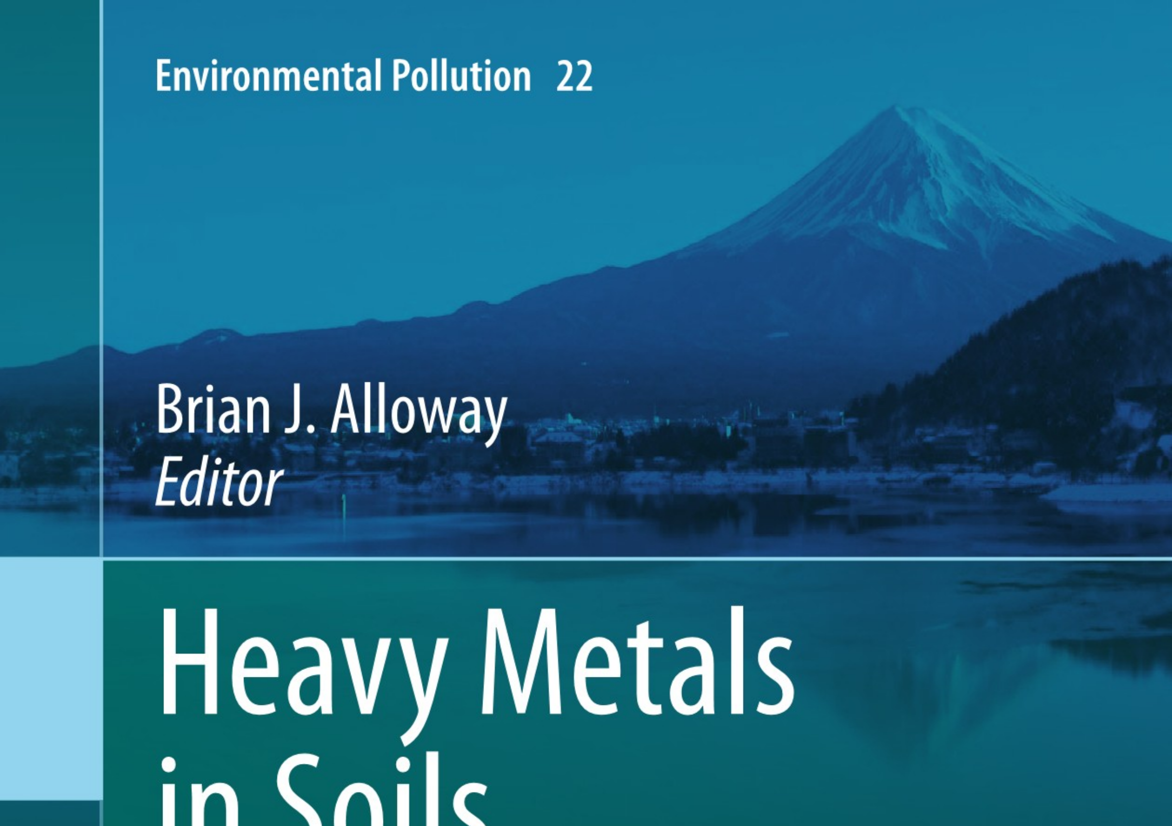

Environmental Pollution 22

Brian J. Alloway
Editor

Heavy Metals in Soils

Trace Metals and Metalloids in Soils and their Bioavailability

Third Edition

Springer

Heavy Metals in Soils

ENVIRONMENTAL POLLUTION

VOLUME 22

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Preface

An understanding of the occurrence and availability of heavy metals and metalloids in soils is of major importance to environmental health, crop and livestock production, food and water quality and ecotoxicology. The concentrations of heavy metal (loid)s in soils can vary widely, even in uncontaminated soils. Marked differences in the geochemical composition of the rocks which form the parent materials of soils and variations in the intensity of soil-forming processes can result in wide ranges of total and available concentrations of most elements in soils, even in those unaffected by contamination. Nevertheless, contamination from many sources can often give rise to some very high concentrations of heavy metal(loid)s which can cause toxicity in soil organisms and susceptible plants, but this depends on the factors affecting the bioavailability of the elements.

This book covers the general principles of the occurrence, soil chemical behaviour and soil-plant-animal aspects of heavy metal(loid)s and more detailed coverage of 21 individual elements, including: antimony, arsenic, barium, cadmium, chromium, cobalt, copper, gold, lead, manganese, mercury, molybdenum, nickel, selenium, silver, thallium, tin, tungsten, uranium, vanadium and zinc.

This is the third edition of this book which was previously published in 1990 and 1995 and it has involved a complete re-write with mainly new authors and several new chapters. The structure of the book is largely the same as in the first two editions with Part I covering ‘Basic Principles’ and Part II covering ‘Key Heavy Metals and Metalloids’. However, the scope of Part I has been broadened with the addition of four new chapters dealing with toxicity in soil organisms (Chap. 5), soil-plant relationships (Chap. 6), heavy metal(loid)s as micronutrients for plants and/or animals (Chap. 7) and the modelling of Critical Loads of heavy metals for risk assessments and environmental legislation (Chap. 8). As in the previous editions, Part II covers arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium and zinc. However, a new Part III has been created to give expanded coverage on ten ‘Other Heavy Metals and Metalloids of Potential Environmental Significance’ which include antimony, barium, gold, molybdenum, silver, thallium, tin, tungsten, uranium and vanadium (with barium and tungsten being new additions).

As with the previous editions, this book will be of great value to advanced undergraduate and postgraduate students, research scientists and professionals in environmental science, soil science, geochemistry, agronomy, environmental health and specialists responsible for the management and clean-up of contaminated land.

January, 2012 University of Reading, UK Brian J. Alloway (Editor)

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Part I Basic Principles

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Abbreviations

AAS	atomic absorption spectrometry (analytical method)
ADI	acceptable daily intake (μg kg^{-1} day^{-1}), the quantity of a compound to which a person can be orally exposed, on the basis of body weight, without experiencing adverse effects on health.
AFA	active fulvic acid
AFS	atomic fluorescence spectrometry
Ag	silver
Al	aluminium
AOC	active organic carbon
AOM	active organic matter
AR	*aqua regia* (acid digestion in pseudototal analysis)
AROMIS	European Commission concerted action project on 'Assessment and Reduction of Heavy Metal Input into Agro-ecosystems'
As	arsenic
AsB	arseonobetaine
AsC	arsenocholine
AR	*Aqua regia* soluble metalloid concentration
ATP	adenosine triphosphate (high-energy compound in living cells)
Au	gold
B	boron
Ba	barium
BC	Before Christ
BCF	bio-concentration factor (also known and transfer coefficient)
BCR	Community Bureau of Reference (of the EU)
BLM	Biotic Ligand Model
BSI	British Standards Institute
Bt	billion tonnes (10^9 t)
β_{ML}	overall metal(M)-ligand(L) stability constant
C	carbon
Ca	calcium

CA	cacodylic acid
CCA	chromated copper arsenate (wood preservative)
CCD	charge coupled device
CCE	Coordination Centre for Effects (of the ICP Modelling and Mapping under the LRTAP Convention)
Cd	cadmium
Cd-U	Urinary cadmium
Ce	cerium
CEC	cation exchange capacity
CHUM-AM	model (which includes WHAM-VI) to simulate combined acidification and metal behaviour for catchments in Cumbria (north-west England)
Cl	chlorine
CL	critical load
$\mathrm{cmol_C\ kg^{-1}}$	centimoles charge per kilogram (units of cation exchange capacity)
Co	cobalt
Cr	chromium
CRM	certified reference material
Cu	copper
CVAAS	cold vapour atomic absorption spectrometry
Da	Daltons (molecular size) 1 Da=1 g/mol
D_{app}	apparent diffusion coefficient ($m^2\ s^{-1}$)
DBT	dibutyltin
DDT	damage delay time
DGT	diffusive gradients in thin films technique
DIN	Deutsches Institut für Normung (German Standards Institute)
DMA(V)	dimethylarsinate
DMT	dimethyltin
DNA	deoxyribonucleic acid
DOC	dissolved organic carbon
DOM	dissolved organic matter (mol kg^{-1})
DPT	diphenyltin
DTPA	diethylentriaminepentaacetic acid (chelating agent used for soil tests)
DU	depleted uranium
DW	dry weight (also DM=dry matter)
EC10	effective concentration yielding 10% inhibition in response
eCEC	effective cation exchange capacity (at pH of the soil)
EDL	electrodeless discharge lamp
EDTA	ethylenediaminetetraacetic acid (chelating agent use for soil tests)
EDXRF	energy dispersive X-ray fluorescence
Eh	redox potential, which is the potential generated between a platinum electrode inserted into the solution to be measured and a standard hydrogen electrode (mV)

EMEP	Meteorological Synthesizing Centre East under the LRTAP Convention
EPS	extracellular polysaccharide (biofilm produced by roots)
ESR	electron spin resonance (spectroscopy)
ETAAS	electrothermal atomic absorption spectrometry
EU	European Union (comprising 27 member states and~500 M inhabitants)
EXAFS	extended X-ray absorption fine structure (spectroscopy)
F	fluorine
FAAS	flame atomic absorption spectrometry
FAO	Food and Agriculture Organisation of the United Nations
Fe	iron
FE	Freundlich equation
FIAM	free ion activity model
FMI	free metal ion
FTIR	Fourier transformed infra-red spectroscopy
FW	fresh weight (or wet weight) usually in analysis of plant tissues
G-Base	British Geological Survey's Baseline Survey of the Environment
GI tract	gastro-intestinal tract in humans and higher animals
GPF	general purpose Freundlich equation
GPS	global positioning system
GPx	glutathione peroxidase (antioxidant enzyme containing selenium)
GSH	glutathione (tripeptide functioning as reducing substrate for GPx)
H	hydrogen
h	hour(s)
ha	hectare (10,000 m^2) equivalent to 2.471 acres
HA	humic acid
HCL	hollow cathode lamp
Hg	mercury
HGAAS	hydride generation atomic absorption spectrometry
Hi	hysteresis index
HIV	human immunodeficiency virus
IAA	indole acetic acid (growth regulating hormone in plants)
IAP	ion activity product
ICP-AES	inductively coupled plasma atomic emission spectrometry (multi-element analytical method)
ICP-MS	inductively coupled plasma mass spectroscopy
INAA	instrumental neutron activation analysis
ISO	International Organisation for Standardisation
IUPAC	International Union of Pure and Applied Chemistry
JRC	Joint Research Centre, Ispra (of the EU)
K	potassium
k_d	distribution coefficient (L kg^{-1})
k_F	Freundlich adsorption constant

K_L	Langmuir adsorption constant
K_s	solubility product
L/A	leaching-ageing factor
LA-ICP-MS	laser ablation inductively coupled plasma mass spectrometry
LDL	low-density lipoprotein
LFE	Langmuir-Freundlich equation
LIBS	laser-induced breakdown spectrometry
LMWOLs	low molecular weight organic ligands
LOAEL	the lowest observed adverse effect level: toxicological threshold
LOD	limit of detection
LOI	loss on ignition (%) a measure of organic matter content
LRTAP	long-range transboundary air pollution (convention of UNECE)
mg kg^{-1}	milligrams per kilogram (equivalent to micrograms per gram or 1 part per million (ppm))
mg L^{-1}	milligrams per litre (or 1 part per million (ppm) in liquids)
MA	mugineic acid (phytosierophores)
MAE	mean absolute error
MBT	monobutyltin
Mg	magnesium
mM	milli-moles
MMA(V)	monomethylarsonate
Mn	manganese
MPT	monphenyltin
Mo	molybdenum
MOS	margin of safety
N	nitrogen
Na	sodium
NADPH	reduced nicotinamide adenine dinucleotide (reducing substrate for the enzymes glutathione reductase and thioredoxin reductase)
NF-*kappa*B	Nuclear factor-*kappa*B (transcription factor enhancing expression of several proinflammatory genes and replication rate of HIV)
Ni	nickel
NICA-Donnan	the Non-Ideal Competitive Adsorption model
NIST	National Institute of Standards and Technology (of the United States)
NMR	nuclear magnetic resonance spectroscopy
NOEC	no observed effect concentrations, i.e. highest dose at which no significant inhibitory effect is observed
NPK	nitrogen, phosphorus and potassium compound fertilisers
O	oxygen
OTC	organotin compound
Os	osmium
P	phosphorus
Pb	lead

PBET	physiologically-based extraction test
Pd	palladium
PC	phytochelatins
pe	the negative logarithm ($-\log_{10}$) of electron activity
pH	$-\log_{10}$ (hydronium ion activity) – measure of acidity
pKa	$-\log_{10}$(acid dissociation constant)
PNEC	predicted non-effect concentration (above which toxic effects may occur in sensitive species)
Pt	platinum
PT	pseudototal (incomplete chemical dissolution e.g., *Aqua regia* digestion)
PTFE	polytetrafluoroethylene (Teflon)
PVC	polyvinylchloride
Ra	radium
RDA	recommended dietary allowance (for humans)
RDI	recommended daily intake (of nutrients for humans)
RDT	recovery delay time
REE	rare earth elements
Rh	rhodium
RM	reference material
Rn	radon
ROS	reactive oxygen species
RSD	relative standard deviation
S	sulphur
Sb	antimony
SBET	simplified bioaccessibility extraction test
SDMM	simple dynamic model of metals (Centre for Ecology and Hydrology, UK)
Se	selenium
SEM-EDX	scanning electron microscope with energy dispersive X-ray analysis
Se-Met	selenomethionine
SeMCYS	Se-methylselenocysteine
SDMM	simple dynamic model for metals
Si	silicon
Sn	tin
SOD	superoxide dismutase (enzyme)
SSA	specific surface area
SUVA	specific ultra-violet absorbance
t	metric tonne (or megagrams, Mg) – 0.984 tons (Imperial)
$T_{1/2}$	half life (of a radioisotope)
TBT	tributyl tin
TBTO	tributyl tin oxide
TDI	tolerable daily intake (of a potentially toxic substance)

TETRA	tetramethyl arsonium ion
TGA	thymine guanine adenine (base triplet in DNA molecule)
TGF-*beta*	transforming growth factor *beta* (cytokine inhibiting immune functions and stimulating formation of the structural molecule collagen found in fibrous connective tissue)
Th	thorium
Tl	thallium
TL	target load
TMAO	trimethyl arsine oxide
TMT	trimethyltin
TOC	total organic carbon
TOTs	tetraorganotin compounds
TPN	total parenteral nutrition (supplying nutrients in solution into a vein and by- passing the GI tract)
TPT	triphenyl tin (compounds)
TPTA	triphenyltin acetate
t-RNA	transfer RNA
TSP	total suspended particles (in air)
U	uranium
UGA	uracil guanine adenine (base triplet in RNA molecule)
UKAS	United Kingdom Accreditation Service
UKSHS	United Kingdom Soil and Herbage Survey
UNECE	United Nations Economic Commission for Europe
USDA	United States Department of Agriculture
USDoE	United States Department of Energy
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
V	vanadium
W	tungsten
W6-MTC	customised program based on WHAM6
WDXRF	wavelength-dispersive X-ray fluorescence
WHAM6	version 6 of the Windermere Humic Aqueous Model designed to calculate equilibrium chemical speciation in surface/ground waters, sediments and soils
WW	wet (fresh) weight (same as FW)
XANES	X-ray adsorption near edge structure
XRD	X-ray diffraction (analysis of crystal structures)
XRF	X-ray fluorescence (spectrometry)
Zn	zinc
ZPC	zero point of charge

Part I
Basic Principles

Chapter 1
Introduction

Brian J. Alloway

Abstract This new (third) edition of 'Heavy Metals in Soils' provides an up to date and in-depth coverage of analytical methods, concentrations in soils, soil chemistry and effects on plants, animals and humans of the 21 most environmentally important heavy metals and metalloids. Although retaining a similar structure to the two earlier editions (1990 and 1995) it has been completely re-written by a team of mainly new authors. Its scope has been expanded by the inclusion of 4 new chapters in Part I (Basic Principles) dealing with soil organisms, soil-plant relationships, heavy metal(loid)s as micronutrients and critical loads. Part II, (Key Heavy Metals and Metalloids) covers the 11 most important elements and Part III (Other Heavy Metals and Metalloids of Potential Environmental Significance) deals with a further 10 less well known, but nonetheless important elements. Figures are given for total world mining production of most of these heavy metal(loid)s over the period from 1973 to 2010. Opinions differ on the appropriateness of the term 'heavy metals' and these are discussed together with a brief consideration of significant developments in the study and management of heavy metal(loid)s in soils over the 22 years since the first edition.

Keywords Heavy metals • Metalloids • Soil • Plants • Animals • Micronutrients • Editions • Chapters • Authors • Toxicity • Deficiencies • Mine production

An understanding of the natural (geochemical) and anthropogenic sources of heavy metals and metalloids in soils, their soil-plant relationships and possible toxicity or deficiency problems associated with them is just as important for environmental protection, human health and agricultural productivity today as it was in 1990 when

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the first edition of 'Heavy Metals in Soils' was published [1]. As more and more analytical data for soils and plants become available in the world literature it is increasingly apparent that considerable areas of soil in many parts of the world have been contaminated with heavy metals and metalloids which, in many cases, pose potential toxicity problems. On the other hand, however, deficiencies of essential heavy metals, such as zinc (Zn), copper (Cu) and manganese (Mn) and metalloids, such as selenium (Se) in agricultural soils are affecting agricultural productivity and human health in many countries.

The most important factor determining whether toxicities or deficiencies of elements will occur in plants on a particular soil is the plant-available concentration in this soil. This depends on the total content of the element, the adsorptive capacity of the soil and physico-chemical factors, such as pH and redox potential, which control the balance between adsorbed and soil solution fractions of heavy metals and metalloids. This book provides in-depth coverage of the key factors affecting the occurrence, soil-plant relationships and possible toxicities or deficiencies of the most environmentally important heavy metals and metal(loid)s. It is divided into three parts: Part I: 'Basic Principles', Part II: 'Key Heavy Metals and Metalloids' and Part III 'Other Heavy Metals and Metalloids of Potential Environmental Significance'.

Part I (Basic Principles) covers (in order): the geochemical and anthropogenic origins of heavy metals and metalloids in soils (Chap. 2), soil chemistry (Chap. 3), methods of chemical analysis (Chap. 4), effects on soil organisms (Chap. 5), soil-plant relationships (Chap. 6), a brief overview of the heavy metal(loid)s which are essential for plants and/or animals (Chap. 7) and finally, Chap. 8 deals with 'critical loads', which are the total input rates of heavy metals and metalloids in soils and the environment which can be sustained without harmful effects.

Part II (Key Heavy Metals and Metalloids) comprises nine chapters covering the sources, properties, soil-plant relationships, human and animal toxicology and other environmental aspects of the 11 most environmentally important heavy metal(loid)s. These include: arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), mercury (Hg), lead (Pb), manganese (Mn), nickel (Ni), selenium (Se) and zinc (Zn). Finally, Part III (Other Heavy Metals and Metalloids of Potential Environmental Significance) deals with the less well known, but nevertheless environmentally important elements: antimony (Sb), barium, (Ba), gold (Au), molybdenum (Mo), silver (Ag), thallium (Tl), tin (Sn), tungsten (W) uranium (U) and vanadium (V).

The term 'heavy metal' has been used for many years and is generally recognised as referring to the group of metals and metalloids of relatively high atomic mass (>5 g cm^{-3}) especially the transition metals, such as Pb, Cd and Hg, that can cause toxicity problems [5, 7]. However, 'heavy metals' is difficult to define precisely and some experts consider it inappropriate [5]. Although several alternative group names, including 'toxic metals' and 'trace metals' have been put forward, there are also problems with their use. Chemists argue that a new classification based on the periodic table is needed to enable properties, such as toxicological effects of elements to be predicted [5]. However, on the other hand, many professionals who have to deal with contaminated soil and other environmental media find the group name ‘heavy metals’ to be a convenient “peg” on which to ‘hang’ data for the range of metals and metalloids likely to cause toxicity problems. It is highly likely that many of these people will probably continue to use it, even though it is poorly defined. One consequence of this is that ‘heavy metals’ tends to be used mainly in a pejorative sense implying ‘bad’ metals which contaminate and hence spoil the quality of land [6]. This is unfortunate because several of the heavy metals are also essential for plants and/or animals and need to be present in adequate quantities. Other non-pejorative terms, such as ‘trace metals’ are sometimes used in preference. Some non-metals, such as As, Sb and Se which have the appearance and/or some of the properties of metals, but behave chemically like non-metals, have sometimes been included within the group name ‘heavy metals’. This is now considered to be too imprecise and so they are usually referred to as ‘metalloids’ to distinguish them from heavy metals. The term ‘heavy metal(loid)s’ is used widely in this book as a convenient shorthand when both heavy metals and related (high density) non-metals are being considered together.

‘Trace elements’ is another widely used (and non-pejorative) term which includes the heavy metal(loid)s and also lower density metals and non-metals, such as boron (B) and halogens such as iodine (I) and fluorine (F) which do not necessarily cause the same environmental and toxicological problems as the heavy metal(loid)s. In plant and animal nutrition, there is a convention for referring to the essential heavy metals and metalloids as ‘trace elements’, but this is not as precise as ‘micronutrients’. From a geochemical point of view, the heavy metal(loid)s are all trace elements, that is they normally occur in trace amounts (usually $<1{,}000$ mg kg^{-1}) in rocks and soils (except for natural concentrations in ore minerals, which form ore deposits). However, the biological use of the term “trace element” applies to elements normally occurring at relatively low concentrations (usually <100 mg kg^{-1}) in the dry matter of living organisms.

From a historical perspective, some heavy metals such as Au, Ag, Cu, Sn and Pb have been used by mankind for thousands of years (e.g., Au around 8,000 years, Cu >6,000 years). The places where these metals were mined and smelted or where artefacts were made from them will have been contaminated by these metals. Other geochemically associated heavy metal(loid)s such as As and Zn, which were present in some of the ore deposits, but not intentionally exploited, will also have contaminated the local environment. Analyses of carbon and pollen-dated layers in peat cores from ombrotrophic bogs in Europe have revealed that atmospheric pollution of Cu and Pb from mining and smelting has occurred over a period of more than 4,000 years [4, 9]. Peaks of contamination occurred at historically important times such as the Bronze Age, the Roman Empire, the Industrial Revolution and the ‘modern’ period with its diverse sources and greatly increased pollution loads. Apart from anthropogenic sources, soils in areas underlain by rocks with anomalously high contents of heavy metal(loid)s will also have become enriched through natural geomorphological and pedogenic processes over an even longer timescale.

Table 1.1 World mine production of heavy metals and metalloids (t of element content, except where stated)

Element	Symbol	World production 1973 [11]	1994 [3]	2004 [3]	2010 [10]
Antimony	Sb	–	106,000	112,000	135,000
Arsenic	As	–	43,000	37,500	54,500
Barium*[a] (59%)	Ba	–	4,300,000	6,900,000	6,900,000
Cadmium	Cd	17,200	18,100	17,200	22,000
Chromium*[b](46.5%)	Cr	–	9,570,000	17,000,000	22,000,000
Cobalt	Co	–	18,500	46,900	88,000
Copper	Cu	7,116,900	9,430,000	14,500,000	16,200,000
Gold	Au	–	2,300	2,470	2,500
Lead	Pb	3,487,000	2,800,000	3,150,000	4,100,000
Manganese*[c](35–40%)	Mn	–	7,190,000	11,000,000	13,000,000
Mercury	Hg	9,300	1,760	1,750	1,960
Molybdenum	Mo	–	104,000	139,000	234,000
Nickel	Ni	710,000	906,000	1,400,000	1,550,000
Selenium	Se	–	1,880	1,500	2,260
Silver	Ag	–	13,900	19,500	22,200
Thallium (kg)	Tl	–	15,000	15,000	10,000
Tin	Sn	233,800	184,000	250,000	261,000
Tungsten	W	–	26,000	60,000	61,000
Vanadium	V	–	33,900	44,000	56,000
Zinc	Zn	5,709,400	6,810,000	9,100,000	12,000,000

From: US Geological Survey [10, 11] and World Resources Institute [12]

*Tonnages of mined metal ores, rather than in metal(loid) content

[a] Barite = $BaSO_4$ (59% Ba)

[b] Chromite = $FeCrO_4$ (46.5% Cr)

[c] Mn ore (oxides) (35–54% Mn)

Table 1.1 shows total annual production of many of the heavy metal(loid)s covered in this book over the period 1973–2010 [3, 10, 11]. Copper production is the highest of all the metals shown and has more than doubled along with that of Zn and Ni over this 37 year period. Tungsten production doubled between 1994 and 2010, Ag increased by around 60% and Au production remained more or less even over this period. Tin and Pb showed a decrease between 1973 and 1994, with gradual increases after this to higher total production tonnages by 2010. The marked decrease of more than five times in the production of Hg between 1973 and 1994 and then relatively similar total production in the subsequent 16 years is particularly noteworthy and is due to changes in the use of Hg and the introduction of stricter environmental controls.

In contrast to anthropogenic contamination of soils, it is now recognised that large areas of agricultural land are deficient in one or more plant micronutrients [2]. As the world population and its concomitant demand for food continues to increase, it is important to ensure that levels of plant-available micronutrients such as boron (B), Cu, Zn, Mn, Fe and molybdenum (Mo) in soils are adequate. This has become a major problem in some parts of the world where higher yielding crop cultivars are being grown on less fertile soils and deficiencies in Zn, Cu, B and other micronutrients are becoming widespread (see Chaps. 7, 12, 13 and 17). Concentrations of elements essential for livestock and humans will also be lower in deficient crops, which is particularly important in the case of Zn which is required by both plants and animals/humans (Chap. 17) and Se, which is only required by animals/humans (see Chap. 16).

Since the first edition of this book was published in 1990, there have been many important developments in the study and management of heavy metal(loid)s in soils and these include:

- Multi-element analysis of soils and plants (by ICP-AES, ICP-MS and XRF) is now much more common both for research and advisory (extension) purposes, in fact ICP-AES is now the most widely used spectroscopic technique for the analysis of heavy metal(loid)s in soils, plants and related materials (See Chap. 4, Sect. 4.7.4).
- The publication of soil geochemical atlases for several countries and regions and analytical data from the soil testing of large numbers of representative samples from farmer's fields provide valuable indications of the relative proportions of deficient and contaminated soils (See Chap. 2).
- Major advances have been made in modelling the dynamics of heavy metal(loid)s in soil-water and soil-plant systems with models such as the Free Ion Activity Model (FIAM), the Windermere Humic Aqueous Models (WHAM 1–6) and the Biotic Ligand Model (BLM) (see Chaps. 3 and 8). These are very useful in the estimation of critical loads and in the remediation of contaminated and deficient soils.
- The publication (in English) of large numbers of papers on heavy metal(loid) contaminated soils in China, eastern Europe and other regions about which relatively little was known until recently, provides a wider global perspective on sources, dynamics and effects of heavy metal(loid)s in soils (see Chap. 2).
- Increased awareness of the significance of atmospheric inputs of heavy metal(loid)s and the development of the methodology for determining critical loads (See Chaps. 2, 8, 16 and 17) has focussed attention on minimising soil contamination.
- Increased research on the ecotoxic effects of heavy metal(loid)s on soil organisms (See Chaps. 5, 6 and 13) has shown that several important soil ecosystem processes mediated by microorganisms may be disrupted at relatively low levels of contamination when crop plants appear to be unaffected by toxicity.
- The European Union (EU) instigated a series of voluntary risk assessments on several heavy metals, including Ag, Cd, Co, Cu, Mn, Mo, Ni, Pb and Zn. These assessments drew together the latest findings on the inputs of these metals from the major sources, concentrations in soils and critical (ecotoxicological) concentrations from throughout Europe (see Chaps. 8, 10, 13 and 17). These have been superseded by the EU REACH Regulations which deal with the Registration, Evaluation, Authorisation and Restriction of Chemical substances and became law (within the EU) in 2007. These regulations aim to improve the protection of human health and the environment through improved and earlier identification of the intrinsic properties of chemical substances and also to enhance the competitiveness of the EU chemicals industry.

- Metalliferous mine tailings dams have failed in various countries (e.g. Romania and Spain recently) resulting in large areas of alluvial soils downriver being grossly contaminated with heavy metal(loid)-containing tailing particles. The massive contamination of previously uncontaminated land has provided some very valuable research opportunities.
- Increased recognition of the importance of micronutrient deficiencies in humans, especially of Zn and Se has fostered research into methods for the biofortification of crops with these metal(loid)s (see Chaps. 7, 16 and 17) and Alloway [2].
- Increased planning and regulatory emphasis on the recycling of brownfield sites, has stimulated research into the clean-up and remediation of heavy metal(loid)-contaminated soils [8].
- Developments in armaments, such as the use of depleted uranium (DU) in anti-tank ammunition and armour for tanks has necessitated research into the behaviour of this material in the environment including pathways to humans (see Chaps. 2 and 26).
- Synthetic organo-tin compounds (OTCs) have been used in increasing amounts in industry, marine antifouling paints and agriculture since their introduction in the 1960s and significant amounts have found their way into some aquatic and terrestrial environments. The OTCs which enter soils can be taken up by plants and enter human diets. It is therefore important to monitor their concentrations and investigate any potential toxicity hazards [3](see Chap. 24).

This book contains a great deal of up-to-date information on heavy metal(loid)s in soils, plants and the wider environment which will be of great value to research workers, agronomists, environmental engineers, environmental protection specialists and regulators. It will also be a very useful source of information for advanced undergraduate and postgraduate students.

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Chapter 2
Sources of Heavy Metals and Metalloids in Soils

Brian J. Alloway

Abstract Heavy metals and metalloids in soils are derived from the soil parent material (lithogenic source) and various anthropogenic sources, most of which involve several metal(loid)s. There are many different anthropogenic sources of heavy metal(loid) contamination affecting both agricultural and urban soils. However, localised contamination from a predominant single source, such as a metal smelter can have a marked effect on soils, vegetation and possibly also on the health of the local population, especially in countries where there are inadequate emission controls and soil quality standards. In general, soils at industrial sites can have distinct groups of heavy metal(loid) contaminants, which depend on the respective industries and their raw materials and products. Soils in all urban areas are generally contaminated with lead (Pb), zinc (Zn), cadmium (Cd) and copper (Cu) from traffic, paint and many other non-specific urban sources. Although the heavy metal(loid) composition of agricultural soils tends to be more closely governed by the parent material, inputs from sources such as deposition of long-distance, atmospherically-transported aerosol particles from fossil fuel combustion and other sources, organic material applications and contaminants in fertilisers can also be significant. Removal of Pb from petrol and paints, changes in the type and structure of industries and strict regulations on atmospheric emissions and waste water discharges have resulted in a general reduction in the loads of heavy metal(loid)s reaching soils in many countries. However, historic contamination still affects soils in many areas and may have impacts for decades or even centuries afterwards.

Keywords Lithogenic • Anthropogenic • Atmospheric deposition • Contamination • Urban • Ores • Mining • Industry

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2.1 Introduction

All soils contain more or less the full range of heavy metal(loid)s in the periodic table, but the concentrations vary widely and some may be below the limit of detection for certain analytical procedures. Concentrations of elements in soils can be divided into 'total' and 'available', which is the fraction of this total content which is potentially available to plants (see Chaps. 3 and 4). Total concentrations include all forms of the element in a soil, such as ions bound in the crystal structure of primary and secondary minerals; those adsorbed on the surfaces of secondary minerals such as clays, oxides and carbonates, those bound in solid state organic matter, and free ions and soluble organic and inorganic complexes in the soil solution. In most cases, much of the total content of an element will not be available for immediate uptake by plants. The 'available' concentration of an element in the soil is an estimate of the fraction of that element which is present as either free ions, soluble complexes or in readily desorbable (labile) forms. Availability is affected by many factors including pH, redox status, macronutrient levels, available water content and temperature (see Chap. 3). Plants can also exert significant effects on the availability of metal(loid)s through the release of exudates from the roots (see Chap. 6). Soil analysis to determine 'available' concentrations of elements usually involves a partial extraction with dilute solutions of reagents which have been correlated with plant uptake and/or yield in certain species, or measurement of specific soil parameters which can be used in a model to predict free ion and available concentrations (see Chaps. 3 and 6). Although total concentrations are often a poor indication of the potentially plant-available or 'bio-accessible' fractions of a metal(loid) in a soil, they do provide a useful indication of whether a soil has anomalously high or low concentrations. This will show whether this soil is contaminated and/or geochemically enriched and thus poses a possible risk of toxicity to some species of plants, soil fauna or microorganisms (Chaps. 5 and 6). On the other hand, low total concentrations indicate that a soil has either developed from a parent material with a low total content of an element, or has become depleted during pedogenesis and is relatively free from contamination. In either case, there is a greater chance of essential heavy metal(loid)s (Zn, Cu, Co, Mn, Mo and Se) being deficient in soils with low total contents especially where soil conditions do not favour plant availability (see Chap. 7).

2.2 Total Concentrations of Heavy Metals and Metalloids in Soils Around the World

It is important to stress that 'total' concentrations can be determined by two different chemical methods and by one instrumental method using X-ray fluorescence spectrometry (XRF). Only one chemical method, involving digestion in concentrated nitric acid (HNO_3) and hydrofluoric acid (HF), dissolves all soil constituents and gives a 'true' total concentration (Chap. 4, Sect, 4.5.1). The other more widely used analytical procedure involves digestion in hot *aqua regia* (concentrated HNO_3 + HCl) which dissolves most of the soil constituents except those strongly bound in silicate minerals. This is sometimes referred to as the 'pseudo-total' content, or qualified as being determined in *aqua regia* (often abbreviated to 'AR' in tables) (Sect. 4.5.2). Although not providing absolute total concentrations, this method extracts all the elements that are likely to become bioavailable even in the long term.

Table 2.1 gives the median and maximum concentrations of 20 heavy metal (loid)s from surveys in different countries and regions and also average values for these elements in world soils. It was not possible to include gold (Au) in this table due to lack of sufficient data.

From the data in Table 2.1, barium (Ba) and manganese (Mn) have the highest median contents and silver (Ag) the lowest, but antimony (Sb), and thallium (Tl) also have low median total contents of <1 mg kg^{-1}. A comparison of the concentrations of specific metal(loid)s in different countries or regions shows that median concentrations can vary widely. For example median values of Ba show a nearly 13-fold range, being lowest in agricultural soils of the Baltic region (46 mg kg^{-1}) and highest in the northern California (601 mg kg^{-1}). The maximum individual Ba concentration from all the data sets is 7,610 mg kg^{-1}, which was also found in northern California [32]. Cadmium (Cd) shows a wide range of median values (0.13–1.1 mg kg^{-1}), but the highest individual value encountered (in agricultural soils) is 41 mg kg^{-1}, which was found in England and Wales [56]. However, Cd contents of up to 360 mg kg^{-1} have been found in soils at Zn–Pb mine sites [67]. Lead shows an almost fivefold median range (8.4–40 mg kg^{-1}), but the highest individual Pb value encountered in any of these surveys was 16,300 mg kg^{-1} in England and Wales. Chromium shows an eightfold variation (12–96 mg kg^{-1}) with the highest value of 5,910 mg kg^{-1} in northern California. Although the range of median Zn values in Table 2.1 is less than threefold (33–88 mg kg^{-1}) maximum Zn contents of 3,648 and 6,173 mg kg^{-1} have been found in England and Wales and the USA, respectively. The variations between countries and regions reflect differences in the geochemical composition of the soil parent materials and the degree of soil contamination from various sources (see Sect. 2.3.2 below). The highest median contents of Ba, Co, Cr, Mn, Ni and V in Table 2.1 are in the soils of northern California and reflect the diverse range of rock types (lithogenic sources) in this region which range from ultramafic to acid igneous. The high maximum As, Cu, Pb and Zn contents also found in northern Californian soils are due to metalliferous ore deposits in the Sacramento Valley drainage basin, which are both lithogenic and anthropogenic (mining) sources of metal(loid)s [32]. In contrast, relatively low concentrations of most heavy metal(loid)s were found in Florida, which is probably due to the sandy nature of the soils and their severe leaching during podzolization. Median contents of selected elements in the Florida soils (in mg kg^{-1}) were: Cd 0.004, Cu 1.9, Pb 4.9 and Zn 4.6 [11].

Although the world and regional average or median metal(loid) concentrations can be of general use in providing a basis for comparison of soil test data at

Table 2.1 Median and maximum total heavy metal concentrations in topsoils in various countries and average values for world soils (mg kg^{-1})

	Europe	Baltic states	Ireland	England and Wales	Netherlands	NL(bkgd)[a]	Denmark	N. California	USA	World (av[b])
No. of samples	852	773	1,310	5,692	100	100	393	1,300	1,903	–
Ag	0.27 (<3.15)	<1 (<1.04)	–	–	–	–	–	–	–	0.1
As	6.0 (<27.3)	1.9 (<24)	7.25 (<123)	–	5.6 (<39)	20	3.3 (<48)	6.0 (<106)	–	4.7
Ba	65.0 (<1,700)	46 (<311)	230.2 (<1,297)	121 (<2,973)	32.4 (<620)	190	–	601 (<7,610)	–	362
Cd	0.145 (<14)	0.13 (<1.1)	0.326 (<15)	0.7 (<41)	0.14 (<2.5)	0.6	0.16 (<0.85)	0.2 (<11.2)	0.16 (<41)	1.1
Co	7.0 (<255)	4.1 (<39)	6.2 (<59)	9.8 (<322)	2.4 (<22)	15	–	16 (<166)	7 (<347)	6.9
Cr	22.0 (<234)	12 (<126)	42.6 (<222)	39.3 (<838)	15.7 (<106)	55	9.9 (<64)	96 (<5,910)	24 (<4,107)	42
Cu	12 (<239)	7.8 (<142)	16.2 (<272)	18.1 (<1,508)	10.2 (<141)	40	7 (<93)	37 (<3,088)	17.3 (<1,836)	14
Hg	0.037 (<1.35)	–	0.086 (<3.5)	–	0.045 (<1.2)	0.15	–	–	0.075 (<3)	0.1
Mn	382 (<6,480)	255 (<1,560)	462 (<21,077)	577 (<42,603)	–	–	–	752 (<4,430)	372 (<8,071)	418
Mo	0.62 (<21.3)	<3 (<74)	0.91 (<21)	–	<0.5 (<3.9)	–	–	0.7 (<10)	–	1.8
Ni	14 (<2,560)	8 (<619)	17.5 (<176)	22.6 (<440)	4.94 (<66)	35	5 (<76)	50 (<4,955)	18.3 (<4,497)	18
Pb	15 (<886)	8.4 (<76)	24.8 (<2,635)	40 (<16,338)	15.6 (<451)	50	11.3 (<102)	23 (<2,354)	10.1 (<1,650)	25
Sb	0.6 (<31)	<10 (<10)	0.53 (<5.3)	–	<1.3 (<2.8)	–	–	0.7 (<6.9)	–	0.62
Se	–	0.14 (<7.6)	0.74 (<17)	–	–	–	–	0.2 (<2)	–	0.7
Sn	3 (<106)	1.1 (<6.8)	1.68 (<17.8)	–	<1 (<38)	6.5	–	1.0 (<110)	–	–
Tl	0.66 (<24)	0.38 (<2.5)	0.43 (<2.7)	–	<0.5 (<1.8)	–	–	0.3 (<2.1)	–	0.6
U	2 (<53.2)	1.4 (<56)	1.96 (<64)	–	–	–	–	1.8 (<11.4)	–	3.7
V	33 (<281)	18 (<203)	52.2 (<240)	–	27.7 (<168)	80	–	135 (<490)	–	60
W	<5 (<14)	<5 (<40)	0.59 (<7.7)	–	–	–	–	0.8 (<18)	–	1.2
Zn	48 (<2,270)	33 (<254)	62.6 (<1,384)	82 (<3,648)	40.3 (<316)	140	26.8 (<135)	88 (<3,350)	56.5 (<6,173)	62
Reference	[84]	[78]	[99]	[56]	[8]	[8]	[4]	[32]	[9]	[43]

References: Salminen et al. [84]; Reiman et al. [78]; Zhang et al. [99]; McGrath and Loveland [56]; Brus et al. [8]; Bak et al. [4]; Goldhaber et al. [32]; Burt et al. [9] and Kabata-Pendias [43]

[a] Official background concentrations for the Netherlands [7]

[b] Average concentrations for world soils [38]

specific sites, they are of little value when it comes to interpreting soil analyses with regard to contamination and possible toxicity, or anomalously low contents and possible micronutrient deficiencies. It is necessary to collect sufficient samples from apparently uncontaminated sites in the locality being investigated in order to determine a local background value for each metal(loid) to provide a basis for comparison. Some countries have determined 'official' background and/or maximum permissible concentrations, which are used for the interpretation of soil analytical data (Chap 4. Sect. 4.2). An example of these are the statistically-determined background values for the Netherlands shown in Table 2.1 [8]. It is common for the total concentrations of heavy metal(loid)s in soils not affected by anthropogenic contamination or particularly diverse geology to span more than one order of magnitude [30].

2.3 Sources of Heavy Metals and Metalloids in Soils

The total contents of heavy metal(loid)s in a soil are the sum of the concentrations of elements derived from minerals in the geological parent material on which the soil has developed (lithogenic source) and inputs from a wide range of possible anthropogenic (contamination) sources. These include atmospheric deposition of aerosol particles ($<30\ \mu\text{m}$ diameter), raindrops containing heavy metal(loid)s, or gaseous forms of elements, direct applications of agricultural fertilisers, agrichemicals and various organic materials including sewage sludges, livestock manures, food wastes and composts. Technogenic materials such as ashes, mine wastes and demolition rubble can be contaminants in existing (pedogenic) soils or can form the parent materials of new, man-made soils (Anthrosols).

The total concentration of a metal(loid) in a soil is the sum of all these various inputs minus the losses through off-take in harvested or grazed plants, erosion of soil particles by wind or water, leaching down the soil profile in solution and losses by volatilization of gaseous forms of elements. These are summarised in the following descriptive equation:

$$\begin{aligned} M_{total} = {} & \left(M_{pm} + M_{atm} + M_{sed} + M_f + M_{ac} + M_{tm} + M_{om} + M_{ic}\right) \\ & - \left(M_{cr} + M_e + M_l + M_v\right) \end{aligned}$$

Where: M = metal(loid), pm = parent material, atm = atmospheric deposition, sed = deposited sediment, f = fertilisers, ac = agricultural chemicals, tm = technogenic materials, om = organic materials, ic = other inorganic contaminants, cr = crop removal, e = soil erosion, l = leaching, and v = volatilisation.

2.3.1 Lithogenic Sources of Heavy Metals and Metalloids

On a spatial basis, the lithogenic source (geological minerals in the soil parent material) is the dominant factor determining the total concentration of heavy metal(loid)s in world soils. Ten ‘major’ elements: oxygen (O), silicon (Si), aluminium (Al), iron (Fe), calcium (Ca), sodium (Na), potassium (K), magnesium (Mg), phosphorus (P), and titanium (Ti) constitute over 99% of the total element content of the earth’s crust. The remainder of the elements in the periodic table are called ‘trace elements’ and together comprise a total of only 1% by mass of the earth’s crust. Their individual concentrations do not normally exceed 1,000 mg kg^{-1}, except in ore minerals, which are natural concentrations of minerals containing these trace elements. The parent material is the rock or unconsolidated drift material that has undergone weathering and pedogenesis to form the mineral skeleton of the soil. Weathering involves the chemical decomposition of minerals, the release of some of their constituent elements in soluble forms and the formation of new (secondary) minerals through chemical reactions between the products of weathering. The part of the mineral not chemically decomposed remains as an insoluble residue and any metal(loid)s retained in it are unlikely to become soluble and available to plants for a long time. In addition to concentrations of major and trace elements, the mineralogical composition of the soil derived from its parent material also determines its texture (percentages of sand, silt and clay-sized particles) and has a major influence on the physical and chemical properties of soils. Perhaps the most important chemical property is the ability of the soil to adsorb cations and anions, which is directly linked to the type and amount of secondary minerals including clays, carbonates and hydrous oxides of Fe and Mn, the soil pH and redox conditions (See Chap. 3). This adsorptive capacity of the soil will have a profound effect on the bioavailability of metal(loid)s.

Typical concentrations of a range of heavy metal(loid)s found in the upper earth’s crust and the most common types of igneous and sedimentary rocks are shown in Table 2.2. In the earth’s upper crust, Ba and Mn have the highest concentrations of all the elements listed and Ag and Cd, the lowest, which is also reflected in their concentrations in world soils shown in Table 2.1. Zinc is quite notable for being present in relatively high concentrations compared with other heavy metals, such as Cu, Pb and Ni. When the different types of rocks are considered, among the groups of igneous rocks shown in Table 2.2, Cu, Mn, V and Zn are highest in the gabbros and basalts, whereas, Co, Cr and Ni are highest in the ultramafic group (peridotites and serpentinites).

Trace elements are incorporated into the crystal structure of rock-forming primary minerals, which have crystallized from magma, mainly by substitution of the major constituent ions, such as Fe, Al and Si. The ferromagnesian minerals such as olivine, hornblende and augite have relatively large numbers of different trace elements associated with them including the micronutrients, which are elements essential for plants and animals (see Chap. 7) [66]. As a result of their relatively high contents of both macronutrients and micronutrients and their relatively rapid weathering, the soils derived from basalts and other rocks containing these minerals tend to be very fertile. As the proportion of Si increases in primary minerals, they become more resistant to weathering and tend to have lower contents of trace constituents. Quartz, the crystalline form of SiO_2, generally has relatively low contents of trace elements (such as Ti, Li and B) associated with it and is the

Table 2.2 Geological (Lithogenic) sources of heavy metals and metalloids (mg kg^{-1})

Element	Upper crust	Granite, granodiorite	Gabbro, basalt	Ultramafic rocks	Sandstone	Shales	Black/Oil Shales	Limestones	Coal
Ag	0.07	0.04	0.1	0.06	0.25	0.07	1.9	0.12	–
As	2	3	0.7	0.7	0.5	13	<500	1.5	10
Ba	668	600	330	5	300	550	67	90	250
Cd	0.1	0.1	0.2	0.05	<0.04	0.25	<240	0.1	1
Co	12	4	45	110	0.3	20	67	0.1	10
Cr	35	10	250	2,300	35	100	<700	5	20
Cu	14	12	90	40	2	45	<300	6	20
Mn	527	400	1,500	1,200	100	850	–	15	40
Mo	1.4	1.5	1.2	0.3	0.3	2	<570	0.3	3
Ni	19	5	130	2,000	2	70	<300	5	20
Pb	17	20	4	0.05	10	22	<100	5	20
Sb	0.3	0.3	0.2	0.1	0.05	1	<10	0.15	2
Sn	2.5	3.6	0.9	0.3	0.6	5	<10	0.3	8
U	2.5	4	0.5	0.02	1.3	3.2	<1,250	1	2
V	53	70	260	80	20	130	<2,422	15	40
Zn	52	50	100	60	20	100	<2,314	40	50

References: Wedepohl [96]; Tauber [89]; Krauskopf [47]; Rose et al. [82]; Fouad and El-Rakaiby [26] most abundant primary mineral in the earth's crust. It is highly resistant to weathering, although over a prolonged period in hot, wet tropical conditions, even quartz is eventually weathered.

Sedimentary rocks are formed by the lithification of sediments comprising rock fragments, resistant minerals (such as quartz), secondary minerals such as clays and/or chemical precipitates such as Fe_2O_3, $CaCO_3$ and $MgCO_3$ arising from the weathering of igneous rocks. Since around 75% of the rocks outcropping at the earth's surface are sedimentary, they form a much higher proportion of soil parent materials and are therefore more important in determining soil composition than igneous rocks. In many parts of the world, outcrops of sedimentary rocks are covered by superficial ('drift') deposits of various types, including wind-blown loess, boulder clay, glacial sands and gravels, colluvium and alluvium and it is these that form the actual soil parent material. These superficial deposits are also primarily derived from sedimentary rocks. In Table 2.2 it can be seen that sandstones tend to have the lowest concentrations of most metal(loid)s and that some black shales and oil shales have the highest concentrations of several potentially toxic elements such as As, Cd, Cu, Mo, Pb, uranium (U), V and Zn.

2.3.1.1 Rock Types of Major Significance as Lithogenic Sources of Heavy Metal(loid)s in Soils

Black Shales

Black shales, including bituminous and oil shales, have high organic matter and clay contents and are significantly enriched in a range of heavy metal(loid)s and other trace elements. They can give rise to significantly elevated concentrations of Ag, As, Au, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V, W, Zn, rare earths (REE) and platinum (Pt)-group elements in the soils developed on them. They were mostly formed in marine basins and are often referred to as 'metalliferous marine black shales'. Some of these rocks contain sufficiently high concentrations of metal-containing minerals to be mined as metal ores. Others have acted as source rocks for hydrothermal mineralization deposits of metal ores. The Kupferschiefer ("copper shale") is an example of a metal-rich black shale, and it has been mined in various places in Germany and Poland for Cu, Pb and Ag since medieval times. Organic-rich, black shales were formed in shallow sea water with a reducing environment which is partly responsible for their accumulations of heavy metal(loid)s. Deposits of black shales of various geological ages outcrop widely throughout the world with particularly large deposits in Russia, USA, Canada, Australia, China, Brazil and northern Europe. In Manitoba, Canada, outcrops of black shales, ranging in age from Ordovician to Tertiary (360 M yrs), with an area of 150,000 km^2, show considerable variation in Mo contents, with the oldest and youngest showing the lowest median values ($\sim$ 1 mg kg^{-1}). Those of intermediate ages (Devonian to Cretaceous) had similar median values ($\sim$ 5 mg kg^{-1}), but the Cretaceous black shales had individual Mo contents varying by three orders of magnitude [30].

Smaller occurrences in many other countries give rise to localised areas of heavy metal(loid)-enriched soils either developed directly on shale outcrops or on drift deposits containing shale fragments and their weathering products (clay and silt-sized particles). The origin of this black shale drift can include residues of eroded overlying strata, glacial drift and alluvium. Relatively thin beds (facies) of black shale can also occur in some major clay deposits (e.g. Kimmeridge Clay of Jurassic Age) and give rise to local anomalies in heavy metal(loid) concentrations. Molybdenum-induced Cu deficiency in ruminants (see Chaps. 7 and 21) occurs widely on Mo-enriched soils derived from shales, especially those with black shale facies. In Ireland, black shale facies of the Clare shales (Upper Carboniferous) contain high concentrations of Mo and Se (<200 mg Mo kg^{-1} and <220 mg Se kg^{-1}) which can cause toxicity (and/or induced Cu-deficiency) problems in livestock grazing pastures on soils derived from these rocks [23].

Black shales have attracted wide attention as sources of elevated Cd concentrations in soils and examples include: up to 22 mg Cd kg^{-1} in soils on the Monterey Shale in California, USA [73], 24 mg Cd kg^{-1} on Carboniferous shales in Derbyshire, UK [55], 11 mg Cd kg^{-1} in alluvial soils in an area of uraniferous black shales in South Korea [45] and 60 mg Cd kg^{-1} in soil (and <187 mg Cd kg^{-1} in rock) in an area of black shales and carbonaceous siltstone in Wushan County in south western China [88]. These soils in south western China also contain anomalously high concentrations (in mg kg^{-1}) of Ni up to 388, Zn 962, Mo 99 and Sb 15. Control soils nearby contained concentrations of up to (in mg kg^{-1}): Cd 0.76, Ni 39, Zn 108, Mo 1.1 and Sb 3.4. Crops grown in soils on black shales in this area had elevated concentrations of Cd (up to 76.5 mg kg^{-1} DM in maize) and Mo (up to 5.4 mg kg^{-1} DM in beans) which are a major cause of concern for the health of consumers [88].

Many black shale facies and related carbon-rich sedimentary rocks are significantly enriched in U and those with particularly high contents are referred to as 'uraniferous' shales. Concentrations of >300 mg U kg^{-1} have been found in uraniferous black shales in South Korea. Black shales of Upper Jurassic age in West Siberia contain high concentrations of rare earth elements (REE) (<534 mg kg^{-1}) with cerium (Ce) being the most abundant (<220 mg Ce kg^{-1})[98]. A uraniferous organic-rich black shale of Upper Cretaceous age from the Nakheil phosphate mine in Egypt was found to contain high concentrations of several heavy metals (in mg kg^{-1}): U 41, Mo 570, Cd 233 and Zn 2,314 [26] (Table 2.2). In most cases, U-rich sedimentary rocks, such as shales and phosphorites also contain significant amounts of the radioactive element thorium (Th) which is usually present at around three times the concentration of U (see Chap. 26).

Coals are also closely related to black shales in being formed from organic-rich sediments in shallow reducing environments. They are relatively enriched in several heavy metal(loid)s (Table 2.2), but the contents in different coal formations vary widely. Some coals contain significant amounts of U and Th and the ash from these coals could contain up to ten times as much U (see Chap. 26). They can also be mineralized with the deposition of minerals containing As and other heavy metal (loid)s [53]. Although coals do not form significant areas of soil parent materials on the land surface, they do affect the composition of large geographical areas of soils through air pollution (and subsequent atmospheric deposition) from coal combustion for electricity generation, industrial steam generation and/or domestic heating [53].

Limestones

Limestones comprise mainly grains of calcite ($CaCO_3$) mostly derived from microscopic marine organisms. The marine basins in which these organisms and chemical precipitates of $CaCO_3$ accumulate can also receive significant inputs of heavy metal (loid)s and can thus give rise to limestones with elevated concentrations in some locations. Sulphides can occur in some limestones and clay-rich calcareous marls are often found to be a rich source of heavy metal(loid)s. In many parts of the world, limestones have been extensively mineralized from the deposition of sulphide heavy metal(loid) ore minerals from hydrothermal fluids in the limestone sedimentary beds (see Sect. 2.3.2.2 Metallogenic Mineralization). This carbonate-hosted mineralization is referred to as being of the "Mississippi Valley-Type". During weathering, when the limestone and sulphide ore minerals undergo dissolution and oxidation, the metal(loid)s become dispersed in the residual soil and/or leached into groundwater.

Baize and Chrétien [3] report anomalously high concentrations of Cd, Co, Ni, Pb and Zn in soils on the Sinemurian (Lower Jurassic) limestone platform in Bourgogne region of central France. The organic-rich, calcareous residual soils (Rendic Leptosols) have developed over limestone which had previously been mineralized by hydrothermal fluids or sedimentary processes. Weathering and pedogenesis have resulted in these soils having high concentrations of heavy metal(loid)s (in mg kg^{-1}): Cd 3–4.7, Co 20–50, Ni 62–410, Pb 107–10,180, thallium (Tl) 47–55 and Zn 420–3,820, which are very high for soils unaffected by anthropogenic contamination [3, 92]. Soils in an area with a similar geological history near Alés, in France, were also found to have elevated concentrations of several heavy metals including Tl (<18.2 mg kg^{-1}). In contrast, a survey of Tl in 244 samples of arable soils across France showed a median concentration of 0.29 mg Tl kg^{-1}, a mean value of 1.5 mg Tl kg^{-1} and a 90th percentile of 1.54 mg Tl kg^{-1} [92].

Soils developed on Jurassic Oolitic limestone in adjacent areas of the Jura Mountains in Switzerland and France have been found to contain anomalously high concentrations of Cd (up to 22 mg kg^{-1}) and Zn (up to 864 mg kg^{-1}), but the Cd and Zn concentrations in the limestone rock were much lower (<4.9 mg Cd kg^{-1} and <207 mg Zn kg^{-1}). The enrichment of the Calcaric Cambisol soil in this area, relative to its parent material, is probably due to vertical pedogenic processes involving the weathering of underlying rock and debris from upslope limestones and the accumulation of resistant Zn-containing minerals [41, 76].

Phosphorites

Phosphorites are sedimentary rocks containing high concentrations of phosphate minerals, mainly apatite ($Ca_5(F, Cl, OH)(PO_4)_3$) which have formed in several possible ways, usually on the ocean floor, and are often accompanied by other sedimentary strata which may include limestone, shales, cherts and sandstones. Large accumulations of bird excreta (guano) over a very long time-scale have reacted with underlying limestones and given rise to some important phosphorite deposits in some places such as certain Pacific islands. These deposits have been utilised as raw materials for the manufacture of P fertilisers and most have been completely consumed. Phosphorites are generally enriched in several heavy metal (loid)s to a greater extent than black shales, for example Ag by a factor of 20 times, U by 30 and Cd by 50 [85]. Silva et al. [17] compared concentrations of metals in samples of phosphorites from a mine in Tunisia with other phosphate rocks from around the world and the maximum concentrations found (in mg kg^{-1}) were: Cd 62.5, Cr 490, Cu 110, Ni 180, Pb 500, U 150 and Zn 1,850. Perhaps more important than their contribution to the heavy metal(loid) content of soils developed on them, is the impact of these rocks on soils of all types when they are used as raw materials for manufacturing P fertilisers (see Sect. 2.3.2.2 Inorganic Fertilisers). Page et al. [73] refer to mean concentrations of 25 mg Cd kg^{-1} in phosphorites with maximum values of <500 mg Cd kg^{-1}.

Very high Cd concentrations have been found in soils developed on phosphorites derived from guano in Jamaica. Concentrations of <930 mg Cd kg^{-1}, of lithogenic origin were found in soils which had not been contaminated from anthropogenic sources. The Hope phosphorite (rock) from Manchester Parish in Jamaica contained (in mg kg^{-1}): Cd up to 6,200, Zn 12,300 and U 166 [31]. A similar deposit, the Spitzbergen phosphorite, also in this part of Jamaica, contained up to 16,540 mg Cd kg^{-1} and 6,103 mg Zn kg^{-1}. Owing to their very high Cd content, these phosphorites have been described as ‘cadmiferous’.

Ultramafic Rocks

Ultramafic rocks of various types, including serpentinites, peridotites and pyroxenites, outcrop in several parts of the world. Although, on a global scale the soils developed on them do not occupy a very large total area, they are particularly notable because of their relatively high concentrations of Ni, Cr, and Co, low Ca:Mg ratios and low levels of P and K which only adapted plant species (‘serpentine flora’) can tolerate. The high Co, Cr, Cu and Ni values in northern Californian soils shown in Table 2.1 are due to ultramafic parent materials. The UK Soil and Herbage Pollutant Survey (UKSHS) found that mean Cr and Ni concentrations were higher in the rural soils of Northern Ireland than in the rest of the UK due to the greater occurrence of mafic and ultramafic soil parent materials there [83].

Concentrations of up to 10,000 mg Ni kg^{-1} (1%) have been found in soils developed on ultramafic rocks whereas normal Ni concentrations in soils on other parent materials are frequently <500 mg Ni kg^{-1} [75]. In California, Cr concentrations in ‘serpentine’ soils ranged between 1,725 and 5,910 mg kg^{-1} [32, 72]. In Galicia, northern Spain, serpentine soils contain up to 1,162 mg Cr kg^{-1}, 940 mg Ni kg^{-1} and 150 mg kg^{-1} Cu, compared with up to 50–100 mg Cr and Ni kg^{-1}

and 5–25 mg Cu kg^{-1} for local control soils on other parent materials [65] (see also Chap. 11).

Sedimentary Ironstones

All Fe oxide-rich sediments, including ‘ironstones’ which are defined as containing >30% Fe oxides, are generally found to have accumulated relatively high concentrations of As, Ba, Cu, Mn, Mo, Ni, Pb, V and Zn [80]. Sedimentary ironstone formations are found in many parts of the world and many of them are exploited as Fe ore deposits. In Lincolnshire, in the UK, ironstone deposits of Lower Jurassic and Lower Cretaceous ages have accumulated significant concentrations of As and soils developed on them have up to 342 mg kg^{-1} total As. However, this As has an extremely low bioaccessibility and hence does not constitute a significant hazard to health even though maximum total concentrations are 17 times higher than the UK soil guideline value of 20 mg As kg^{-1} [7].

Metallogenic Mineralization

Metalliferous ores can give rise to anomalously high concentrations of heavy metal (loid)s in soils when outcrops of rocks containing these ores undergo natural (geochemical) weathering *in situ*, or the products of weathering are dispersed locally by geomorphological processes and undergo subsequent weathering. However, much larger areas can be affected by anthropogenic pollution when these ores are mined and smelted. Ores are naturally occurring concentrations of minerals with a sufficiently high concentration of metal(loid)s to render them economically worthwhile exploiting. ‘cut-off’ grades of metals in an ore mineral, which are the contents above which it is economical to exploit a mineral deposit, have been gradually decreasing as the demand for metals has increased and the technology of mineral extraction has improved. For example, the average grade of ore mined by the Cu industry throughout the world has decreased from around 13% Cu in 1770 to <1% Cu in 2007 [77]. This trend of mining lower grade ores has resulted in increasingly greater percentages of waste being produced per tonne of metal extracted and larger areas disrupted and contaminated by mining operations. Mineral deposits often contain exploitable concentrations of several ore minerals (in addition to the principal ore) allowing a range of different metals to be produced. Minerals containing concentrations of metal(loid)s below their cut-off grades are referred to as ‘gangue minerals’ and in the past these were usually discarded after mining along with country rock. As a consequence, the wastes from historic mining operations often contain significant concentrations of a wide range of heavy metal (loid)s which constitute a potential environmental hazard, but, on the other hand, may now be worth reprocessing for metal production. From Table 2.3 it can be seen

Table 2.3 Common ore minerals of heavy metals and metalloids and the elements associated with them

Metal	Ore minerals[a]	Associated heavy metals/metalloids
Ag	Argentite (Ag_2S), PbS	Au, Cu, Sb, Zn, Pb, Se, Te
As	Arsenopyrite (FeAsS), AsS, Cu ores	Au, Ag, Sb, Hg, U, Bi, Mo, Sn, Cu
Ba	Barite ($BaSO_4$)	Pb, Zn
Cd	Sphalerite (ZnS)	Zn, Pb, Cu
Co	Cobaltite ((Co,Fe) AsS)	Fe, As, Sb, Cu, Ni, Ag, U
Cr	Chromite (Fe, Cr_2O_4)	Ni, Co
Cu	Bornite (Cu_5FeS_4), Chalcocite (Cu_2S) Chalcopyrite ($CuFeS_2$), Cu[b]	Zn, Pb, Cd, As, Se, Sb, Ni, Pt, Mo, Au, Te
Hg	Cinnabar (HgS), Hg[b], Zn ores	Sb, Se, Te, Ag, Zn, Pb
Mn	Pyrolusite(MnO_2)	Co, Ni, Zn, Pb
Mo	Molybdenite (MoS_2)	Cu, Re, W, Sn
Pb	Galena (PbS)	Ag, Zn, Cu, Cd, Sb, Tl, Se, Te
Sb	Stybnite (Sb_2S_3)	Ag, Au, Hg, As
Sn	Cassiterite (SnO_2)	Nb, Ta, W, Rb
U	Uraninite (UO_2)	V, As, Mo, Se, Pb, Cu, Co, A
V	Vanadinite ($Pb_5(VO_4)_3Cl$), p and Fe ores, crude oil etc.	U, Pb
W	Wolframite ((Fe, Mn) WO_4)	Mo, Sn, Nb
Zn	Sphalerite (ZnS), Smithsonite ($ZnCO_3$)	Cd, Cu, Pb, As, Se, Sb, Ag, In

References: Peters [74], Rose et al. [82] and others

[a] Selected ore minerals – most heavy metals have several different ores but the associated elements apply to most sources of the metals/metalloids

[b] Native metal

that many heavy metal ore minerals and gangue minerals (such as arsenopyrite) are sulphides and consequently their oxidation during weathering gives rise to acid soils (and acid mine drainage) which promotes the solubility and mobility of cationic forms of metals. Almost all ore minerals also contain significant concentrations of several other metals and metalloids as inclusions in their crystal structure, as shown in Table 2.3. These ‘guest’ elements, together with associated gangue minerals, are the reason that soils in mineralized areas and those contaminated by mining and smelting usually contain a wide range of heavy metal(loid)s at elevated concentrations.

In addition to elevated concentrations of heavy metal(loid)s from mining contamination (Sect. 2.3.2.2 Non-ferrous Metalliferous Mining and Smelting), the weathering of ore minerals will result in the dispersion and plant uptake of metal (loid)s at undisturbed mineralized sites and this is sometimes referred to as ‘natural pollution’. For example the weathering of a low-grade PbS (galena) ore deposit and natural dispersion down-slope of weathering products over several thousand years since the last glaciation has resulted in the formation of patches of barren ground within a forest in southern Norway [48]. Concentrations of $<100{,}000$ mg Pb kg^{-1} have accumulated in these patches which are too toxic for plants, but a tolerant strain of the grass *Deschampsia flexuosa* grows in adjacent areas with lower Pb concentrations (Alloway, 1976, personal communication).

2.3.2 Anthropogenic Sources of Heavy Metals and Metalloids

Heavy metal(loid)s from anthropogenic sources can be described as either contaminants or pollutants, but there is a convention for using 'contaminants' (and contamination rather then pollution) in the context of soil and land. The importance of contamination is clearly shown in a comparison of analytical data for relatively large numbers of background soils with the results for soils affected by anthropogenic contamination from various sources (urban, agricultural, mining or smelting activities) across the USA by Burt et al. [9]. The surface horizons of representative soil profiles (pedons) of 312 non-anthropogenic and 392 anthropogenically-affected soils, respectively, had the following median total concentrations (in mg kg^{-1}): Cd 0.16 and 0.22, Cu 16 and 33, Pb 10 and 48 and Zn 60 and 73. Mercury contents were 44 and 170 μg kg^{-1}, respectively. The maximum values for some of these metals in the anthropogenic group were up to 32 times higher (for Cd) than in the background soils, with Cu and Pb being around ten times higher.

For soil contamination to occur the metal(loid)s have to be transported from a source to the soil at a particular location. The main mechanisms by which heavy metal(loid) contaminants are transported from source to the soil site are:

- moving air currents (wind) and deposition of dust, aerosol sized particles (<30 μm) and gaseous forms of metals (e.g. Hg),
- moving water (runoff and/or flooding rivers) followed by deposition of metal(loid)- containing soil down-slope or on alluvial soil in the case of flooding rivers,
- down-slope movement of metal-rich rock and contaminated mineral material or soil by gravity,
- intentional placement by tractors, sprayers, manure spreaders, lorries and earth-movers of heavy metal(loid)-containing materials.

Contamination can be either extensive (affecting large areas) or localised.

2.3.2.1 Extensive Contamination

Atmospheric Deposition

Atmospheric deposition is the most extensive form of contamination because long-range transport can result in particles being carried very long distances (thousands of km), although much contamination from this source tends to be more localised (few km). Sources of metal(loid)s emitted into the atmosphere (usually as particles) include: coal and oil-fired electricity generating stations, industrial emissions from smelters, foundries and other pyrometallurgical industries, motor vehicle engine exhaust emissions and dusts from tyre and brake lining wear, smoke and other emissions from industrial and domestic heating, accidental fires, bonfires and corrosion of metal structures, such as galvanised (Zn-coated) roofs. The transfer of metal(loid)-containing particles from the atmosphere to soils or water can be by wet, dry or occult deposition, but when monitored, it is often collected and measured as combined ‘bulk deposition’. Although large areas can be affected, in most cases, except for very local sites, deposition rates are the lowest of all those from the different transport mechanisms listed above because of the dilution of atmospheric emissions in a large mass of moving air. However, the contamination process often continues for longer than the other mechanisms and the total inputs from this route can be very significant. The spatial distribution of pollutants reaching soil in this form is also the most evenly spread and metal(loid) concentrations are highest in the surface layer of the soil profile (see also Chap. 8 on Critical Loads).

Some examples of the inputs of heavy metal(loid)s from atmospheric deposition are given in Table 2.4. It is difficult to compare sets of data for atmospheric deposition from different countries because a variety of different sampling methods have been used and there is no generally accepted monitoring protocol. There is often a wide variation in metal deposition within some countries. For example, in different parts of Norway, deposition of Pb, Cd, As, Sb and Bi can vary by more than one order of magnitude even when the effects of local pollution sources are excluded (Steinnes, pers comm.). Some methods of monitoring are based on the analysis of mosses (which trap atmospheric particles in their leaves) and others use funnels of various types to collect bulk deposition. Total suspended particulates (TSP) are normally monitored by specialised pumped filtration systems which separate suspended particles into different size ranges, which are later analysed separately.

Analytical surveys in Europe have shown that concentrations of Cd and Pb in mosses decreased between 1990 and 2000, with Pb declining to a greater extent. However, Hg concentrations remained relatively constant across Europe during the period 1995–2000 [34]. The data for England and Wales and those for New Zealand shown in Table 2.4 are all based on the collection of bulk deposition using inverted Frisbee-type collectors. However, these collectors have been found to over-estimate the small particulate fraction due to the capture of some locally suspended and re-deposited dust and soil particles. In the light of this, the ‘original’ data of Alloway et al. [1] have subsequently been adjusted by Nicholson et al. [70], using more recent dry deposition data and the results of surveys of mosses in the UK. These moss surveys in 1995 and 2005 showed a decrease in deposition with time in the UK [34]. The effects of these calculations by Nicholson et al. [70] were to reduce the original England and Wales deposition values by between 80% (Pb) and 35% (Cu), with no change in Hg deposition. These adjusted data are shown in Table 2.4.

The values in Table 2.4 for Finland show much lower levels of deposition than in all the other sets of data and is probably a reflection of lower levels of atmospheric pollution. However, the results from all the different countries show higher levels of Zn deposition than of any other heavy metal(loid). Of particular interest is the comparison (in the original Alloway et al. 2000 data) between the 34 sites in rural locations in England and Wales (remote from obvious sources of contamination) and the site 2 km downwind from a large Zn–Pb smelter in south west England. Bulk deposition near the smelter was greater than the national mean for England

Table 2.4 Atmospheric deposition of heavy metals and metalloids in several countries (g ha^{-1} year^{-1})

	England and Wales[a]		England smelter[b]	Switzerland	Finland	New Zealand[c]	All China[d]	Yangtze River Delta	Los Angeles[e]
	(34)								
	Original	Adjusted	(1)	(16)	(8)	(7)	(72–148)	(43)	(6)
As	3.1	0.9	27	–	–	–	28 (4–117)	15.7 (3.8–58.4)	–
Cd	1.9	0.7	66.9	0.8	0.2	0.2	4.0 (0.4–25)	4.1 (0.9–20.7)	–
Cu	56.8	37	138	18.0	5.0	35.4	108 (2.3–409)	139 (40–589)	76.7
Hg	1.0	1.0	2.2	–	–	–	1.4 (0.2–5)	0.3 (0.04–0.9)	–
Ni	16.0	8.0	15.1	11.0	1.5	9.5	58 (6.3–138)	46 (15–114)	18.9
Pb	54.0	11.0	1,766.8	28.0	5.7	23.0	202 (5.1–756)	359 (83–2,530)	69
Zn	221.3	112.0	3,557.0	119.0	20.0	1025.0	647 (29–1,484)	895 (144–3,730)	438

References: Alloway et al. [1]; Gray et al. [33]; Nicholson et al. [68, 70]70; Luo et al. [54]; Lim et al. [52]; Huang et al. [38]

NB sampling protocols differ between most countries

[a] Mean of 34 sites (with duplicate samplers) over 42 months (1995–1998); Original = data in Alloway et al. [1]; Adjusted = Original data adjusted using other later dry deposition and moss surveys

[b] Smelter data from Alloway et al. [1]

[c] Mean of seven New Zealand pastoral sites over 2 years

[d] Non-systematic sampling 1999–2006 representative of all of China

[e] Total suspended particulates measured for 24 h in each of four seasons at six urban sites (August 2003–June 2003)

and Wales by a factor of 35 for Cd, 32 for Pb, 16 for Zn, 8.7 for As and 2.4 for Cu [1]. The data in Table 2.4 for New Zealand show values with similar orders of magnitude for most metals, except that Zn is much higher than the mean and maximum values for England and Wales, but lower than for the smelter site. Unlike England and Wales, New Zealand is neither highly populated, nor heavily industrialised, but the very high Zn deposition is considered to come from the dispersion of Zn from the corrosion of galvanised (Zn-plated) roofing material which is widely used in New Zealand [33]. This is supported by the TSP data for a suburb of Paris, France, which showed relatively high Zn concentrations considered to be due to the large number of galvanised roofs in the city and its suburbs [2].

An inventory of inputs of trace elements to agricultural soils in China showed that 58–85% of the inputs of As, Hg, Pb and Ni, 35% of Cd, 40% of Zn and 43% of Cr were derived from atmospheric deposition. Table 2.4 shows that Zn deposition in China was also higher than that of any other element measured. Total annual deposition of Zn in China amounted to around 79,000 t, which comprised around 40% of total inputs of Zn to soil. The highest Zn input (96,000 t) was from livestock manures [54].

The values in Table 2.4 for all of China and the separate data for the Yangtze Delta, one of the fastest developing regions in China, both show levels of heavy metal(loid)s which are generally much higher than for England and Wales and all the other sampling locations, except in the case of Hg in the Yangtze Delta. The monitoring in the Yangtze Delta was more systematic and therefore likely to be more reliable than the data for the whole of China. In comparing these two sets of data, the Yangtze is higher than the whole of China for all elements except As and Ni. Concentrations in the Yangtze Delta are higher than those for England and Wales (Alloway et al. data)[1] by factors of 5 for As, 2.2 for Cd, 17.6 for Cr, 2.4 for Cu, 2.9 for Ni. 6.6 for Pb and 4 for Zn. Although the sampling protocols were different, it is obvious that soil contamination from atmospheric deposition is much greater in China than in England and Wales or even Los Angeles, which is slightly higher than England and Wales for all elements except Ni. Multivariate statistical analysis of the Yangtze Delta data showed that As, Hg, Cd, Mo, S and Zn were associated with road traffic emissions, Cr and Ni with pyrometallurgical processes, Fe and Mn from the resuspension of soil particles, and Pb and Se from coal burning [38]. Coal and oil combustion can be significant contributors of As, Cd, Cr, Hg, Ni, Pb, Se, Th, U and V in atmospheric deposition, depending on the composition of the coal used [27, 28]. In China, coals have been found to contain $<3.5\%$ As [53]; in the UK, coals can contain <137 mg Pb kg^{-1} [21] and in the USA coals can contain <73 mg Se kg^{-1} [15] and average contents of 1.3 mg U kg^{-1} and 3.2 mg kg^{-1} thorium (Th) [28].

In Europe, the AROMIS project calculated the following rates of inputs of metals from the atmosphere to agricultural land (in g ha^{-1} year^{-1}) as: Cd 0.2–3.3, Cr 0.5–8.9, Cu 4–379, Ni 1.5–68, Pb 6–415, and Zn 20–50. However, the original Alloway et al. [1] results were used (together with other data) in these calculations. Atmospheric deposition was the second most important source (after livestock manures) of Cu and Zn (1–39% Cu and 8–49% Zn) in agricultural soils in the 22 European countries involved in the study [19].

Using different monitoring methods, Pb in suspended atmospheric particles near Paris was shown to have decreased by a factor of 13, from 200 ng m^{-3} in 1994 to 15 ng Pb m^{-3} in 2003 [2]. In the north-western Mediterranean, near Nice, France, metals of anthropogenic origin (Cd, Pb and Zn) showed a marked decrease in suspended particles over the last two decades: Pb by 900%, Cd by 66% and Zn by 54%, but lithogenic elements such as Al, Fe, Mn, and Co showed no overall trend [35]. In contrast to Europe, the average concentrations of Pb, Cu, Zn and Mn in TSP in Beijing, China, were found to have increased during the period 2002–2005, but showed a decrease in 2006. These average concentrations were five to ten times higher than in several other Asian countries including Bangladesh, Vietnam, Hong-Kong, Korea, Taiwan, Pakistan and Japan. The maximum average Pb and Zn contents in TSP (694 ng Pb m^{-3} and 1,214 ng Zn m^{-3}) occurred in China, the maximum average Cu content (235 ng m^{-3}) occurred in Taiwan and the maximum Cr (299 ng m^{-3}) occurred in Japan. The concentrations of metals were highest in the $PM_{2.5}$ fraction, with the highest $PM_{2.5}$ Pb being found in Hong Kong (91,260 ng Pb m^{-3}) [39]. These data indicate that the atmospheric pollution levels are not decreasing in many parts of Asia and that the most rapidly developing cities and industrial regions have the highest levels of atmospheric heavy metal pollutants (See also ‘critical loads’ in Chap. 8).

Flooding and Sediment Deposition

Heavy metal(loid)-containing particles from various sources are carried in suspension in rivers and when these flood much of the suspended sediment in the water overflowing onto land will be deposited on alluvial soils. One of the most common historic sources of heavy metal(loid) contamination of alluvial soil is sediment from metalliferous mines. These sediments are finely ground particles of ore, gangue minerals and country rock which were separated from the bulk of the metal ore during the processing of the material extracted from the mines. These fine particles of mine waste are known as ‘tailings’ and in the past they were often discharged straight into streams and rivers. In the UK, The Rivers Pollution Prevention Act of 1876 required all effluent from mineral separation at mines to be channelled through two ponds in succession to allow sediment to settle-out before being discharged into rivers. This was effective in reducing sediment loads in the rivers by around 90%, but unfortunately the law did not specify what should be done with the sediment cleaned out of the ponds. This was usually dumped in piles beside the water courses which then resulted in the tailings being eroded from these piles by rain and wind and to continue to contaminate the rivers for more than 130 years following the introduction of the law.

Modern mining methods normally involve the indefinite storage of tailings in large lagoons behind dams, but occasionally these dams fail causing widespread soil and water contamination by deep layers of ‘tailings mud’ as happened at the Aznalcóllar Mine in southern Spain in 1998 and other places around the world since then. It can be seen from the international literature that contaminated mine sediment is a very common source of heavy metal(loid) contamination of alluvial soils all over the world, but some of the worst affected valleys are those where mining activity dates back possibly 200 years or more. In a review of metal-mining contaminated sediments in England and Wales, Hudson-Edwards et al. [39] refer to concentrations of heavy metal(loid)s in alluvial soils and overbank sediments in catchments contaminated by metal mining (in mg kg^{-1}) of: Cd <117, Cu <5,318, Pb <26,800 and Zn <38,000.

2.3.2.2 Localised Contamination

Agriculture and Horticulture

Intentional Placement of Organic Materials Such as Livestock Manures and Sewage Sludges

Livestock Manures. These are a ubiquitous source of heavy metal(loid) inputs on livestock farms and the amounts of elements involved are strongly influenced by the quantities added to animal feed. In the case of pigs and poultry in Europe, relatively large amounts of Cu and Zn have been routinely fed in the past, with concentrations of up to 140 mg Cu kg^{-1} and 800 mg Zn kg^{-1} in ‘creep’ feed for piglets prior to weaning, decreasing to around 200 mg Zn kg^{-1} for older fattening pigs. Since the levels to satisfy nutritional requirements are only 4–5 mg Cu kg^{-1} and 40–60 mg Zn kg^{-1}, the additional amounts are added to the feed to act as a growth promoter [19]. In 2003, much lower maximum permitted levels in animal feeds were introduced in the EU. For pigs, these are now in the range (in mg kg^{-1}): 25 Cu (17 weeks–6 months) to 170 Cu (up to 12 weeks), for poultry: 25 Cu and 150 Zn, for cattle: 15–35 Cu and 150 Zn, and for sheep: 15 Cu and 150 Zn [70]. In the USA, an organic As-containing compound (‘roxarsone’) has been widely fed as a growth promoter to broiler chickens since the 1960s, but it was banned in the European Union in 1999. This implies that elevated amounts of As are added to soils when poultry litter (manure) typically containing 30–50 mg As kg^{-1} is recycled to soil [5, 29].

Table 2.5 shows data for the heavy metal concentrations in livestock manures of different types in Europe (AROMIS project) and China [19, 54]. The AROMIS project collected a much larger number of samples from representative farms in 21 European countries. A comparison of the two sets of data show much higher levels of all metals except Zn in the Chinese manures. Perhaps most noteworthy is Cd which is around ten times higher in the Chinese manures. However, both data sets show that, in general, pig slurry contains the highest levels of Cu and Zn, with maximum values in the European samples exceeding 1,000 mg Cu kg^{-1} and 5,000 mg Zn kg^{-1}, mainly due to high levels of Cu and Zn additives in the feed. Similar values were also found for pig FYM. Poultry manure contained more Zn than cattle manure and levels in both the Chinese and European samples were similar. Both the AROMIS project in Europe and work by Luo et al. [54] in China

Table 2.5 Heavy metal concentrations in livestock manures in Europe (AROMIS project) and China (mg kg^{-1} dry solids)

Manure		Cd	Cr	Cu	Ni	Pb	Zn
Europe							
Cattle FYM	W. mean[b]	0.3	7.5	23	4.4	3.8	119
	Range	(0.04–3.1)	(0.1–170)	(0.3–191)	(0.2–28)	(0.1–92)	(9.6–691)
	No.	348	200	345	175	331	345
Cattle slurry	W. mean	0.4	6.9	42	6.2	5.6	207
	Range	(0.04–5.5)	(0.2–170)	(0.1–741)	(0.1–57)	(0.1–75)	(2.0–1,908)
	No.	680	431	720	475	679	721
Pig slurry	W. mean	0.3	9.4	193	12	3.0	934
	Range	(0.02–4.0)	(0.2–37)	(12–1802)	(0.1–50)	(0.3–112)	(5.0–5,832)
	No.	1,128	235	1,143	180	1,126	1,143
Broiler chicken and turkey FYM	W. mean	0.4	20	89	6.2	3.7	353
	Range	(0.1–1.2)	(1.3–80)	(8.4–760)	(2.2–21)	(1.0–24)	(52–790)
	No.	102	49	105	46	102	105
China (2003)							
Cattle manure (42[a])	Mean	3.4	15.2	46.5	14.1	15.7	152
Pig manure (61)	Mean	4.8	46.6	473	12.5	10.1	843
Chicken manure (70)	Mean	3.4	46	102	15.9	20.6	309

References: Eckel et al. [19]; Luo et al. [54]

[a] Number of samples

[b] Weighted mean

found that livestock manures were the most important inputs to soils for Cu (29–72% in Europe and 69% in China) and Zn (29–65% in Europe and 51% in China).

Sewage Sludges. Sewage sludges (or ‘biosolids’) are the insoluble residues from the treatment of waste waters at sewage treatment plants. Due to their beneficial contents of N, P and organic matter, they are frequently recycled to agricultural land where they have a significant fertiliser value. However, the concentrations of heavy metal(loid)s are a major constraint in the amounts of sludge that can be applied to soils (see Table 2.6). The heavy metal(loid)s in sewage sludges are the result of inputs from human excreta, domestic ‘grey’ water from baths, showers and dish-washing, run-off water from roofs and roads and industrial waste waters discharged into the sewers and processed in sewage treatment plants (STPs). Sludges from different STPs can vary considerably in composition depending on the sources of discharges in their catchment area. Heavy metal(loid) contents of sludges at individual STPs, also vary significantly on a weekly or even daily basis as a result of differences in the composition and volume of discharges into sewers. Regulations introduced in Europe, the USA, Australia, New Zealand and many other technologically developed countries over the last 20 years or more have established both maximum concentrations of selected ‘heavy metals’ allowed in sludges which are applied to agricultural land and maximum permissible concentrations of

Table 2.6 Average contents of heavy metals in sewage sludges in member states of the European Union

Sludges (mg kg^{-1} dry solids)					Soils (mg kg^{-1})					
					Proposed new soil limits 1[d]					
				Current EU soil limits[c]	*Moderate changes*			*More significant changes*		
Metal	EU weighted[a] mean	Range[b]	EU limits[c]	pH 6–7	pH5–6	6–7	>7	pH5–6	6–7	>7
Cd	2.0	0.4–3.8	20–40	1–3	0.5	1	1.5	0.5	1	1.5
Cr	73	16–275	1,000–1,750	–	50	75	100	50	75	100
Cu	330	39–641	1,000–1,750	50–140	30	50	100	30	50	100
Hg	–	0.3–3	16–25	1–1.5	0.1	0.5	1	0.1	0.5	1
Ni	36	9–90	300–400	30–75	30	50	70	30	50	70
Pb	104	13–221	750–1,200	50–300	70	70	100	70	70	100
Zn	811	142–2,000	2,500–4,000	15–300	100	150	200	20	20	200

References: Eckel et al. [19]; Milieu et al. [63]; Langenkamp [50]

All values are ‘total’ concentrations based upon *aqua regia* digestion

[a] Weighted mean for EU based on data for sludges reported by Member States (Eckel et al. [18])

[b] Range of average metal contents for individual EU Member States

[c] Directive 86/278/EEC

[d] JRC Ispra proposed limits for soils

'heavy metals' in soils receiving sludges. These regulations are intended to avoid the accumulation of excessive concentrations of elements which could cause either ecotoxicity in soils and/or phytotoxic effects in crops. However, sewage sludges have been applied to land in some countries for more than 100 years and during this time some of these sludges and the soils to which they were applied would almost certainly have had higher concentrations of some heavy metal(loid)s than are permitted nowadays. In 2010, total sewage sludge production in the 27 Member States of the EU was around 11.6 Mt (dry solids), of which 88% was produced in the 15 states which were members before the expansion of the EU in 2004 [63].

The data in Table 2.6 show much narrower ranges of heavy metal(loid) contents in the sewage sludges of EU member states from relatively recent analyses than the range for the world [43] which includes values from the literature over many years. The weighted mean values for EU sludges are all well below the preferred EU limit values with only Cu and Zn coming within 33% of the lower limit values. It is important to note the very high maximum values from the world range, but these probably date back to a time before the introduction of regulations in many countries to reduce the heavy metal(loid) concentrations in both the wastewater (sewage) and the sludges derived from it. The EU limits are now quite old, dating back to 1986. There has been much work done on revising them, but so far, no new Directive has been issued. The proposed new limit values (shown in Table 2.6) show that greater importance is now attached to soil pH due to its effect on heavy metal(loid) availability and in all cases the maximum permitted soil total concentrations are lower than the 'old' maximum values in the 1986 Directive. Even in soils with pH >7, where most metals will be least available, the Cd limit is reduced from 3.0 to 1.5 mg kg^{-1}, Cu from 140 to 100 mg kg^{-1} and Zn from 300 to 200 mg kg^{-1}. Individual EU Member States are allowed to have more conservative limits than those shown and some countries, such as the Netherlands, have actually banned the application of any sludges to soil. However, there will still be residues from sludges applied before this regulation came into being. In addition to the elements included in Table 2.6, Kabata-Pendias [43] gives the world ranges for other heavy metal(loid)s in sludges (in mg kg^{-1} DW) including: As <26, Ba <4,000, Mn <39,000, Sn <700 and V <400.

Inorganic Fertilisers. Macronutrient fertilisers are ubiquitous sources of heavy metal(loid) inputs into agricultural soils in most parts of the world, except for some of the poorest developing countries where little fertiliser is used. The macronutrients most commonly used to improve plant growth and yield are the 'primary macronutrients' nitrogen (N), phosphorus (P) and potassium (K). Compounds of these nutrients are applied to the soil either individually as required, or more frequently together in various combinations as 'compound fertilisers', such as NPK or NP and so on. In 2007/2008 the world supply of macronutrient fertilisers was 206.4 Bt and was predicted by the FAO to rise to 240.7 Bt by 2012 [25]. The 'secondary' macronutrients calcium (Ca), magnesium (Mg) and sulfur (S) are also applied as fertilisers, although Ca is most commonly applied as lime (usually as $CaCO_3$) to raise the pH of acid soils and Mg may also be applied in dolomite

Table 2.7 Concentrations of heavy metals/metalloids in phosphatic and nitrogen fertilisers, limestones and manures in all countries and median concentrations in EU fertilisers (mg kg^{-1})

	Phosphatic fertilisers		Nitrogen fertilisers		Lime fertilisers		Manures
	World range	EU median	World range	EU median	World range	EU median	World range
As	2–1,200	–	1–120	–	0.1–24	–	3–150
Ba	200	–	–	–	120–250	–	270
Cd	0.1–170	13	0.05–8.5	0.9	0.04–0.1	0.2	0.3–0.8
Co	1–12	–	5–12	–	0.4–3.0	–	0.3–24
Cr	66–600	60	3–19	3.4	10–15	6.5	5.2–55
Cu	1–300	26	1–15	2.0	2–125	5.6	2–60
Hg	0.01–1.2	–	0.03–3	–	0.05	–	0.09–26
Mn	40–2,000	–	–	–	40–1,200	–	–
Mo	0.1–60	–	1–7	–	0.1–15	–	0.05–3
Ni	7–38	22	7–38	6.0	10–20	6.3	7.8–30
Pb	7–225	13	2–1,450	1.9	20–1,250	8.2	6.6–350
Se	0.5–25	–	–	–	0.08–0.1	–	2.4
Sn	3–19	–	100–5,420	–	0.5–4	–	3.8
U	10–800	–	–	–	–	–	–
V	2–1,600	–	–	–	20	–	–
Zn	50–1,450	236	1–42	5.0	10–450	22	15–250

References: Kabata Pendias [44]; Eckel et al. [19]

($MgCO_3$. $CaCO_3$) for the same purpose. In addition to these macronutrient fertilisers and liming agents, essential trace elements (micronutrients) are also applied to either the soil or plant foliage in specialised micronutrient fertilisers and a range of compounds of B, Cu, Co, Fe, Mn, Mo, Ni and Zn are used for this purpose (see Chaps. 7, 12, 13 and 17).

Most of the inorganic compounds used in macronutrient fertilisers contain significant concentrations of contaminant heavy metals and metalloids, although in some cases this can be beneficial where the ‘contaminant’ is a micronutrient such as Zn, but it depends on the amounts supplied. Phosphatic fertilisers generally contain the highest concentrations of most heavy metal(loid)s including As, Cd, U, Th and Zn. Sedimentary phosphate rock (phosphorite) deposits, which are by far the largest source of P for fertilisers, are widely recognised as being enriched in a large number of elements (see Sect. 2.3.1.1 Phosphorites). As a result of the contaminants contained in fertilisers, frequently fertilised arable soils can accumulate significant concentrations of some heavy metal(loid)s if the contents in the fertilisers were relatively high.

In Table 2.7, it can be seen that P fertilisers around the world can contain a wide range of most heavy metal(loid)s with the greatest variations being in Cd (1700-fold variation), V (800-fold) and As (600-fold). Relatively high Cd contents in many P fertilisers are a major cause of concern. In Australia, P fertilisers made from guano-derived phosphorites have had Cd contents of <300 mg Cd kg^{-1} in the recent past and contributed 30–60 g Cd ha^{-1} to soils [57] (see also Sect. 2.3.1.1 Phosphorites and Chap. 10, Sect. 10.3). It is interesting to note that

Nicholson et al. [69] found that inputs of Cd to soils in England and Wales were nearly as high from lime as they were from P fertilisers. This was due to the much larger amounts of lime applied to soils than P fertilisers and not due to particularly high Cd contents in the lime. The high Zn contents often found in P fertilisers have been a useful source of this micronutrient in sandy and calcareous soils in many parts of the world. However, a recent move towards using 'high analysis' P fertilisers, such as mono- or diammonium phosphate, which have lower contents of Zn and other heavy metal(loid) contaminants, will necessitate the application of more Zn fertilisers in future, but on the other hand, they cause less soil contamination.

The AROMIS project showed that the mean input of heavy metals from fertilisers on a total of 37 farms (both livestock and crops) were (in g ha^{-1} $year^{-1}$): Cd 2.2, Cr 24, Cu 4.3, Ni 6.7, Pb 5.2 and Zn 49. The metal concentrations in superphosphate that were used in the calculation of these values (in mg kg^{-1}) were: Cd 23, Cr 233, Cu 41, Ni 60, Pb 39 and Zn 557 [19].

Micronutrient fertilisers supplying the 'essential' metals, mainly Cu or Zn, will give rise to significant inputs of these metals, but they would normally only be used where the available Cu or Zn status of the soil is low. In England and Wales, around 5% of cereal growing sites are deficient in Cu and applications of Cu fertiliser compounds add a total of around 28 t Cu per year to soils in these two countries [70].

Industrial by-products, such as flue dusts from electric-arc furnaces and various slags, have been used to make Zn fertilisers and can give rise to unacceptably high concentrations of various potentially toxic heavy metal(loid)s including Pb (<5.2%) and Cd (<0.22%). If these materials are regularly used, in addition to rectifying a deficiency of Zn, the soil could end up by being significantly contaminated with both Pb and Cd. Some proprietary micronutrient mixes can also have significant impurities, such as <55 mg/kg Cd, <0.36% Pb and <83 mg As kg^{-1} [94].

Agricultural Chemicals – Fungicides. Various inorganic heavy metal(loid) and organo-metallic compounds have been used as fungicides on field and plantation crops. These include: Pb arsenate ($AsHO_4Pb$), Cu acetoarsenate ($C_4H_6As_6Cu_4O_{16}$ 'Paris Green'), 'Bordeaux Mixture' ($CuSO_4.5H_2O + Ca(OH)_2$), Cu oxychloride ($3Cu(OH)_2$. $CuCl_2$) and phenyl mercuric chloride (C_6H_5ClHg). Soils from apple orchards in Virginia, USA treated with heavy metal(loid) fungicides and insecticides were found to contain the following median and maximum concentrations, respectively: (in mg kg^{-1} except for Hg): Cu 26.3 (<156), Zn 59.3 (<220), As 21.9 (<263), Pb 88.7 (<1,150) and Hg 59.5 μg kg^{-1} (<674 μg kg^{-1}). The elevated As and Pb were due to residues from the use of $AsHO_4Pb$ [80].

Copper-based fungicides have been used in vineyards since 1885 and a literature review by Komárek et al. [46] found reports of concentrations of <3,216 mg Cu kg^{-1} in vineyard soils, but most contained <700 mg Cu kg^{-1}. The highest values (>3,000 mg Cu kg^{-1}) were from a vineyard in Brazil which was more than 100 years old. A single application of Bordeaux Mixture to vines in the Champagne region of France added 3–5 kg Cu ha^{-1} and between three and ten applications were usually made each year. In Northern Spain, vineyard soils which had received Cu-based fungicides washed off foliage over many years had a mean Cu content of 205 mg Cu kg^{-1} (42–583). Sediments derived from eroded vineyard soils on slopes contained a mean concentration of 423 mg Cu kg^{-1} (74–947). The degree of Cu-enrichment was linked to the organic matter, silt and clay contents. Release of Cu from soil and sediments was greatest below pH 5.5 due to acidification and above pH 7.5, it was due to solubilization of soil organic matter in alkaline conditions [22].

In addition to fungicides used in vineyards and orchards, wood preservative containing Cu, Cr and As used on fences and poles can also contribute significant amounts of these elements to soils, albeit with a heterogeneous distribution. Solutions of $CuSO_4$ and $ZnSO_4$ are sometimes also used for fungicidal footbaths for cattle and become dispersed in the area around the footbaths [70].

'Zineb' an organo-Zn compound ($C_4H_6N_2S_4Zn$) and 'Maneb' an organo-Mn compound ($(C_4H_6MnN_2S_4)x$) are also used as foliar-applied fungicides on crops, but the inputs of these metals from these sources are not as large as those of Cu, Pb and As used in earlier fungicide treatments, although the latter two elements are not now used as agrichemicals. Lead arsenate [$Pb_5OH\ (AsO_4)_3$] was used as a pesticide from 1900 to 1960 mainly to control insect pests in orchards. Codling [14] reported concentrations of <676 mg Pb kg^{-1} and <133 mg As kg^{-1} in two orchard soils with a history of Pb–As pesticide applications.

Organotin compounds, such as triphenyltin (TPT), are also used as fungicides on some agricultural crops and these eventually degrade to inorganic Sn which accumulates in soil (see Chap. 24).

Other Agricultural Inputs. Lead shot from game and 'clay pigeon' (plastic flying targets) shooting over agricultural land is an important source of Pb and other heavy metal(oid)s including As, Mo, Sb and Ni (see Sect. 2.3.2.2 Military Activity and Sports Shooting). Corrosion of galvanized (Zn-coated) structures, such as fences and roofs adds significant amounts of Zn to soils receiving runoff or suspended particles (see Sect. 2.3.2.1 Atmospheric Deposition). Various wastes including, meat production sludges, egg, dairy, vegetable and other food processing wastes, paper crumble, waste gypsum and waste water treatment cake are applied to soils in some places and all contribute significant amounts of certain heavy metal(loid)s [70].

Urban Soils

Concentrations of several heavy metal(loid)s are often found to be significantly higher in urban soils than those in rural or agricultural soils. Opinions vary on the groups of heavy metal(loid)s considered to be characteristic of urban contamination, but most include Pb, Cd and Zn. Kabata-Pendias and Mukherjee [44] give Ba, Cd, Pb, Sb, Ti and Zn as being characteristic urban contaminants, whereas Chen et al. [12] give As, Cd, Cu, Hg, Pb and Zn as the most common in urban areas in China. Kabata-Pendias and Mukherjee [44] refer to work by several authors showing cities to vary in the combinations of heavy metal(loid) contaminants they have, for example: Berlin: Cd, Cu, Hg, Ni, Pb, Sn, Th and Tl; Minsk: Cd, Pb and Zn; Novosibirsk: As, Cd, Cu, Hg, Mo, Pb, Zn; St Petersburg: Ba, Cr, Cu, Pb, V, W and Zn, and Warsaw: Ba, Cd, Cr, Cu, Ni, Pb and Zn. However, elevated levels of Pb are common to all these cities.

Unlike soils at or near to industrial sites where there is often an obvious link between the main contaminants and the industrial process, there are many possible causes of soil contamination in urban areas and there may not be a single source which could explain the anomalously high metal(loid) concentrations. The most common sources of metals and metalloids in urban areas include:

- Deposition of dust and aerosol particles (from fossil fuel combustion, motor vehicles etc.),
- Corrosion of metal structures, including galvanised roofs and fences,
- Technogenic (man-made substrate) materials incorporated in the soil or in dusts,
- Contaminants from the former agricultural or horticultural use of the land,
- Fertilisers and composts used on urban gardens,
- Deposition of solid or liquid wastes onto soils,
- Paints and other decorative materials,
- Bonfires, accidental fires and wartime bombing.

It is important to emphasise that elevated concentrations of heavy metal(loid)s in urban soils are both an indication of inputs from a range of different sources and also that some of these sources, such as atmospheric aerosols, may have affected the health of people directly, for example by inhalation, and not just afterwards via contaminated soil. Once sorbed in the soil, elevated concentrations of metal(loid) s can affect human health when the soil itself is ingested directly on unwashed vegetables, on unwashed hands, through intentional soil eating (pica), by inhalation of resuspended soil particles in dust, or though uptake into garden vegetables [91].

Technogenic Materials

Mineral materials such as quarry waste, construction residues, demolition wastes, furnace slags, ashes and harbour dredgings are often referred to as ‘technogenic’ materials. These are important sources of heavy metal(loid) contamination in urban and industrial areas. They may have been dumped on land in the past, or transported over land in large quantities and used for foundations of buildings, to level sites or build roads. Technogenic wastes are also closely associated with industrial sites as discussed in Sect. 2.3.2.2 Industrial Contamination. Deposits of these materials, including spillages *en route* and dusts dispersed into the atmosphere from them can greatly influence the heavy metal(loid) content of soils. Meuser [59] gives typical data for technogenic mono-substrates in Germany which show that brick and concrete rubble have relatively low contents of heavy metal(loid)s (in mg kg^{-1}): Cu <70, Pb <110, but bottom ash from coal burning has higher levels (As <25, Cu <100, Pb <180). Fly ash from coal-fired electricity generating stations can contain: Cd <14, Cr <200, Cu <474, Ni <583, Pb <1,100 and Zn <1,800, but even higher contents are found in fly ash from garbage incineration As <230, Cu <1,300, Pb <8,300, and Zn <27,000. Radionuclides in coal, such as U and Th are also concentrated by a factor of five to ten times in bottom ash and fly ash from coal combustion [86]. Metallurgical slags can contain the highest concentrations of all: As <7,000, Cu <1.2%, Pb <5% and Zn <13% [59]. If coal fly ash is used in urban areas for construction it can lead to both air pollution (in dust) and soil contamination. Where cities and industrial sites develop over time, there will often be a sequence of layers of technogenic materials under the land surface as new buildings and industrial processes are built on the sites of earlier ones. Demolition, accidents such as fires and explosions and wartime bombing can result in a very heterogeneous distribution of heavy metal(loid)s and persistent organic pollutants. Readers are referred to "Contaminated Urban Soils", by Helmut Meuser (published by Springer in 2010) for a more detailed coverage of this topic [59].

Case Studies on Heavy Metals and Metalloids in Urban Environments. A comparison of heavy metals in urban and adjacent rural soils in the city of Turin (Torino) in Italy, showed that Pb was the heavy metal present in the most elevated concentrations within the city, followed by Zn and Cu. Median concentrations and ranges (in mg kg^{-1}) were: Pb 117 (31–870), Zn 149 (78–545) and Cu 76 (34–283). A 'Pollution Index (PI)' based on urban soil content divided by the rural soil content gave a PI of 7.5 for Pb, 2.9 for Zn and 3.3 for Cu [6].

Several surveys of urban soils have been conducted in the United Kingdom (UK), these include the UK Soil and Herbage Survey (UKSHS) of soil samples from rural, urban and industrial sites [83], the British Geological Survey's Baseline Survey of the Environment (G-BASE) [24] and a study by Culbard et al. [16] of soils (and associated house dusts) in gardens in England, Scotland and Wales. The summarised results from the UKSHS and G-BASE studies are shown in Table 2.8 and the Culbard et al. [16] data in Table 2.9.

Table 2.8 shows the UKSHS and the G-BASE data for urban soils in the UK. The median values from the G-BASE data, based on 8,368 soil samples from 20 urban centres, give a more reliable indication of the extent of heavy metal(loid) contamination in urban environments in the UK than the 28 samples in the UKSHS survey. Interestingly, these G-BASE median values in urban soils are higher than those from the UKSHS for all metal(loid)s in both urban and industrial soils, and some very high maximum contents of all elements listed were found. However, many of the urban centres in the G-BASE survey had a history of industrial activity [91]. The UKSHS concentrations for Cd, Cr, Ni and Zn in rural soils are lower than those from the much larger systematic grid survey of 5,692 agricultural soils in England and Wales [56] shown in Table 2.1. This is probably an indication of the variation in lithogenic and anthropogenic sources in this grid survey. The earlier study by Culbard et al. [16] involved more than 4,000 garden soils and associated house dusts in up to 100 houses in each of 50 cities, towns or villages in England, Scotland and Wales. They generally found relatively high concentrations of Pb and Zn in all these soils, but the mean levels in the gardens of houses in the Greater London boroughs were higher than for any other urban area investigated in the study, apart

Table 2.8 Concentrations of selected heavy metals and arsenic in soils at rural, urban and industrial sites in the United Kingdom (mg kg^{-1})

	As	Cd	Cr	Cu	Pb	Mn	Hg	Ni	Sn	V	Zn
Rural Soils											
UKSHS[a] (n = 122)											
Median	**7.09**	**0.29**	**29.2**	**17.3**	**37.4**	**421**	**0.10**	**15.8**	**2.0**	**39.2**	**65.9**
95th percentile	26	1.15	73	51	138	1,532	0.28	7.28	7.3	97	195
Urban soils											
UKSHS (n = 28)											
Median	**9.78**	**0.29**	**27.1**	**30.4**	**93**	**387**	**0.23**	**22**	**5.41**	**43**	**97**
G-BASE[b] (n = 8,368)											
Median	**14.0**	**0.9**	**78**	**–**	**100**	**–**	**–**	**29.7**	**7.9**	**–**	**133**
Maximum	2,047	134	4,286	–	14,714	–	–	1,038	919	–	23,238
Industrial soils											
UKSHS (n = 50)											
Median	**12.5**	**0.38**	**35.7**	**28.8**	**68.9**	**540**	**0.14**	**27.8**	**3.66**	**47.7**	**114**
95 percentile	57	4.2	74	188	471	1,500	1.31	61	30	105	650

*Additional elements: **Ag** <133, **Ba** <1,210, **Tl** <0.8, **Ce** <387, **Th** <14.5, **U**<7.8, **Sb** <38, **Se** <52.4, **Mo** <24, **W** <11*

[a] UKSHS = United Kingdom Soil and Herbage Survey [83]

[b] G-Base = British Geological Survey Geochemical Baseline Survey of the Environment (G-BASE Project) [24]

Table 2.9 Geometric means and ranges of total lead, cadmium and zinc concentrations in domestic garden soils in England, Scotland and Wales (mg kg^{-1})

	Number of house gardens	Pb	Cd	Zn
All areas[a]	4,127	266 (13–14,100)	1.2 (<1–40)	278 (13–14,600)
London boroughs	579	654 (60–13,700)	1.3 (<1–40)	424 (58–13,100)

From Culbard et al. [16]

[a] All areas includes the 579 gardens in London Boroughs

from obviously polluted areas, such as villages with old metalliferous mine workings. A summary of their results in Table 2.9 shows much higher geometric mean concentrations for Pb and Zn for all areas than in the G-BASE or UKSHS data and even greater levels of Pb and Zn contamination in London boroughs. However, the G-BASE survey did not include the London Boroughs and was not confined solely to gardens like the Culbard et al. study. It also included some samples from, parks, allotments and recreation fields. The maximum Pb values are similar for the G-BASE and the Culbard et al. data, but the maximum Zn value in the G-BASE survey is nearly twice as high, which helps to illustrate the very wide range of concentrations of heavy metal(loid) contamination which can be found in urban areas, especially those with a history of heavy industry. Urban soils in Berlin with debris from bombing in the Second World War contained relatively high mean metal concentrations (in mg kg^{-1}) of: Pb 330 (<3,168), Zn 379 (<3,607), Cd 175 (<757) and Cu 99 (<657) [58] which are of a similar order to those found in London gardens, but the Cd concentrations in Berlin are particularly high and are comparable to the levels of Cd found in Zn–Pb mining contaminated land (Sect. 2.3.2.2 Non-ferrous Metalliferous Mining and Smelting).

Lead is the most distinctive heavy metal contaminant of urban soils and its two most important sources are house paints and exhausts from petrol engines in motor vehicles. Although inputs from these two sources have decreased in recent years as a result of legal controls, street dusts and soils which were contaminated at a time when paints often contained more than 10% Pb and petrol contained <0.85 g Pb L^{-1} will still be present in the urban environment [37, 60]. Horner [37] reported that flakes of paint from houses in London, UK, constructed in the 1860s contained mean Pb contents of 14.1% (<43% Pb), those constructed in the 1920s had 1.93% Pb (<7.2%) and in the 1990s houses the mean Pb content of paint was 0.0135% Pb (<0.03%). In Minneapolis, USA, Meilke et al. [61] had earlier found a link between Pb contents of garden soils and the age of houses since paints containing relatively high levels of Pb would have been used on older, predominantly wooden-walled houses and the paint scrapings and erosion of painted surfaces would have contaminated adjacent soil. Garden soils of painted houses had a median Pb content of 938 mg kg^{-1} (475–6,150) and non-painted houses had 526 mg Pb kg^{-1} (130–1,840). Even the Pb levels in non-painted houses were quite high, which is a reflection of the many different possible sources of Pb in the urban environment.

Mielke et al. [62] showed how the stripping of old house paints with 9–13% Pb could give rise to very high quantities of Pb and other metals in dust. They calculated that the removal of old paint (with 9% Pb) from a wooden house by power sanding could release dust containing 7.4 kg Pb, 3.5 kg Zn, 14.8 g Cu, 9.7 g Cd and smaller amounts of Mn, Ni, Cr, Co and V. They reported a case of a timber framed house built in 1925 which had around 13% Pb in the paint where the family pet died and children were hospitalized due to Pb toxicity as a result of power sanding to remove the old paint. The bare soil around the house contained between 360 and 3,900 mg Pb kg^{-1}. The US EPA standard for soil in play areas is 400 mg Pb kg^{-1}, but Mielke et al. [62] suggested that a lower maximum content of 80 mg Pb kg^{-1} would provide a more appropriate margin of safety for children's health. Several countries banned or severely controlled the use of Pb in paints from the 1940s onwards. Lead in paint was banned in the US in 1978, but was not phased out in the UK until 1987.

In addition to Pb, Hg was also used in some house paints. Prior to 1992 in the USA, latex paints were formulated with Hg, which gradually vapourized. Analysis of paint chip samples from houses in New Orleans showed median concentrations of 26.9 mg Hg kg^{-1} (<214) and 7.66% Pb (<31.7%) in exterior paints and 7.1 mg Hg kg^{-1} (<39.2) and 0.042%Pb (<6.3%) in interior paints [60].

One feature which is readily apparent from the monitoring of blood Pb levels in children living in urban areas is that there is a strong seasonality in sources of Pb pollution. Lead concentrations are usually highest in summer when exterior atmospheric particulate Pb levels are highest, and it is at this time that re-suspension of dust particles from various sources is at a maximum from dry soils [49].

In Mühlburg/Karlsruhe, south west Germany, older houses (especially those built <1920) had the highest Pb contents (160 mg kg^{-1}) in garden soils . Houses, built after 1980 had the lowest (39 mg Pb kg^{-1}) and those built between 1920 and 1980 had intermediate concentrations (118 mg Pb kg^{-1}). These soil Pb contents were much lower than in the American and UK cities quoted above, probably because of the relatively small percentage of painted external wood on houses in this part of Germany and fewer other sources of Pb contamination [71].

Apart from paints, wood preservatives containing Cr, Cu and As (CCA) can contribute to the contamination of soils in both urban and rural environments (see Sect. 2.3.2.2 Agricultural Chemicals-Fungicides). This will contaminate the soil in contact with treated wood (such as fence posts and garden decking) and also contribute to air pollution if the wood is burnt. The ash residue from burning will also be a source of soil contamination.

Many urban areas in China have been subject to considerable heavy metal(loid) contamination from several sources. Chen et al. [12] showed that the main contaminating elements in soils in the urban-rural transition area of Hangzhou in China were As, Cd, Cu, Hg, Pb and Zn but Co, Cr, Ni and Mn were mainly of natural (lithogenic) origin. Nearly 70% of the area was affected by contamination with heavy metal(loid)s.

A study of urban soils in Newcastle upon Tyne, UK, to determine whether a municipal waste incinerator had a detectable effect on heavy metal(loid) contents, found high levels of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn, which are typical of urban areas, but no detectable evidence of greater concentrations down-wind of the incinerator. Hotspots were found for As, Cd, Cu, Hg, Pb and Zn and the median concentrations and ranges (in mg kg^{-1}) of elements measured were: As 15 (5–279), Cd 0.28 (0.01–6.95), Cr 51 (23–230), Cu 77 (20–12,107), Hg 0.32 (0.03–4.99), Ni 26 (11–165), Pb 233 (40–4,134) and Zn 74 (75–4,625) [79].

Motor vehicle tyres and brake linings are significant sources of several heavy metal(loid)s in urban dusts. In Stockholm, Hjortenkrans et al. [36] found that road traffic accounted for 50% or more of Cd, Cr, Cu, Ni, Pb and Zn. Brake linings were major sources of Cu, Zn and probably Sb and tyres were the main contributors of Cd and Zn. In 2005, average annual Zn emissions from rubber tyre wear in Stockholm were 4,200 kg Zn (720–7,700) and Cu was 5.3 kg (0.7–10). From brake linings, the main emissions were 3,800 kg Cu and 1,000 kg Zn. Total Zn emissions from tyres in the whole of Sweden amount to 150 t Zn year^{-1}. In Baltimore, USA, median and maximum concentrations of metals in urban soils (in mg kg^{-1}) were: Pb 89 (<5,650), Cu 35 (<216) and Zn 81 (<1,110) and the highest were mainly related to vehicular sources because the oldest parts of the city have the highest road densities [97].

In addition to the more technologically advances sources of heavy metal(loid)s, such as traffic and paints, inputs from coal and wood smoke (together with organic pollutants and oxides of S) and the associated ashes are also significant sources in all areas of human habitation.

Industrial Contamination

The distribution of heavy metal(loid)s in soils in industrial and urban areas tends to be far more heterogeneous than in agricultural soils, owing to the localized nature of some of the types of pollution. Although atmospheric deposition would be expected to be more evenly distributed, at least in the area down-wind of the emission source, the complex air currents around buildings, roads with fast-moving traffic and structures such as chimneys contribute to uneven deposition. Mean concentrations of Cu, Pb, Hg, Ni, Sn and Zn in urban and industrial soils are usually significantly elevated relative to those in rural soils (Table 2.8). Although some surveys have distinguished between urban and industrial soils, very often urban soils have received considerable inputs of heavy metal(loid)s from industrial sources in addition to those from urban and domestic activities, especially in old urban areas where there has been a historical mix of residential and industrial land use and this distinction between urban and industrial is often not valid.

The occurrence of heavy metal(loid) contamination in soils at industrial sites varies with the type of industry and can arise from dusts and spillages of raw materials, wastes, final product, fuel ash as well as emissions from high temperature processes, accidents and fires. Examples of possible combinations of heavy metal (loid) contaminants associated with different industries include:

Chemical industry (general): Ag, Sb, Se
Chlor-alkali (Cl_2 and NaOH) industry: Sb, As, Bi, Ba, Cd, Cu, Pb, Hg, Ag, Sn
Sulphuric Acid works: As, Cu, Pb, Ni, Pt, V, Zn
Nitric acid works: As, Cr, Co, Cu, Mo, Ni, Rh, V, Zn

Phosphoric acid works: As, Ba, Cd, Cu, Pb, U
Ceramics: Cd, Cr, Cu, Pb, Hg, Ni, Zn, Ce, Eu
Electrical components: Cu, Zn, Au, Ag, Pd, Pb, Sn, Y, Cr, Se, Sm, Ir, In, Ga, Re, Sn, Tb,Co, Mo, Hg, Sb, Hf, Ru, Ta, Te
Steel works: As, Cr, Pb, Mn, Mo, Ni, Se, Sb, W, V, Zn
Pesticide works: As, Cu, Cr, Pb, Mn, Zn, V, Th
Battery manufacture: Pb, Sb, Zn, Cd, Ni, Hg, Ag
Printing and graphics: Se, Pb, Cd, Zn, Cr, Ba
Catalysts: Pt, Sm, Sb, Ru, Co, Rh, Re, Pd, Os, Ni, Mo, Ag, Zn
Pigments and paints: Pb, Cr, As, Sb, Hg, Se, Mo, Cd, Ba, Zn, Co
Polymer stabilizers: Sn, Pb, Cd, Zn, Ba
Non-ferrous metal smelting: Ag, As, Ba, Cd, Cu, Cr, Hg, Mo, Sb, Se, Sn, Tl, V, U, W, Zn
Waste disposal (incineration etc.): As, Cd, Cu, Be, Hg, Ni, Sb, Se, Ce, Mo, W, Pb, Tl, Zn

(various sources)

Kabata-Pendias and Mukherjee [44] give values from the literature for the highest concentrations of heavy metal(loid)s found in soils contaminated from industrial sources in Canada, China, Japan, Poland, UK and USA (in mg kg^{-1}) as: As <2,500; Cd <1,800; Co <300; Cu <3,700; Hg <100; Ni <26,000 and Zn <80,000.

In the UKSHS data shown in Table 2.8, concentrations of Cu, Pb, Hg and Sn in soils from selected urban and industrial sites in the UK were found to be on average two to three times higher than those in rural soils [83]. Soils at representative industrial sites showed wide ranges of the 37 different elements studied semi-quantitatively using ICPMS analysis. In addition to the data in Table 2.8, concentrations of up to 133 mg Ag kg^{-1} were found, with the highest at a chemical works, apart from this one site, all the other industrial sites only showed concentrations of <2.1, rural soil 0.3 and urban soil ca. 0.1 mg Ag kg^{-1}. Barium concentrations of <1,210 mg kg^{-1} were found at an electricity generating station, with the next highest (641 mg Ba kg^{-1}) at a chemical works (rural values <281 mg Ba kg^{-1}; urban values 95 mg kg^{-1}). Uranium concentrations of up to 3.3 mg U kg^{-1} were associated with the non-ferrous metal industry (rural soil <0.8 mg U kg^{-1}; urban soil 2 mg U kg^{-1}). Antimony concentrations <38 mg kg^{-1} were found near an incinerator, 22 mg Sb kg^{-1} associated with a steel works and 17 mg Sb kg^{-1} at a chemical works. Selenium was highest (52 mg kg^{-1}) at a chemical works with the second highest concentration (11 mg Se kg^{-1}) at an incinerator. Rural Se concentrations were <3.3 mg Se kg^{-1}, but Se was below the limit of detection in urban soils. The highest tungsten (W) concentrations (<11 mg kg^{-1}) were found at a steel works with incinerators having the next highest concentrations (<6 mg W kg^{-1}). Rural soils had <0.3 mg W kg^{-1} and urban soils 0.2 mg W kg^{-1} [83].

In the town of Mundelstrup, near Arhus in Denmark, the gardens of houses constructed on the site of a former P fertiliser factory were found to be heavily contaminated with Pb (<67,600 mg kg^{-1}) and As (<5,500 mg kg^{-1}). On the basis of the maximum permissible concentrations in garden soils permitted by Danish law in the 1990s (40 mg Pb kg^{-1} and 20 mg As kg^{-1}), a major clean-up of the site was carried out. This involved removing approximately 50,000 m^3 of contaminated soil from the gardens of 30 houses to a maximum depth of 8 m where necessary and replacing with 'clean' soil [13].

Non-ferrous Metalliferous Mining and Smelting

Non-ferrous metalliferous mining and smelting industries are associated with very high levels of heavy metal(loid) contamination of the environment . These industries extract and process metal ores and gangue minerals which generally contain several metal(loid) elements in high concentrations. Some non-ferrous metalliferous mines are situated in upland areas where the surrounding land is not normally used for arable cropping and only suitable for extensive grazing. Therefore the impact of mining contamination on agriculture in these cases is less than in areas of high quality arable land or urban development. However, villages and towns to house the workers have grown up at or around many major mine and/or smelter sites in developing countries and it is often found that garden and agricultural soils nearby are severely contaminated with heavy metal(loid)s.

A potential hazard to human health was found in garden soils of houses built on the site of a former Zn–Pb mine site at Shipham, near Bristol in southwest England. Median and maximum total concentrations of Cd, Pb and Zn (in mg kg^{-1}) in the gardens were: Cd 91 ($<$360), Pb 2,340 ($<$6,540) and Zn 7,600 ($<$37,200), but soils around the mine itself contained Cd $<$618, Pb $<$1.24% and Zn $<$5.84% [90]. Cadmium concentrations in vegetables grown in domestic gardens in Shipham contained an average of 0.25 mg Cd kg^{-1} DM, which was nearly 17 times higher than the UK national average Cd content. The vegetables with the highest concentrations contained 15–60 times more Cd than those grown in uncontaminated soils nearby [67]. The sources of the contaminating heavy metal(loid)s were the ore minerals galena (PbS) and smithsonite ($ZnCO_3$).

In South China, the Dabaoshan mine in the vicinity of Shaoguan city has given rise to marked contamination by Cu, Zn, Cd, Pb and As. Mean and maximum concentrations (in mg kg^{-1}) of: Cu 703 ($<$1,313), Zn 501 ($<$1,663), Pb 386 ($<$621) and Cd 4.7 ($<$7.6) were found in wetland rice (paddy) soils. Garden soils showed similar high mean total concentrations of (in mg kg^{-1}) of: Cu 348 ($<$594), Zn 696 ($<$921), Pb 297 ($<$384) and Cd 4.4 ($<$7.6). Contamination was highest in the vicinity of the mine and decreased exponentially with distance from the inflow of mine waste water. The concentration factors for the metals in vegetables decreased in the order Cd $>$ Zn $>$ Cu $>$ Pb with leafy vegetables accumulating higher concentrations (relative to the soil) than non-leafy vegetables. It was evident that there was a significant risk to the health of people consuming vegetables produced near to this mine [100].

Metal smelting usually involves converting sulphide ore minerals to oxides by roasting them in air followed by reduction of these oxides in a furnace and separating the different molten metals. In historic times, inefficient processing caused widespread air, water and soil pollution, which is still detectable today. There are very many reports of studies at historic mine and smelter sites in the literature and total concentrations of several percent of some of the metals are often found. For example, soils around the Pb mine at Lavrion in Greece, which was worked intermittently from 3000 BC until AD 1977, had a median Pb content of 7,410 mg kg^{-1} with a maximum of 15.2% Pb [93]. A Pb smelter in Calcutta, India, was known to cause Pb toxicity in people, especially children in an adjacent residential area with a population of around 50,000. Soils in this residential area had very high heavy metal(loid) concentrations (in mg kg^{-1}) of: Pb <47,000; Zn <10,300; <833; As <9,740; Hg <277. However, the concentrations of Pb, As, Mo, Cu, Hg, Cd, Sn and Ag all decreased with increasing distance from the smelter [10]. Mercury is used in the recovery of Au from sedimentary sources of the metal in small-scale operations and is mainly a contamination problem in streams and rivers, as in the Amazon basin (see Chap. 15).

Military Activity and Sports Shooting

Battlefields, bombed cities and military training areas are all sites of gross contamination by heavy metal(loid)s and organic pollutants. The sources are shells, bullets and bombs, unexploded mines, cartridge cases, damaged vehicles, leaking fuel and burning buildings. As with residual contamination from metalliferous mining and smelting, soils on battlefields also remain contaminated for hundreds of years or more even though all visible traces of the damage may have been removed and the sites redeveloped, as happened in northern Europe after the First and Second World Wars. The main metal(loid)s involved are Pb, Cu, Zn, Ni, Sb, depleted-U (DU), Hg, As and Bi. Depleted-U has only been used since the First Gulf War (1991) for anti-tank ammunition. Although depleted in highly radioactive ^{235}U, there can still be a considerable amount of radioactivity and also chemical toxicity associated with this material (see Chap. 26). Bullets used by the military in Switzerland contain 95% Pb, 2% Sb, 3% Cu and 0.5% Ni [42]. At shooting ranges, the soil on embankments (‘stop butts’) behind the targets is usually the most heavily contaminated with an average content in Switzerland of 1% Pb (<10% Pb). In a study of embankment soils (<0.5 mm fraction) at seven shooting ranges the variations in concentrations of metals (in mg kg^{-1}) were: Pb 1,900–515,800; Sb 35–17,500; Cu, 160–4,450; Ni 54–770; Bi, 6–5,140; Tl <3–2,150, and Hg <1.5–410 [42].

Copper in the topsoil of an area of 625 km^2 around Ypres, Belgium (site of a prolonged First World War battle) showed a significant elevation in median Cu content of soil (12 mg Cu kg^{-1}) to 18 mg Cu kg^{-1} in the battlefield and this amounted to an input of 2,800 t of Cu in the top 0.5 cm. Concentrations of <830 mg Cu kg^{-1} were found in soils in the major war zone, but <3,600 mg Cu kg^{-1} was found in the surrounding area [95].

In addition to warfare and military training, considerable quantities of Pb and other metals (As, Sb, Mo and Ni) are added to soils in shotgun pellets (or bullets) used for sports shooting. This includes both game bird and ‘clay pigeon’ (flying plastic target) shooting. Concentrations of more than 1% Pb in soil are sometimes found at sites of shooting clubs, but where occasional shooting of game birds is practiced the pellets are randomly distributed in the topsoil and give very heterogeneous analytical results depending on whether a pellet is present in the sample or not. In England and Wales, Pb shot from shooting is the single most important source of Pb in agricultural soils with over 3,000 t Pb deposited annually [70]. It is estimated that individual pellets may take between 100 and 300 years to completely corrode and for the Pb and other constituent metal(loid)s including As and Sb, to be dispersed in the soil [81] (see Chap. 3, Sect. 3.2.5.2).

2.4 Concluding Comments

This chapter has attempted to show that there are many possible sources of the heavy metal(loid)s found in soils. On a global area basis, the geological soil parent material (lithogenic source) is probably the most important determinant of heavy metal(loid) concentrations in agricultural and rural soils, but many ubiquitous anthropogenic sources also exist, including atmospheric deposition of both long and short-range transported particulates, fertilisers, livestock manures and sewage sludges. However, in the urban environment there are many more possible sources of heavy metal(loid)s and they are also likely to be very heterogeneously distributed. Lead is the most characteristic heavy metal(loid) contaminant of urban soils, usually together with Cu and Zn. The concentrations of metal(loid)s in urban soils are a reflection of the integration of all the different sources of metals that people are exposed to. Finally, soils at industrial sites can vary widely in their concentrations of many metal(loid)s, depending on the nature of the industry, both past and present. This can be an important consideration in the redevelopment of brown field and derelict industrial sites for residential and urban use.

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Chapter 3
Chemistry of Heavy Metals and Metalloids in Soils

Scott D. Young

Abstract It is a simple matter to conceptually classify trace metal fractions in soil in terms of their relative ‘availability’. However, the challenge has always been to translate this qualitative understanding into predictive models of metal solubility, ideally based on proven mechanistic processes of specific adsorption, ion exchange, precipitation, colloidal flocculation, reduction, intra-aggregate diffusion etc. This chapter starts with a brief examination of the surface properties of the main metal adsorbents in soil, including humus, and the colloidal minerals Fe/Mn oxides, alumino-silicate clays, zeolites and sparingly soluble Ca salts. The interaction of these phases with the transient soil variables (e.g., pH, redox potential, temperature) in controlling metal solubility is discussed alongside the overarching influence of time. The sheer complexity of these co-dependencies still confounds our efforts to resolve an exact description of metal solubility and speciation and the range of modelling approaches which has emerged from this ‘confrontation’ is outlined. Currently the literature still presents an uneasy co-existence of relatively simple descriptions of metal solid $\leftrightarrow$ solution equilibrium along with thermodynamically consistent mechanistic models. To compensate for their limited predictive power in the face of soil heterogeneity, the empirical equations are often extended to incorporate key soil properties (soil organic carbon content, pH etc.) as determinants of the model parameters – with surprising success. The principal challenge for mechanistic models is to resolve a meaningful basis for their description of metal dynamics *which can be confirmed experimentally*. However, an equally important goal is to reconcile the demanding requirements for their operation with the paucity of such data in geochemical studies and datasets. With much wider use in recent years the remaining shortcomings of the mechanistic models are becoming more apparent and this has created new experimental imperatives.

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These include characterising the small proportions of high affinity sites on adsorbents and developing descriptions of mixed adsorbents beyond a purely additive approach. The future promises continued improvement of models describing trace metal dynamics in soils and their increasing incorporation into human and environmental risk assessment tools.

Keywords Adsorption • Desorption • Reaction kinetics • Diffusion • Labile metal • Solubility • Humus • Hydrous oxides • Phyllosilicates • Zeolites • Soil pH • Redox potential • Humic acid • Freundlich • Langmuir • WHAM-VI • NICA-Donnan • Assemblage models

3.1 Introduction

This chapter outlines the nature of metal and metalloid interactions with soil and current approaches to modelling these interactions.

3.1.1 Background to the Study of Metal Interactions with Soil

Heavy metals and metalloids are adsorbed strongly by the organic, and inorganic, colloidal constituents of soil. The resulting moderation of mobility and bioavailability of metals in the environment must rank as one of the most important 'ecosystem services' attributable to soils with implications for both micronutrient availability and potential toxicity to terrestrial and aquatic organisms. The overall strength with which metals are retained in soils is a reflection of:

(i) 'residual' properties attributable to the metal source material (primary minerals within the soil parent material, smelter fallout, sewage sludge, mine spoil, urban anthropogenic artefacts etc.);
(ii) the intrinsic affinity of individual metal ions for soil adsorption surfaces and for soluble soil ligands;
(iii) the suite of adsorption surfaces present in soils (humus, metal oxides, alumina-silicate clays etc.);
(iv) the more 'transient' properties of the soil, including pH, redox potential, water content, temperature, biological activity, salt concentration etc.
(v) soil-metal contact time.

A complete understanding of the mechanisms through which intrinsic and transient soil properties influence metal solubility still eludes us, despite decades of investigative effort. Nevertheless, as in all applied sciences, the emergence of new analytical techniques has gradually improved our ability to predict the behaviour of metals in soils. For example, synchrotron-based spectroscopy (EXAFS; XANES) is able to elucidate the bonding environment and valence of sorbed metals, electron microprobe and laser-ablation-ICPMS reveal the elemental make up of individual particulates, isotopic dilution and diffuse-gradient technology (DGT) quantify the kinetics and reactivity of surface-adsorbed metal ions and ion chromatographic and Donnan Membrane techniques enable speciation of metals in the soil pore water. An increasing number of studies utilise these techniques *in combination* to reveal a fuller picture of the interactions between metals and soils. This new wave of analytical information feeds directly into the development of increasingly powerful geochemical modelling approaches. Such models fulfil a dual role in (i) providing predictive information on metal fractionation (in solids) and speciation (in solution) and (ii) revealing the research imperatives for those studying metal sorption reactions.

Chapter three deals primarily with adsorption and precipitation reactions as the two recognised mechanisms whereby metals and metalloids are retained in soil. The latter process involves added complexity in a soil environment where compounds may (i) precipitate on pre-existing surfaces, (ii) exist as heterogeneous solid-solutions rather than pure phases and (iii) will in turn be subject to surface 'contamination' through adsorption reactions. Thus the boundaries between the two processes are rather diffuse and they may eventually be described in a more unified manner. For trace metals the more important reaction is usually adsorption and this is reflected in the greater weight given to Sect. 3.2 which describes the main types of adsorption surfaces and the manner of their interaction with metals. The effects of transient soil conditions on adsorption strength are outlined in Sect. 3.3 and current approaches to modelling the interaction of trace metals with soils are described in Sect. 3.4.

3.1.2 Overview of Metal and Metalloid Interaction with Soils

An emerging view of metal 'fractionation' in the solid phase, and 'speciation' in the solution phase, is illustrated in Fig. 3.1 below.

M_{inert} is 'inert' metal, held in a form which only responds to changes in solution conditions over periods of years, possibly through mineral weathering, organic decomposition or changes in redox state. Examples include:

(i) trace levels of metal ions buried within the structure of primary (or secondary) minerals by isomorphous substitution and released only by mineral weathering;
(ii) resistant primary (e.g., sulphide) or secondary (e.g., phosphate, carbonate) metal compounds solubilised by slow oxidation reactions or dissolution over extended periods;
(iii) recalcitrant organic compounds (containing metals);
(iv) resistant anthropogenic contaminants such as metal fragments, vitrified particles etc.

$M_{non\text{-}lab}$ represents 'non-labile' metal that is not held reversibly and therefore shows apparent sorption hysteresis. It is held in forms which are 'kinetically

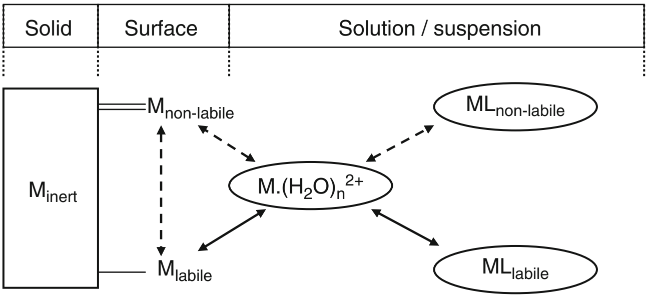

Fig. 3.1 Schematic representation of three-phase divalent metal ion equilibria in soils. *Broken* and *solid reversible arrows* represent kinetically constrained and 'instantaneous' reactions respectively; '*ML*' represents metal ions bound to soluble ligands

constrained' and so responds to changing conditions slowly (days to months). However, desorption can occur without changes in redox status or decomposition of the absorbing substrate. Non-labile metal may exist within soil solids or even in solution/suspension linked to ligands (ML) such as humic/fulvic acid or contained within micron and sub-micron sized particulates [69]. Examples may include:

(i) dehydrated metal ions which have diffused into the interior spaces or structural framework of minerals (e.g., metal hydrous oxides, collapsed planar aluminosilicates, selected voids within zeolites etc.) or become occluded through co-precipitation reactions;
(ii) some surface-adsorbed metals held strongly, perhaps through multiple covalent linkages, on mineral or organic surfaces;
(iii) an *internal* constituent of single or mixed metal compounds that are in solubility equilibrium with the soil solution;
(iv) non-reversibly held metal complexes in solution and sub-micron particulates in suspension.

M_{labile} represents 'labile' metal ions which respond reversibly (adsorption or desorption), and almost instantly, to changes in solution equilibrium and do not show 'adsorption hysteresis' [1]. These may exist in a wide range of chemical forms, including soluble ligand complexes (ML; inorganic and organic). Examples will include:

(i) all exchangeably (electrostatically) held hydrated metal ions in clay interlayers and in the diffuse double layers of humus acids;
(ii) some specifically-adsorbed metal ions on clay edges, Fe/Mn/Al hydrous oxide surfaces and humus;
(iii) metal ions on the surface of metal compounds which are in solubility equilibrium with the soil solution;
(iv) reversibly held metal complexes in solution including most inorganic species and a proportion of the metal bound to dissolved humic and fulvic acid.

Factors governing the distribution of inner-sphere surface complexes between ‘labile’ and ‘non-labile’ forms are still under investigation. However, the isotopically-exchangeable fraction of metals (Cd, Zn, Cu, Pb) always greatly exceeds the fraction exchangeable with salt cations (Ca^{2+}, Mg^{2+}) [82] implying that the ‘labile pool’ of metal must include (some) specifically-adsorbed metal. Furthermore, current models of metal binding to dissolved humic and fulvic acids are parameterised with datasets which assume complete reversibility of metal ion adsorption. This implies that even the most strongly bonded metal ions are nevertheless ‘labile’; of course this may not be the case.

$M.(H_2O)^{2+}$ represents free hydrated metal ions. These are often regarded as the ‘immediately’ bioavailable form of metal ions but there is good evidence that complexes in solution (ML_{labile} and possibly $ML_{non\text{-}labile}$) also contribute to apparent bioavailability. Obviously all forms in the soil solution ($M.(H_2O)^{2+}$, ML_{labile}, $ML_{non\text{-}labile}$) are subject to transportation in drainage water.

3.2 Adsorption of Metals on Soil Constituents

Trace metals are adsorbed on the surface of colloidal particles in soils, principally humus, hydrous oxides of Fe, Mn and Al, alumino-silicate clays and some sparingly soluble salts such as calcium carbonate.

3.2.1 Humus

3.2.1.1 Bulk Properties of Humus

Humus is the organic product of ongoing plant and animal decay in a soil environment. In contrast to the mineral constituents that adsorb metals, humus is markedly concentrated in the top 20 cm layer of most mineral soils, unless it has been redistributed by pedogenic processes, as in podzols. Soil organic matter content can vary from <1% (sandy subsoils) to over 90% (peats). The major elemental composition of humus includes carbon (C) (50–60%), oxygen (O) (30–40%) and both H and nitrogen (N)(c. 5%). Structurally, humic materials are around 20–30% aliphatic, 10–20% carbohydrate and 20–40% aromatic. About 20% of H is bound to O as carboxyl (Hu-COOH) and acidic (possibly phenolic) hydroxyl groups (Hu-OH), the rest is bound directly to C [113]. Humus is intensely heterogeneous and exists in a continuum of particulate, colloidal and molecular forms. These only broadly equate to the well known operational (extractable) fractions humin, humic acid (HA) and fulvic acid (FA) described in many texts [109, 113]. Comparatively little is known about the relatively hydrophobic ‘humin’ fraction, in particular. Furthermore, this simple fractionation scheme is complicated by the variable degree of molecular aggregation, and colloidal flocculation, to which humic substances are prone depending on soil pH, ionic strength, temperature and level of saturation with polyvalent cations.

3.2.1.2 Surface Chemistry of Humus Acids

The distribution and spacing of O-substituted acid groups are key determinants of the surface chemistry of colloidal and molecular HA and FA. Close juxtaposition of Hu-COOH and Hu-OH groups causes ‘mesomeric’ and ‘inductive’ electron-withdrawing effects, which create stronger acidity (lower pKa values). By contrast, electrostatic restriction from *charged* neighbouring groups, and hydrogen bonding, weaken the acidity of HA and FA (higher pKa values). In combination these effects extend the range of pH values over which surface charge is generated. Therefore, oxy-acid groups on humus dissociate across a wide pH range: pH 2–8 (Hu-COOH) and pH 7–11 (Hu-OH) generating an almost linear increase in negative charge from pH 3 to pH 10, often with the faint suggestion of an equivalence point (Hu-COO$^-$) around pH 8. As a result, the strength of metal binding varies accordingly across the pH range (Sect. 3.3.1) with stronger adsorption at high pH.

3.2.1.3 Metal Binding by Humic and Fulvic Acids

Metals are thus bound to a range of sites on humus composed of a mix of oxygen, nitrogen and sulphur donor atoms. Potentiometric studies and a range of spectroscopic techniques (FTIR, EXAFS, XANES, ESR, NMR and others) have provided detailed, but not always consistent, information on the nature of metal binding. The negative charge on humus generates simple coulombic attraction of cationic metals, especially alkali and alkaline-earth cations. However, specific inner-sphere, complex formation of most heavy metals is likely and the presence of functional groups in close proximity suggests the formation of multidentate and multinuclear chelate sites. Binding of heavy metals is probably dominated by the formation of two or even three bonds to a mix of carboxyl and acidic hydroxyl groups. A prevailing idea for many years was that divalent trace metals were mainly bound in chelate structures on aromatic rings (essentially phthalic and salicylic acid units) although this has been difficult to confirm. The independence of binding parameters on humic acid concentration suggests that metals do not bridge between two humic molecules in solution but rather bond to single or multiple groups on one humic molecule [21].

There is also evidence for bonding to sites containing N (especially Cu) and sulphur (S) (especially Hg) but the relative importance of these ligands is unresolved [113]. Mercury (Hg) is thought to be associated with reduced S-containing ligands in humus [105]. Furthermore, Bernaus et al. [15] demonstrated, using XANES, that methylated forms of Hg (CH_3HgCl) were covalently bound to humic acids, probably through thiol groups, into biologically unavailable forms. There is even evidence that (anionic) arsenate might be linked to DOC, possibly through bridge cations [20].

The relative importance of organic matter in metal binding has been demonstrated many times although this will clearly depend on the composition of the colloidal phases in individual soils. Spectroscopic techniques (e.g., EXAFS; [97]) show that even relatively weakly bound metals such as zinc (Zn) are predominantly held as organic complexes in soil. Removal of organic matter (e.g., by peroxide treatment) causes a profound reduction in metal adsorption capacity (e.g., for Cd; [87]). It is commonly found that strength of metal binding is affected by humus content and therefore by management practices which enhance humus [64].

3.2.1.4 'Active Organic Matter'

The organic fractions primarily responsible for metal binding, humic and fulvic acids, may be around 75% of the soil organic matter on average [109], but this varies between soils. Determining the proportion of what is termed the 'active organic carbon' (AOC) in soil solid and solution phases remains a challenge. To optimise their model of metal binding in a study of 98 upland soils from England and Wales, Tipping et al. [114] had to assume a range of AOC in the solid phase of 9–86%. Amery et al. [5] improved their prediction of metal (Cu) complex formation by equating the 'active fulvic acid' (AFA) fraction with 'specific ultra-violet absorbance' (SUVA, at 254 nm) as an index of 'aromaticity' in the dissolved organic carbon (DOC).

3.2.1.5 Humus Mineral Interactions

Humic and fulvic acids are strongly adsorbed on mineral surfaces, mainly through chemi-sorption to hydrous oxide minerals (Fe, Al, Mn) and probably through co-flocculation with inorganic colloids. Mixed effects on metal and metalloid solubility arise as a result. Organic matter may interfere with the formation of 'stable' metal precipitates such as lead (Pb)-phosphates (chloropyromorphite; [65]). On the other hand, there is evidence for enhanced adsorption on mixed assemblages of fulvic acid and Fe oxide [122, 125]. Anionic metalloids (arsenate, selenate) and metals (chromate) must compete with humic and fulvic acids for their preferred adsorption sites on Fe or Mn hydrous oxides. A current priority in trace metal modelling is to provide a coherent description of mixed humus-mineral assemblages, such as humic acid adsorbed on the surface of Fe/Al/Mn hydrous oxides [126].

3.2.1.6 Dissolved Organic Carbon (DOC)

Soil colloids exist in a flocculated state; only small proportions (0.001–0.1%) of humic and fulvic acids are dissolved in solution at any given time. However, the presence of this dissolved organic carbon (DOC) has profound implications for transport of metals that strongly bind to humic and fulvic acids. In the case of Cu , for example, commonly up to 99% of Cu in the soil solution is complexed to fulvic acid [111]. In the context of risk to aquatic systems, strong bonding of metals to organic matter has always been recognised as a ‘double-edged sword’ in that the overall effect of strong bonding on metal mobility will depend on the solubility of the humus itself [63]. Metal transport in rivers and accumulation in floodplain soils are probably determined by the movement of humus acids and their subsequent deposition. Schroder et al. [99] found very strong correlations between humus content and metal loading in floodplain topsoils around the rivers Meuse and Rhine (Netherlands). Thus, predicting DOC solubility and the ratio of HA to FA in solution is another current challenge for heavy metal modelling in soils [86].

3.2.2 Hydrous Oxides and Hydroxides

3.2.2.1 Bulk Properties

Manganese Oxides

Manganese oxides in soil exist in a range of forms between $Mn^{II}O$ and $Mn^{IV}O_2$, mainly in octahedral co-ordination. Phase changes are initiated by sufficient Mn atoms undergoing alteration of valence state (2, 3, or 4) to cause morphological transformation [77]. They are highly prone to dissolution, as Mn^{2+}, under reducing conditions (Eh $<$200 mV), and re-precipitation within oxidising zones in the soil. Local accumulation of Mn (and Fe) may result from (re-) adsorption of reduced forms (Mn^{2+}, Fe^{2+}) from solution on to manganese and ferric oxide surfaces followed by re-oxidation and (thus) crystal growth of the original oxide surface. This leads to their characteristic appearance as coatings and nodules in subsoils subject to periodic water logging, often in association with Fe hydroxides. Much of the Mn hydrous oxide content of soil is amorphous although lithiophorite [Al_2 Li $Mn_2^{IV}Mn^{III}O_6(OH)_6$], birnessite [$(Na, Ca)(Mn^{III}, Mn^{IV})_7O_{14}.2.8H_2O$], and others have been identified in contrasting soil environments. Lithiophorite is more common in older soils and birnessite in younger soils [33].

Iron Oxides

Iron oxides may be described as the inevitable end product of weathering in soils. Older, more heavily weathered soils often contain a greater free Fe oxide content than younger soils; the most obvious example is the tropical Ferralsol (Oxisol). Part of weathering, alongside dissolution and loss of silicic acid (H_4SiO_4), is the oxidation of ferrous iron (Fe^{II}) in alumino-silicates (e.g., the octahedral layer of biotite) to the ferric form (Fe^{III}) and precipitation as a range of ferric oxide minerals. Thus Fe oxide is usually fairly evenly distributed through the profile of aerobic soils but is subject to the same re-distributive effects under fluctuating redox regimes as Mn oxides. In surface water and ground water gley soils Fe oxides may be concentrated on the outside of peds, and line the surface of major drainage pores and root channels, while in soils with an iron-pan, as the name suggests, they may exist as a consolidated layer determined partly by leaching with organic acids and partly by the prevailing redox state of the soil. Iron oxides often occur in poorly crystalline or amorphous forms but recognised crystal forms also exist. Goethite (α-FeOOH) is perhaps the only stable form in aerobic soils, Haematite (α-Fe_2O_3) is most common in hotter climates, Lepidocrocite (γ-FeOOH) is precipitated during the oxidative ‘phase’ of waterlogged soils and Ferrihydrite ($Fe_5(O_4H_3)_3$) is associated with re-precipitation in podzol Bf horizons and the bed of streams, ditches and ochre in field drains [101].

The bulk distribution of Fe and Mn oxides within soil profiles therefore contrasts markedly with the normal distribution of humus. However, local co-accumulation due to adsorption of humus on to oxide surfaces is also common.

3.2.2.2 Surface Chemistry

An electrical charge on Fe and Mn oxides arises firstly from adsorption and release of H^+ ions from oxygen atoms at the interface between the mineral and the bathing solution (soil pore water). Hydrous oxides are amphoteric; they carry both positive and negative charges and the net surface charge is largely symmetrical around a zero point at a characteristic pH value [10]. This implies that three possible states apply to oxygen atoms on the surface of (e.g., Fe) oxides (Ox-Fe-OH):

$$\mathrm{Ox-Fe-OH^{2+}} \xleftrightarrow{\pm H^+} \mathrm{Ox-Fe-OH^0} \xleftrightarrow{\pm H^+} \mathrm{Ox-Fe-O^-}$$

The point of zero charge (pzc) for most Fe oxides is between pH 7 and pH 8.5 implying that they are positively charged in most soils. The pzc values of Mn hydrous oxides are lower than Fe oxides (pH 1.5–4.6) [77] which means they carry a net negative charge in most soils. Surface charge on oxides is also affected by salt concentration – i.e., the concentration of non-specifically adsorbed (electrostatically attracted) ‘counter-ions’ such as Na^+ and Cl^- – and temperature. Both these dependencies arise because the thermal diffusive forces resisting counter-ion accumulation close to charged surfaces have a greater influence at low salt concentration in the bulk solution and at higher temperature.

3.2.2.3 Metal Binding

Both Mn and Fe hydrous oxides have a high adsorption affinity for heavy metals which are bound as inner-sphere mono- and bi-dentate surface complexes. It is only recently that spectroscopic techniques have been able to determine the precise nature of metal bonding on Fe/Mn oxide surfaces. Arcon et al. [7] used EXAFS and XANES to show that arsenic (As) adsorbed in Cornish (UK) soils contaminated with mine spoil was primarily present as arsenate (As^V) bound to Fe oxides and Al

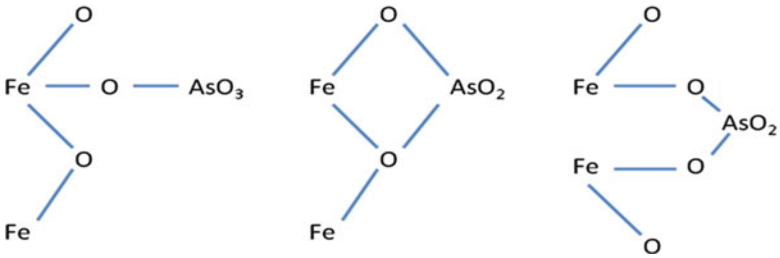

Fig. 3.2 Arsenate bound to the surface of Goethite as monodentate, bidentate-mononuclear and bidentate-binuclear surface complexes (After Fendorf et al.[36])

hydroxides – despite the origins of the As, presumably as As^{III}. Fendorf et al. [36] investigated arsenate and chromate bonding to goethite using EXAFS and suggested three types of bonding mechanism were apparent: monodentate, bidentate-mononuclear and bidentate-binuclear (Fig. 3.2). For both anions the monodentate form was most prevalent at low levels of surface coverage. Arai [6] employed EXAFS to distinguish between nickel (Ni) co-ordinated as face-, edge- and corner-sharing surface complexes on Goethite, Haematite and Ferrihydrite. They concluded that the majority of Ni was bound via edge-sharing, bidentate, inner-sphere $Fe\text{-}O_2\text{-}Ni$ units.

The relative affinity of a metal for specific oxides is likely to be determined by oxide charge relations and the morphology and pore sizes within the oxide surface [42]. The affinity of different metal ions for a specific oxide will also be determined by the speciation of the metal ion in solution. Figure 3.3 below shows the effect of pH on adsorption of ten metals by Goethite [37]. All the metals show an increase in adsorption as pH rises, as a result of reduced competition with H^+ ions and increasingly negative surface potential. The different positions of the curves reflect the intrinsic (chemical) affinity of the individual metals for the adsorption sites and their ability to overcome the positive surface charge on the mineral surface (pzc of Goethite is c. pH 8) and bond to surface oxygen atoms. However, note that the curves for Cr(III) (and Al) are particularly steep. Fischer et al. [37] suggest that, as pH rises, there is hydrolysis to $CrOH^{2+}$ which may be the preferred adsorption species. This does not apply to the other ions which do not hydrolyse within their respective adsorption zones. Thus adsorption affinity follows the sequence: $Hg > Cr > Al > Pb \approx Cu > Zn > Co \approx Ni > Cd > Mn^{II}$. Relatively strong adsorption of trivalent ions, followed by Pb and Cu, and the similarity of Co and Ni behaviour, are features commonly seen in metal *adsorption envelopes* on other oxides.

Particularly strong associations have been noted between Mn/Fe oxides and Co, Ni, As, V, Pb, Cr and Zn [7, 63, 77]. In particular, correlations between Mn and Co in both solid and solution phases in soils are almost invariable high; it is likely that the majority of Co in soils is associated with Mn oxides. In addition to chemical bonding and electrostatic effects reduction-oxidation coupling may also be involved in some sorption reactions. For example, Co^{2+} is oxidised to Co^{III} on the surface of $Mn^{IV}O_2$ and isomorphously incorporated into the oxide structure because Co^{III} is very similar in size to Mn^{IV}. A similar reaction (with Co) was suggested by

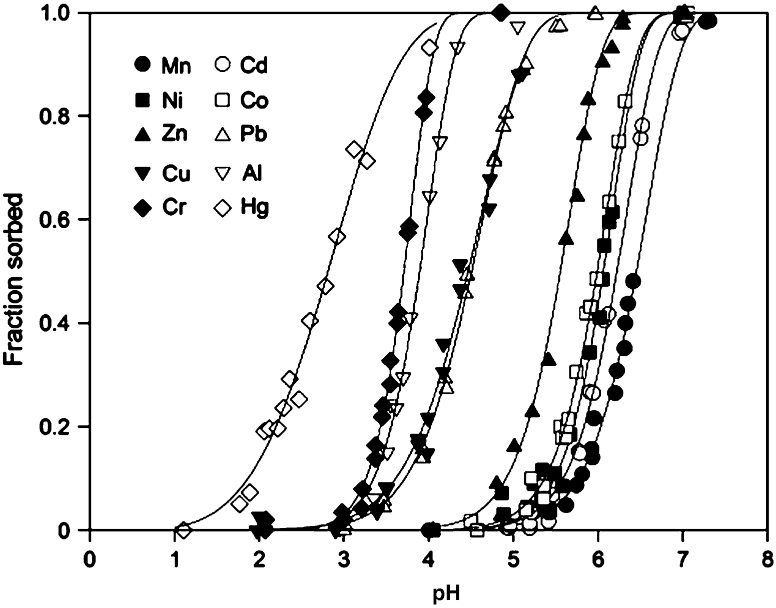

Fig. 3.3 Effect of pH on adsorption of 10 metal ions by Goethite after 2 h reaction. *Solid lines* are a simple exponential model (Fig. 3.1 of Fischer et al.[37], Copyright (2007), with permission from Wiley-Blackwell)

Gerth [42] for ‘Cd substituted’ Goethite. It is recognised that Mn oxides also oxidise Cr^{III} to highly toxic Cr^{VI} [63], however this effect is lessened if the oxide surface is highly substituted with adsorbed Co, Pb, Cu, Ni etc. [83]. Similarly, As^{III} oxidation to As^{V} on oxide surfaces, which will enhance adsorption and reduce potential toxicity, may be possible [33].

There is clear evidence of time-dependent incorporation of metals into oxide structures [10], which can render the sorbed metal ions ‘non-labile’ (Fig. 3.1). This may occur by solid-phase diffusion or by occlusion through co-precipitation. The latter mechanism is particularly important under fluctuating redox regimes because both Fe^{III} and Mn^{IV} hydrous oxides are subject to reductive dissolution and re-precipitation through oxidation over the redox potentials (Eh values) occurring in moist or saturated soils. These effects are discussed in more detail in Sects. 3.3.2 and 3.3.4; modelling metal adsorption is discussed in Sects. 3.4.3 and 3.4.4.

3.2.3 Planar Alumino-Silicate Clays (Phyllosilicates)

3.2.3.1 Bulk Properties

Planar alumino-silicate clays, or ‘phyllosilicates’, are composed of layers of silica tetrahedra and aluminium octahedra in ratios of 1:1 or 2:1. The types of clay minerals most commonly identified are Illite, Vermiculite, Smectite, Chlorite and Kaolinite; all are found in a wide range of soils. These may be very loosely associated with a ‘weathering sequence’ characterised by decreasing isomorphous substitution and variable accessibility of the interlayer space. Thus, Illite is the immediate alteration product of mica and most vermiculites are, in turn, derived from further weathering of Illite, or Mica. Smectites can occur through further alteration or through re-crystallization from solution. Pedogenic Chlorite forms through deposition of non-exchangeable Al-hydroxy polymers in the interlayer space and so is often present in acidic soils. The most common 1:1 clay is Kaolinite which is typically prominent as a result of geological inheritance or through prolonged and severe weathering, as found in tropical Ferralsols (Oxisols), for example [127].

3.2.3.2 Surface Chemistry

The surface area of phyllosilicates can be extremely large – up to 600 $m^2\ g^{-1}$ for Smectites. Isomorphous substitution of the Al^{3+} or Si^{4+} in either the tetrahedral or octahedral layers creates a positive charge deficit which is balanced by cations in the ‘inter-layer space’. Thus, for example, the unit cell composition of a di-octahedral 2:1 clay is:

$$C_{n/v}{}^{v+}\left(Si_{(4-n)}, Al_n\right)Al_2O_{10}(OH)_2,$$

in which there is isomorphous substitution of nAl^{3+} for nSi^{4+} in the tetrahedral layer resulting in a positive charge deficit of ‘n’ and requiring n/v cations with valence v+ in the interlayer space of the clay to balance the negative charge from the structural oxygens and hydroxyls [$O_{10}(OH)_2$].

This gives rise to a ‘cation exchange capacity’ (CEC) which depends on both the negative charge of the layers and the degree of access to the interlayer space. Illite, derived from weathered mica, has the largest surface charge but provides only limited access to the interlayer space because it is mainly collapsed with dehydrated K^+ ions balancing the isomorphous substitution (CEC $=$ 10–40 $cmol_C\ kg^{-1}$). Vermiculite has less remaining isomorphous substitution but the interlayer space is accessible so its CEC is largest (CEC $\approx$ 100–160 $cmol_C\ kg^{-1}$). Smectite has a still lower remaining surface charge but again is wholly accessible (CEC $\approx$ 70–150 $cmol_C\ kg^{-1}$). Chlorite has a limited CEC because of non-exchangeable Al-hydroxy deposits in the interlayer space in acidic soils (CEC $<$ 10 $cmol_C\ kg^{-1}$). Kaolinite is a very pure aluminosilicate with virtually no isomorphous substitution and a very limited ability to hold cations (CEC $=$ 3–15 $cmol_C\ kg^{-1}$). Exchangeable cations are fully, or partially, hydrated and bound as outer-sphere complexes, primarily by electrostatic forces; specificity arises from ion size and ease of dehydration. Larger ions with weaker hydration shells are bound more strongly so that adsorption strength follows the sequence $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ for alkali and alkaline-earth cations respectively.

3.2.3.3 Metal Binding

Cationic heavy metals will be held in the interlayer space of phyllosilicates, as exchangeable cations, but they tend to be poorly represented because of the overwhelming presence of Ca, Mg and K in soils. However, trace levels of metal binding to clays can be considerably more complex. Furnare et al. [39] used EXAFS and XANES to study Cu^{2+} adsorption on Vermiculite and Smectite. They suggested that Cu was covalently bound through inner-sphere complexes to unbonded oxygens at clay edges and corners. They also identified occupancy of octahedral vacancies within the clay structure as well as simple outer-sphere electrostatic retention in the interlayers. The interlayer area can also support highly specific bonding: Ni, Co and Zn are thought to form multi-nuclear species which bind ‘irreversibly’.

There has been considerable interest in *specific* metal binding to clays with Al-hydroxide polymer species in the interlayer space (C_Al_HO systems). It may be that such systems bind some metals more strongly than simple oxides because of their greater surface area for chemi-sorption. Janssen et al. [56] found that Zn and Cu were specifically bound to AlHO in the clay interlayer space but Cd and Pb were only held exchangeably, through outer-sphere linkages, and were easily displaced by other cations. Sako et al. [96] showed specific adsorption of the platinum group elements, originating from catalytic convertors, in a kaolinitic soil (Pd > Rh > Pt). The trend in adsorption with pH was very similar to that expected for oxides (as in Fig. 3.3), with a steep rise in affinity over a single pH unit.

3.2.4 Zeolites

3.2.4.1 Bulk Properties

Zeolites are ‘tectosilicates’, composed of silica tetrahedra which form a hydrated microporous three-dimensional framework, with intra-crystalline morphological features called ‘windows’, ‘cages’, ‘cavities’ and ‘channels’ [76]. The most common zeolites in nature are: analcime, chabazite, clinoptilolite, erionite, mordenite, phillipsite and ferrierite but they rarely comprise more than a few percent of the clay minerals in soils. Usually, zeolites in soils are inherited from parent materials derived from weathered volcanic deposits or from alluvial or eolian deposits [16]; the most commonly found mineral is clinoptilolite. Zeolites can also be ‘pedogenic’; these typically occur in saline-alkaline environments in which analcime is perhaps the most common example [16].

3.2.4.2 Surface Chemistry

Zeolites are negatively charged by isomorphous substitution of Al^{3+} for Si^{4+}. Their generic composition is $C_{x/v}[(AlO_2)_x\ (SiO_2)_y].mH_2O$, where C represents a charge-balancing cation of valence ‘v’. Their surface charge is therefore permanent and the resulting CEC can be extremely large, depending on the degree of Al substitution. Most zeolites have potential CEC values of 200–600 $cmol_C\ kg^{-1}$ which is considerably greater than the phyllosilicate clays (Sect. 3.2.3).

3.2.4.3 Metal Binding

A large proportion of the CEC of zeolites exhibits rapid and reversible cation exchange [22]. However, because of their complex 3-D structure zeolites also exhibit some specific adsorption capacity with respect to individual metal cations. The dimensions of the various ‘cages’, ‘channels’ etc. within the zeolite structure determine selectivity for different sizes of cation to a large degree. This form of selectivity has been called ‘ion sieving’ [16]. Fletcher and Townsend [38] demonstrated apparent irreversibility of trace metal sorption on Faujasite after only short contact times. Ören and Kaya [85] found evidence of surface precipitation of Zn in natural clinoptilolites above pH 6.0. By following changes in isotopic exchangeability with $^{109}Cd^{2+}$, Ahmed et al. [1] demonstrated Cd adsorption hysteresis and prolonged time-dependent ‘fixation’ in a synthetic zeolite. The ‘fixation’ was well described as a reversible first order kinetic process and was thought to be associated with Cd ion dehydration and ingress to smaller pores within the zeolite structure.

The comparative rarity of zeolites in soils belies their potential importance in metal sorption and the application of this property to soil remediation [13] and water protection [58]. Natural zeolites have found widespread application in recovering trace metals (Pb, Cd, Zn, Ni, Co, Cr^{III}, Cu and Fe^{II}) from wastewaters [90, 116] and the treatment of low-high level nuclear waste liquids [30, 51]. There have been several studies of the application of zeolites as amendments for metal-contaminated soils [25, 67].

3.2.5 Sparingly Soluble Calcium Salts and Metal Precipitation Reactions

3.2.5.1 Adsorption on Ca Salts

Sparingly soluble Ca salts are found in soils that are calcareous ($CaCO_3$), gypsiferous ($CaSO_4.nH_2O$) or are heavily fertilized and contain Ca phosphates (e.g., hydroxyl apatite). Metals may bond to the surface of Ca salts either because of similarity to Ca (e.g., Cd) or because of a high affinity for the salt ligand (e.g., Pb for PO_4). However, they may also precipitate on the Ca mineral surface as discrete compounds or form mixed solid-solutions.

There have been comparatively few studies of heavy metal adsorption on simple Ca compounds. Ahmed et al. [2] demonstrated that Cd is adsorbed in an isotopically exchangeable form on calcite but also undergoes time-dependent fixation within the calcite structure; they worked within the normal range of solution Cd concentrations found in soil pore water, below the ion activity product at which $CdCO_3$ might precipitate. Papadopoulos and Rowell [88] suggested that a 'mixed solid-solution' of $Cd_nCa_{n-1}(CO_3)$ formed at higher Cd concentrations.

3.2.5.2 Discrete Metal Compounds in Soils

For metals to form discrete stable precipitates in soils the ion activity product (IAP) in the soil pore water must exceed the solubility product (Ks) of the compound (IAP $>$ Ks). With the exception of the structural cations Fe, Mn and Al, this rarely occurs in uncontaminated soils because trace metals are present at comparatively small (total) concentrations and the free ion activity of trace metals in soil water is generally very small because of strong surface adsorption by soil constituents. Other factors may prevent formation of discrete metal compounds even if conditions are otherwise favourable for precipitation. Thus, Lang and Kaupenjohan [65] suggested that organic acids in soils could prevent crystal growth of the lead phosphate compound chloropyromorphite $[Pb_5(PO_4)_3Cl]$.

However, trace metals can exist as 'guest elements' within the matrices of other soil minerals. This is thought to occur through:

(i) the process of isomorphous substitution, which occurs during the formation of the mineral;
(ii) slow solid phase diffusion into pre-existing minerals following adsorption;
(iii) occlusion within minerals during dissolution-precipitation cycles caused by fluctuating pH and/or Eh regimes.

It is not disputed that discrete metal compounds exist in soils ,but their longevity, stability and the extent to which they can control metal solubility are poorly understood [32]. Soil processes act to dissolve *introduced* compounds which then become adsorbed on the soil colloidal phase even in quite heavily contaminated situations. Degryse et al. [31] showed that about 50% of Pb was isotopically exchangeable in soils heavily contaminated by smelter output and battery plants, despite having neutral pH values. Similarly, Sarret et al. [97] fractionated Zn in a soil contaminated by smelter output and showed by EXAFS that only 15% of the soil Zn was present as residual primary minerals while 54–92% was isotopically exchangeable and mainly bound to humus. Smolders and Degryse [106] showed that up to 40% of the Zn in tyres (mainly ZnO) becomes labile in soils within 1 year.

Nevertheless, unusual metal compounds have been identified in soils with extremely high residual contaminant loads or subject to contemporary inputs. For example, amorphous $FeAsO_4$ was found in mine spoil contaminated soils with 8.8% As using EXAFS/XANES [7]. Sphalerite (ZnS) and Franklinite

($ZnFe_2O_4$) were identified in soils close to Zn smelters with >6,000 mg kg^{-1} using EXAFS and electron microprobe analysis [95]. Murakami et al. [80] also used electron probe microanalysis to identify particulates in roadside dust with >0.2% Cr and Pb, thought to originate from vehicle exhaust soot, brake lining and paint. Councell et al. [27] discuss the importance of vehicle tyre wear as a source of anthropogenic Zn in soils. Uzu et al. [118] found a range of Pb compounds (PbS, $PbO.PbSO_4$, PbO, $PbCO_3$) in PM_{10} and $PM_{2.5}$ particles from a battery recycling plant and confirmed a link between particle size and bioavailability to plants.

Many studies have confirmed the presence of Pb compounds in particular. Some of these concern residual introduced material but many also focus on the pedogenic formation of discrete Pb phosphates. Chloropyromorphite formation has been encouraged by the introduction of soluble forms of phosphate to limit Pb solubility in urban brownfield soils [63] and land used as shooting ranges [49]. Other forms of Pb identified include: metallic Pb, PbO and $PbCrO_4$ in industrially contaminated soils, identified by SEM-EDX [57]; Hydrocerrussite [$Pb_3(CO_3)_2(OH)_2$] resulting from weathering of shotgun pellets, identified by micro X-ray fluorescence [120]; Pb oxide in soils subject to smelter fallout [53].

3.2.6 Conclusions on Adsorption of Metals on Soil Constituents

As a very broad generalisation, the principal adsorption sites for trace metals may be on humus at low pH (<6) and on Fe oxides at high pH (>6). Thus, in a review of the behaviour of metals in tropical soils Rieuwerts [93] examined the perceived risk that (cationic) trace metals may be highly available in some oxisols and ultisols specifically because of the low pH and the relatively low content of humus. However, evidence for metal movement down the soil profile was inconclusive and it appeared that iron oxides provided effective adsorption sites despite low soil pH. Buekers et al. [18] examined fractionation using the geochemical model WHAM-VI (Sect. 3.4.3) to partition metals in the solid phase between humus, oxides and aluminosilicate clays. Similarly, Fig. 3.4 shows the fractionation of Cu, Pb and Cd, predicted by WHAM-VI, for a hypothetical soil (see Fig. 3.4 description) assumed to have metal concentrations at the UK sludge regulation limits. The model illustrates substantial differences between the three metals. Copper has the strongest affinity for humic and fulvic acids. Lead is bound almost exclusively by Mn oxide at low pH and Fe oxide at $pH > 7$. Cadmium is the most weakly bound metal, such that below pH 5 there is even substantial non-specific bonding to the alumina-silicate clay fraction (Sect. 3.2.3.3); however, above pH 7 Cd sorption is dominated by the Fe oxide fraction. The substantial differences that exist between metals and the dependence of fractionation on soil properties are clear; these are examined in more detail in the following section.

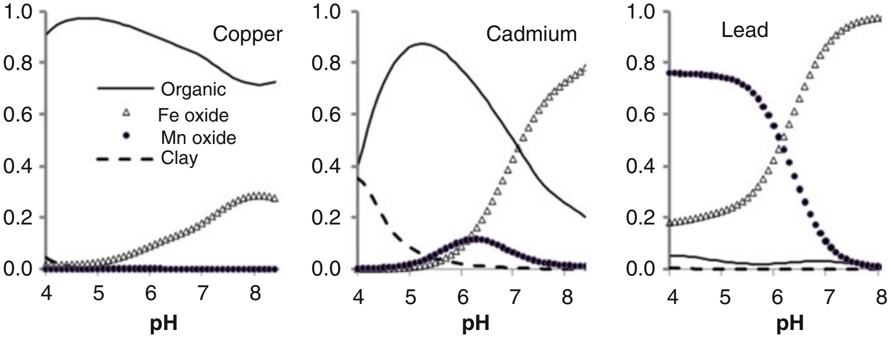

Fig. 3.4 Proportional distribution of Cu, Cd and Pb between organic matter (*solid line*), Fe oxide (Δ), Mn oxide (●) and alumino-silicate clay (*broken line*) in the soil solid phase, as a function of pH, according to WHAM-VI. Hypothetical soil conditions included 1.2 kg suspended in 1 L solution; 5% humus with 30% HA and 20% FA (50% inert); 20% clay, 3.5% Fe oxide and 0.075% Mn oxide. The metals Cu, Cd and Pb were at the current UK 'sludge limits' (135, 3 and 300 mg kg^{-1}). Solubility of Al^{3+} and Fe^{3+} were controlled by $Al(OH)_3(s)$ and $Fe(OH)_3(s)$. The solution phase contained 20 mg L^{-1} FA and 0.005 M Ca^{2+}, 0.0005 M K^+ balanced by 0.0095 M NO_3^- and 0.001 M Cl^-

3.3 Effect of Soil Conditions on Metal and Metalloid Adsorption

3.3.1 Soil pH Value

Soil acidity is measured on the 'pH' scale, normally in a 1:2.5 (w/v) soil:solution suspension, using a combined H^+-sensitive glass electrode and Ag-AgCl reference electrode, where:

$$\mathrm{pH} = -\log_{10}(\text{hydrogen ion activity}) = -\log_{10}(\mathrm{H}^+) \qquad (3.1)$$

Soil pH is both affected by, and indicative of, specific ecosystems or land use practices (Table 3.1).

3.3.1.1 Effect of Soil pH Value on Metal Solubility

Soil pH value has a greater influence on the solubility of heavy metals than any other factor. This would be predictable considering simple metal oxide, hydroxide and carbonate (MCO_3) solubility reactions.

$$\text{eg} \quad MCO_3(s) + 2H^+ \Leftrightarrow M^{2+} + CO_2(g) + H_2O$$

However, as discussed by Degryse et al. [32], the stoichiometry of $M^{2+} \leftrightarrow H^+$ exchange is usually less than the value of 2.0 required for many precipitation reactions which indicates the importance of specific adsorption in controlling metal ion solubility.

Table 3.1 Broad relationship between ecosystem characteristics and soil pH value

Soil pH range	Soil characteristics
<3.5	Acid sulphate soils with active oxidation of ferrous sulphide
3.5–4.0	Acidic peats and podzol surface organic horizons
4.0–5.0	Acid forest soils (e.g., Brown earths)
5.0–6.0	Many examples – e.g., sandy soils under un-limed grassland
6.0–7.0	Many examples – the preferred pH range for arable soils. Many urban soils and brownfield sites
7.0–8.0	Calcareous soils over limestone or chalk parent materials. Many urban soils and brownfield sites
8.0–10.0	Sodic soils with free sodium bicarbonate

For cationic metals a change in soil pH has several important, and independent, effects which influence the apparent strength of adsorption by soil solids. Thus, as pH value ***rises***, the following changes occur.

(i) Surface charge, and electrical potential, will become more negative on the principal adsorption sites on Fe/Mn hydrous oxides, alumino-silicate clay edge sites and humus.

(ii) Competition for adsorption sites from hydronium ions (H_3O^+) and from dissolved 'structural' cations (mainly Al^{3+} and $AlOH^{2+}$) will decline as H_3O^+ ions are neutralised and soluble aluminium ions are (re-)precipitated as $Al(OH)_3(s)$.

(iii) The speciation of the metal cation may change through formation of soluble hydroxy and bi-carbonate complexes, for example. If the principal adsorbing species is the divalent cation (e.g., Cu^{2+}) then this effect will increase overall metal solubility. However, it has also been suggested that the first hydroxide complex of some metals (e.g., $Cr^{III}OH^{2+}$) may be the more important adsorbing species and so changes in metal speciation may produce quite complex effects on adsorption.

(iv) A related effect arises if the increase in soil pH dissolves metal-complexing anions. Again these will bring more metal into solution against the prevailing trend of greater sorption into the solid phase. The principal example here is the soluble components of humus: humic (HA) and fulvic (FA) acids. The solubility of HA and the strength of metal binding by both HA and FA increase as pH rises and the humus acids become more negatively charged and more hydrophilic. This effect is most pronounced for metals that bind most strongly to HA, such as Cu. It has been shown that the distribution coefficient (k_d) of Cu in some soils is close to the k_d value for dissolved organic carbon (DOC) [32, 111]. It may be that some sub-micron inorganic colloids, which both adsorb and contain trace metals, behave similarly although evidence for this is currently still emerging [69].

Notwithstanding some of the more subtle effects listed in (iii) and (iv) above, the dominant effect of an increase in soil pH is a decrease in cationic metal solubility. An example of this trend is shown in Fig. 3.5 below where samples of a soil used for

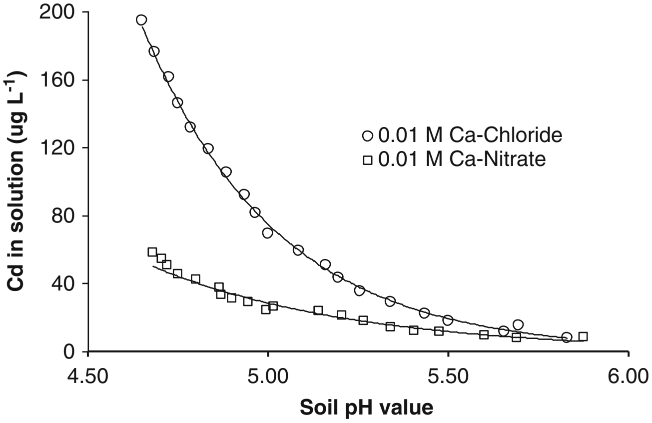

Fig. 3.5 Cadmium concentration in solution as a function of soil pH in batch equilibrations (1:10 w/v suspensions of 0.01 M $Ca(NO_3)_2$ or 0.01 M $CaCl_2$) of an arable soil from a sewage disposal site. The soil was from one of the oldest and most heavily 'sludged' disposal areas ($Cd = 59.3$ mg kg^{-1}; humus = 24.8%) *solid lines* are simple exponential fits

sludge disposal for over a century were suspended in 0.01 M Ca salts and acidified to various levels. The solubility of Cd clearly follows a broadly exponential trend with pH within the range of the measurements.

3.3.1.2 Liming Acid Soils to Lower Heavy Metal Solubility

Mineral soils and peats which have a pH (in water) below pH 6.5 or pH 5.8 respectively normally require liming with $CaCO_3$ for arable agriculture, partly to avoid aluminium toxicity. Similarly, soil may be limed to around pH 7 to avoid toxicity from contaminant metals such as Pb, Ni, Cu, Cd, Zn, Hg, Sn. Examples include restoration of urban 'brown-field' sites, land affected by acid mine drainage, and management of arable land habitually used for sewage sludge disposal.

The alleviation of aluminium toxicity in acid soils can be shown by the simplified reaction illustrated below. Exchangeable aluminium hydroxide ions ($Al(OH)^{2+}$), held in clay inter-layers and by humus functional groups (Humus-COO^-), are precipitated as crystalline or amorphous forms of aluminium hydroxide ($Al(OH)_3$). So the solubility and bio-availability of toxic aluminium is reduced.

$$Ex.Al(OH)^{2+} + CaCO_3(s) + 2H_2O \rightarrow Al(OH)_3(s) + Ex.Ca^{2+} + CO_2 + H_2O \quad (3.2)$$

This involves a series of individual reaction steps, including:

(i) dissolution of $CaCO_3(s)$ to release Ca^{2+} and $CO_3{}^{2-}$ into solution
(ii) cation exchange between $Al(OH)^{2+}$ and Ca^{2+} on clay and humus;
(iii) hydrolysis of CO_3^{2-} to produce OH^- ions and CO_2;
(iv) precipitation of solid aluminium hydroxide, $Al(OH)_3(s)$.

By contrast, when a soil contaminated with divalent heavy metals is limed it is unlikely that precipitation of the (divalent) Pb, Ni, Cu, Cd hydroxides, carbonates or oxides will occur (IAP < Ks). Therefore, it might be expected that Ca^{2+} from liming agents would simply liberate adsorbed metal ions into solution, which would increase the potential toxic hazard. Of course the solubility of the contaminant trace metals almost always *decreases* due to the rise in pH caused by the addition of lime. Fundamental to the successful use of lime to reduce the solubility and bioavailability of potentially toxic metals is the difference in bonding to soil of alkali/alkaline-earth cations (e.g., Ca^{2+}) and most heavy metals. The former are largely held weakly as exchangeable hydrated ions, by electrostatic forces, within alumino-silicate clay interlayers or on charged humus carboxyl groups. Heavy metals, by contrast, are strongly (specifically) bonded to exposed oxy-acid groups on humus and hydrous oxides as inner-sphere (partially dehydrated) complexes. Therefore, addition of lime creates two opposing reactions affecting metal solubility. Calcium ions may release into solution the limited amount of 'exchangeable' trace metals that are held in clay interlayer sites and humus. However this effect is completely negated by the titrating effect of the carbonate ions which neutralise H^+ ions from organic carboxyl and surface hydroxyl groups on Fe/Mn hydrous oxides and thereby free sites for occupancy by strongly binding divalent heavy metals. The latter occurs as a combination of reduced competition from H^+ ions (and $AlOH^{2+}$ ions) and increased electrostatic attraction between negatively charged humus or hydrous oxide sites and metal ions, as discussed above.

The example below represents liming an acidic soil contaminated with lead initially present in an available, in this case *exchangeable*, form. Calcium ions displace exchangeable forms of Pb into solution but carbonate ions neutralise specifically adsorbed H^+ ions on humus carboxyl groups (Hu-COOH), increasing (negative) surface charge and encouraging greater specific adsorption of Pb^{2+} ions.

$$\mathrm{ExPb^{2+} + CaCO_3}(s) + [\mathrm{Hu\text{-}(COOH)_2}] \Rightarrow \mathrm{ExCa^{2+}} + [\mathrm{Hu\text{-}(COO)_2 = Pb}] + \mathrm{CO_2 + H_2O}$$

Liming acid soils to pH 7–8 remains the most expedient way of reducing the solubility of heavy metals, in most situations.

3.3.2 Soil Redox Potential (Eh)

Redox potential (Eh, mV) is an intensive thermodynamic property related to the hypothetical activity of electrons (e^-) through the well known Nernst equation and, in practice, is normally measured with a platinum electrode with Ag/AgCl chloride electrode as reference ($\mathrm{pe} = -\log_{10}(e^-)$).

$$\mathrm{Eh} \quad = \quad \frac{\mathrm{RT}\ln(10)}{\mathrm{F}}\,\mathrm{pe} \quad \approx \quad 59\ \mathrm{pe\ (at\ 25^\circ C)} \tag{3.3}$$

Table 3.2 Principal soil redox reactions and the Eh range in which they typically occur

Soil Eh range (mV)	Soil characteristics
>450	Aerobic soil; oxygen is the principal electron acceptor: $O_2 + 4H^+ + 4e^- = 2H_2O$
200–400	Denitrification: $NO_3^- + 6\,H^+ + 5\,e^- = ½\,N_2 + 3\,H_2O$
100–200	Mn^{IV} oxide reduction and dissolution: $MnO_2(s) + 4\,H^+ + e^- = Mn^{2+} + 2\,H_2O$
−100–200	Fe^{III} oxide reduction and dissolution: $Fe(OH)_3(s) + 3\,H^+ + 2\,e^- = Fe^{2+} + 3\,H_2O$
−150–0	Sulphate reduction to sulphide: $SO_4^{2-} + 10\,H^+ + 8\,e^- = H_2S + 4\,H_2O$
<−250	Acetoclastic methanogenesis: $CH_3COOH = CH_4 + CO_2$

Although the derived value of (e^-) can be used in equilibrium calculations, as if it were a discrete chemical species, it is accepted that Eh values are more safely regarded as an 'index' of redox status when measured in soils. This is partly due to difficulties in measuring Eh [100] and partly because there is always doubt whether redox equilibrium has truly been established [61].

A decrease in soil redox potential (Eh value becomes less positive) typically occurs when soils become wet. The resulting impediment to the diffusion of oxygen into the soil causes the utilization of alternative electron acceptors as organic matter decomposition continues under progressively more anaerobic conditions. The general reduction sequence followed in soils is well established [91]. Table 3.2 shows the broad range of Eh values in which specific redox reactions are 'poised' (buffered) as soils become progressively more anaerobic.

The rate at which the redox potential falls is mainly determined by the nature and availability of the carbon substrate, the degree of restriction on oxygen ingress and the availability of the alternative electron acceptors. It is recognised that some heavy metals become more soluble under anaerobic conditions. Thus Pareuil et al. [89] have suggested that it may be useful to characterise the risk of metal mobilisation in contaminated soils by equilibrating with a range of concentrations of reducing agents, such as ascorbate, to generate a 'redox mobilization edge' (metal solubility vs Eh). However, as redox potential falls naturally, due to microbial activity in saturated soils, several changes occur which may affect metal and metalloid solubility in contradictory ways. These are discussed below.

3.3.2.1 Change in pH

Most redox reactions in soils involve transfer of electrons and protons. This dependence can be described by Eq. 3.4.

$$\mathrm{Eh} = \mathrm{Eo} - \frac{\mathrm{RT}\,\ln(10)}{\mathrm{F}}\left(\frac{n_H}{n_e}\right)\mathrm{pH} \approx \mathrm{Eo} - 59\left(\frac{n_H}{n_e}\right)\mathrm{pH} \quad (\text{at } 25^{\circ}\mathrm{C}) \tag{3.4}$$

Eo is the standard redox potential for the reaction and the ratio n_H/n_e denotes the stoichiometric ratio for electron and proton transfer. In practice it is unlikely that Eq. 3.4 will be followed exactly because (i) there are widely varying concentrations of specific redox couples and (ii) soil pH is strongly buffered by other proton adsorption reactions which are not directly involved in redox reactions [78]. Nevertheless, redox reactions do have a marked effect on soil pH. In fact, soil pH values gravitate to a very restricted *circumneutral* range under anaerobic conditions (c. pH 6.5–7.5) [91]. This is thought to arise from the conflicting effects of (i) a build up of CO_2 partial pressure which lowers pH in alkaline soils by hydrolysis to carbonic acid and (ii) the consumption of H^+ ions by most reduction reactions which raises pH in acid soils (Table 3.2) [94]. Thus for soils which have pH values <6.5 under aerobic conditions, the net result of anaerobism may be an increase in the strength of cationic metal adsorption by humus and metal oxides and an increased possibility of (e.g.) metal carbonate precipitation (Sect. 3.3.1).

3.3.2.2 Dissolution of Fe/Mn Hydrous Oxides

At pH > 6 Fe and Mn oxides are likely to be significant adsorbers of cationic metals and anionic oxyacids (Sect. 3.2.2). If the oxides are reduced and solubilized then two significant effects on metal solubility should occur. Firstly, metals and metalloids adsorbed on the surface will be released as the underlying substrate dissolves. This can be represented as a surface reduction-dissolution reaction for (e.g.,) Pb sorbed on ferric oxide (balancing ions omitted):

$$\mathrm{Fe_2}^{\mathrm{III}}\mathrm{OO{=}Pb(s)} + 4\mathrm{H}^+ + 2\mathrm{e}^- \Leftrightarrow 2\mathrm{Fe}^{2+} + \mathrm{Pb}^{2+} + 2\mathrm{H_2O}$$

The heavy metals may be re-adsorbed on the freshly exposed oxide surface but this must depend on the extent of oxide dissolution and the thickness of the oxide coating. Secondly, the release of large concentrations of Fe^{2+} and Mn^{2+} into solution will present intense competition for metal adsorption sites on humus, clay edges and, of course, on the newly created Fe^{III}/Mn^{IV} oxide surfaces. The overall result of reduction may therefore be increased solubility of trace metals.

When a flooded soil drains, or dries through evaporation, redox potential rises and Fe/Mn oxides re-precipitate. This will cause re-adsorption of liberated metals and if co-precipitation occurs, may even result in ‘fixation’ of metals within oxide particles. Contin et al. [23, 24] suggested that deliberately implementing redox cycles in contaminated soils could be used to lower metal bioaccessibility in some soils. Metal fixation followed the qualitative order Cu $>$ Cd $>$ Zn$>>$ Pb$>>$ Ni using three cycles with anaerobic periods of 40 days each, interspersed with short drying periods. Lee [66] suggested that a similar fixation process may have maintained low metal availability in a kaolinitic paddy soil contaminated by mine tailings.

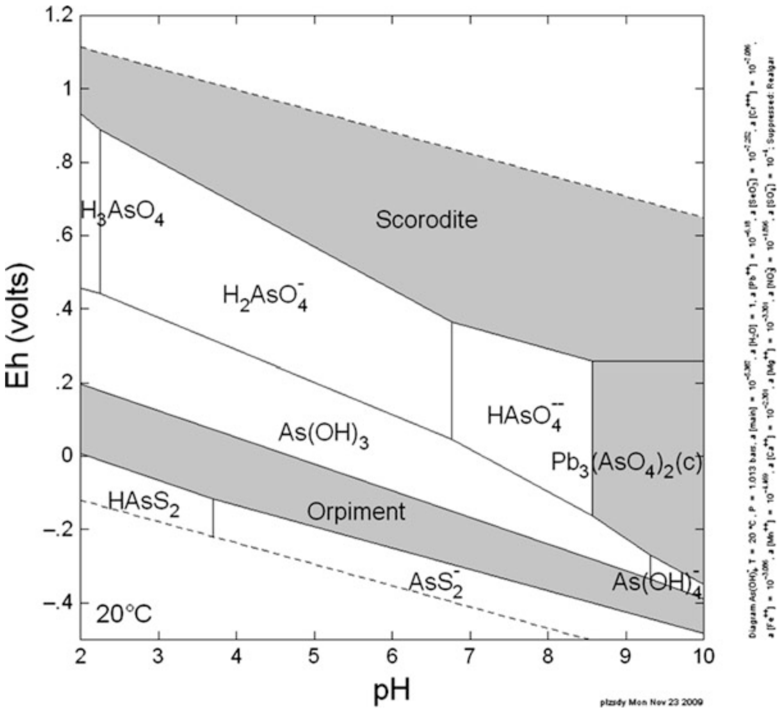

Fig. 3.6 Predominance diagram for arsenic species as a function of pH and Eh (Produced using The Geochemist's Workbench® program)

3.3.2.3 Changes in Metal and Metalloid Valence

Some metals and metalloids undergo valence changes within the range of redox potentials experienced in anaerobic soils – arsenic is a prime example. The stable form of As in aerobic soils is arsenate (mainly $H_2AsO_4^-$ and $HAsO_4^{2-}$ in the pH range 6–7) which behaves very similarly to phosphate ($pKa_2 = 7.2$) and is adsorbed strongly by Fe oxides. As Eh values fall below 250 mV As^V is reduced mainly to As^{III} (arsenite) and possibly methylated forms such as dimethylarsinic acid (DMA; $(CH_3)_2HAsO_2$) and monomethylarsonic acid (MMA; $CH_3H_2AsO_3$). The closest analogue to arsenite is perhaps silicic acid ($pKa_1 = 9.8$), and so As^{III} forms a neutral molecule ($H_3AsO_3^o$) that is very poorly adsorbed. This may be the prime mechanism whereby As is released into groundwater in aquifers which become even mildly anaerobic, as experienced in West Bengal and Bangladesh [60].

$$H_3AsO_4^o + 2H^+ + 2e^- \Leftrightarrow H_3AsO_3^o + H_2O$$

Figure 3.6 shows that transformations between arsenate and arsenite are predicted to occur within the pH-Eh ranges often encountered in wet topsoils, or aquifers with sufficient organic matter to undergo reduction.

Chromium is also subject to changes in valence within the range of conditions found in soils. Reduction of Cr^{VI} to Cr^{III} increases adsorption (as Cr^{3+} or $CrOH^{2+}$) and renders carcinogenic Cr ^{VI} less harmful. Thus Banks et al. [8] found that adding organic manure detoxified Cr^{VI} and promoted greater adsorption. Cobalt is strongly adsorbed within Mn oxides as Co^{III} [42] (see Sect. 3.2.2) and, correspondingly, is usually strongly correlated with Mn^{2+} release under anaerobic conditions [47], partly through reduction of Co^{III} to Co^{2+}. Selenate reduction to selenite should increase adsorption as selenite is a specifically adsorbed anion while selenate is a strong acid anion which is indifferently adsorbed and, at pH 6–7, will remain almost entirely in solution.

3.3.2.4 Release of Complex-Forming Anions and Dissolved Organic Carbon (DOC)

Under anaerobic conditions, anions (phosphate, bicarbonate, fluoride, molydate, humic and fulvic acids etc.), normally adsorbed on Fe/Mn oxides, come into solution as pH rises and the oxides are partially solubilised. In addition, in flooded soils, DOC concentration normally increases as a result of decomposition reactions under oxygen-free conditions. This may have two conflicting effects on cationic metal solubility. Complex formation in solution, especially with HA, FA and other DOC compounds such as propionic and butyric acids [91] will clearly increase the solubility of strongly bound metals such as Cu, Pb and rare earth elements [47]. On the other hand, the formation of new mixed solid phase assemblages, such as humic acid with Fe oxides, may actually increase adsorption of metals [122].

3.3.2.5 Precipitation of Metal Sulphides and Carbonates

Increased soil pH and partial pressure of trapped CO_2 following soil flooding may cause precipitation of metal carbonates [70]; this has been reported for Cd, Zn and Pb [78]. However, under strongly anaerobic conditions ($Eh < -100$ mV), especially in soils with a significant (reducible) sulphate content, it may be possible for metal sulphide precipitation to occur [34]. From solubility modelling, Schroder et al. [100] suggested there was strong evidence for Pb, Zn, Cd and Cu sulphide precipitation in floodplain soils under such conditions. Cornu et al. [26] incubated an industrially contaminated arable soil ($Cd = 3.8$ mg kg^{-1}) under saturated conditions and observed an initial increase in Cd solubility followed by a decline as pe fell below 3. It was thought possible that CdS (Greenockite) may have formed but this could not be confirmed thermodynamically. Theoretically, the trace metals Cd, Zn and Pb should all precipitate before ferrous sulphide formation ‘poises’ the system and thereby prevents further decline in Eh. However, this depends on the free ion activity of the trace metals supported which is difficult to predict when progressive anaerobism usually coincides with changes in soil pH and complexing ligand concentration.

3.3.2.6 Biomethylation

Some metals and metalloids are biologically transformed to methylated forms under anaerobic conditions. These may be more (Hg) or less (As) hazardous than inorganic forms. The range and significance of methylated and organic forms of As are relatively unknown. Many studies have focussed only on arsenite (As^{III}) and arsenate (As^{V}) in studies of As transformations in soils. However, Huang and Matzner [54] identified seasonally dependent microbial methylation of As (MMA, DMA, TMAO) in pore water from wetland soils in Germany, along with several unknown organic forms of As.

3.3.3 Soluble Ligands

In most soils, metal solubility is significantly affected by the presence of complex-forming ligands. The most common organic ligands are fulvic and humic acids which are present in all soil pore solutions; these are discussed in Sects. 3.2.1 and 3.4.3. However inorganic ligands can also increase metal solubility. These typically include SO_4^{2-}, F^-, NO_3^-, Cl^- with HCO_3^- and CO_3^{2-} at high pH. *Chloro-complexation* in particular has received considerable attention because Cd has a moderately high affinity for Cl-, forming soluble $CdCl^+$ and $CdCl_2^0$ complexes with overall stability constants: $\log\beta(CdCl^+) = 1.98$ and $\log\beta(CdCl_2^0) = 2.6$. In fact, Ahmed et al. [1] demonstrated that Cd adsorption (on zeolites) was controlled exclusively by Cd^{2+} and chloro-complexation increased Cd solubility quantitatively. Thus Cd mobilization in soils subject to elevated chloride has been the subject of some concern [107]. Millward and Liu [79] found the mobilization of metals from sediments suspended in seawater followed the sequence $Ni > Cd > Zn > Cu$. Rasa et al. [92] suggested that Cd may be more soluble in roadside soils due to NaCl use for de-icing. However, the net effect on metal solubility in salt-affected environments will be a combination of several independent processes in addition to complex formation, including cation exchange with Na^+, weakening of adsorption by increased ionic strength, possible flocculation or dispersion of colloidal particles and effects on pH and Eh (Sects. 3.3.1 and 3.3.2). Thus Du Laing et al. [34] reviewed the factors affecting metal behaviour in (saline) estuarine soils and noted, for Cd in particular, that mobilization by chloro-complexation is offset by precipitation with sulphide in anoxic saline environments.

Non-humic organic ligands which can mobilize metals may arise from natural root exudates (citrate, malate, oxalate) [131] and from the application of certain pesticides, such as Glyphosate [9]. However, the effect of these ligands on metal solubility will partly depend on the solubility and longevity of the organic acid in soils.

3.3.4 Time, Temperature and 'The Slow Reaction'

3.3.4.1 Time

It is generally recognised that metal ions added to soils in solution will rapidly attain an apparent equilibrium with adsorption surfaces over a period of several hours. However, most metals and metalloids then exhibit further (slower) sorption, over an extended period (months), in which metal ions are transferred from a 'labile' to a 'non-labile' state [32, 117]. This is generally referred to as 'the slow reaction', 'ageing' or 'fixation' [123] and may be partly (or wholly) responsible for the phenomenon of 'desorption hysteresis' commonly observed for metal ions adsorbed from solution on to soil minerals such as calcite, zeolites and goethite [1, 2, 11]. However, it is important to note that 'fixation' is not always a time-dependent process and may also be caused by very rapid reactions such as surface precipitation or possibly strong inner-sphere adsorption. Thus it is often found that a proportion of metal ions, added to soil in solution, become fixed almost instantly – as best judged by isotopic exchangeability. Nakhone and Young [82] noted this effect for Cd fixation in calcareous soils while Ma et al. [71–73] observed a similar process for Cu adsorbed by soils high in organic matter.

There are several mechanisms which may explain the slow reaction, including diffusive limitations, adsorption energy barriers and surface precipitation; in practice these are not entirely independent.

3.3.4.2 Diffusive Limitations

It is recognised that diffusive limitations exist *in solution* as ions slowly penetrate the microporous structure of soil aggregates. This may be especially true for anionic species, such as $HAsO_4^{2-}$ and CrO_4^{2-}, due to repulsion (anion exclusion) from micro-pores lined with negatively charged surfaces [84]. Immediately following adsorption there is likely to be progressive 'surface diffusion' as metal ions redistribute themselves between adsorption sites to achieve lower free energy states. However, it is 'solid phase diffusion', following initial surface adsorption [11], which is usually most closely associated with the extended slow reaction. This involves penetration of the solid phase matrix by replacement of the native cation (or anion) and may occur by true solid phase diffusion but could also occur by occlusion resulting from the continuous process of dissolution and re-precipitation. Diffusive processes may be particularly important at pH values below those required for precipitation reactions; Ma et al. [73] suggested that a diffusive process was solely responsible for slow fixation of Cu in soils below pH 5.

3.3.4.3 Adsorption Energy Barriers to Specific Reactions

Energy barriers to adsorption may occur where there is a specific part of the adsorption mechanism that is rate-limited, such as dehydration, the formation of multiple bonds or slow exchange reactions. Ahmed et al. [1] found that both slow adsorption and desorption of Cd on zeolites was better explained as a first-order kinetic process rather than by continuous diffusion into the zeolite particles. From EXAFS data they provisionally associated the Cd fixation process with retention of dehydrated Cd^{2+} in a specific cavity in the zeolite structure [3].

3.3.4.4 Discrete and Surface Precipitation

Precipitation of metals may occur on existing mineral surfaces or as discrete compounds. In both cases there may be slow reactions involving (i) 'Ostwald ripening' to reduce the surface : volume ratio, (ii) formation of compounds with more stable stoichiometries and (iii) continued penetration of mineral surfaces to form solid solutions. Ma et al. [73] suggested that the slow reaction between Cu and calcareous soils signified Malachite ($Cu_2(OH)_2CO_3$) and $Cu(OH)_2$ formation and 'precipitation/nucleation' reactions generally occurring above pH 6.

3.3.4.5 Effect of Soil Properties on the Slow Reaction

It seems likely that soil components which have little scope for (internal) absorption because of the lack of a porous structure or no clear means of occluding metals will show little if any slow reactions. Thus Covelo et al. [28] found that metals (Cd, Cr, Cu, Ni, Zn, Pb) were most *reversibly* adsorbed on 2:1 alumino-silicate clays and least reversibly adsorbed on Mn oxides. Palagyi et al. [87] investigated sorption of ^{109}Cd by forest and arable topsoils and subsoils, with peroxide treatment to remove humus. They showed that Cd is reversibly held by humus but undergoes time-dependent fixation in mineral constituents. Shirvani et al. [104] demonstrated Cd sorption hysteresis in the Mg-silicates Palygorskite and Sepiolite and in Calcite. Ahmed et al. [2] measured and modelled time-dependent fixation and adsorption hysteresis of Cd on Calcite. Nevertheless, it may also be possible for organic matter to 'fix' metals. Vega et al. [121] expressed irreversible Cd and Cu sorption in soils as a 'hysteresis index' (HI) and showed that although HI was greatest for Cd at high pH and MnO_2 content, it was greatest for Cu at high humus content. Young et al. [130] reported isotopically non-exchangeable Hg in filtered solutions of ^{203}Hg spiked soils which they tentatively interpreted as fixation in DOC. Thus, fixation of metals may also occur simply through strong surface complexation, without occlusion within solids.

Slow fixation reactions have been demonstrated most successfully using isotopic exchange to discriminate between 'labile' and 'non-labile' forms [1, 19, 29].

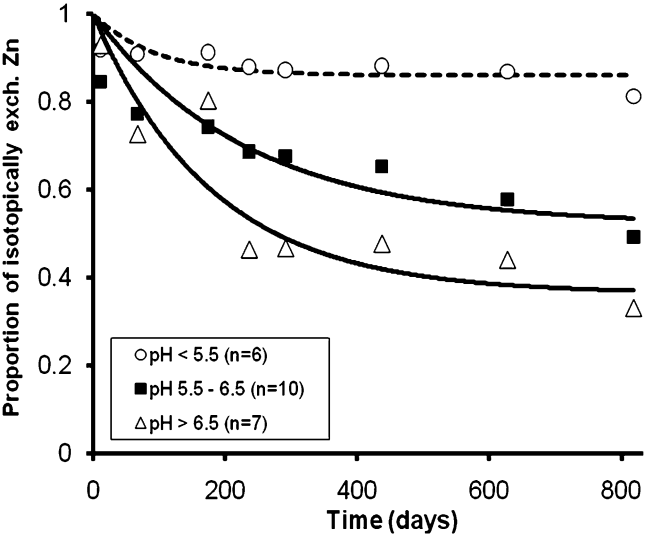

Fig. 3.7 Change in isotopic exchangeability of Zn initially added in solution to 23 soils categorised by pH range. The slow reaction is modelled as a *reversible* first-order kinetic process (*solid lines*)

Figure 3.7 shows the reduction in isotopic exchangeability of Zn, initially added to soils in solution, as a function of pH. As expected, fixation was greater at high pH. However, a crucial point is that the slow reaction had to be modelled as a *reversible* first-order kinetic reaction [1, 2, 29]; the decline in metal lability does not tend to zero but to an apparent steady state in which non-labile metal ions re-enter the labile pool. This also supports the universal finding that historically contaminated soils typically have substantial proportions of isotopically exchangeable metal. Therefore metal ions determined as non-labile should be regarded as 'kinetically restricted' in their interaction with the soil solution phase rather than permanently 'fixed'. This reinforces the distinction between 'non-labile' and 'inert' in Fig. 3.1; Degryse et al. [32] discuss this issue in more detail.

3.3.4.6 Temperature

A higher temperature increases the proportion of the metal ions which have sufficient energy to overcome energy barriers to adsorption or desorption and therefore movement in general. This effect can be described in terms of an activation energy (Ea, kJ mol^{-1}). The rate constant for adsorption or desorption (k) is related to temperature through the well known Arrhenius equation:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \tag{3.5}$$

A is the 'pre-exponential factor', with the same units as the rate constant (k). Temperature will therefore also affect the final position of the equilibrium if the value of Ea for adsorption differs from that for desorption. Equation 3.5 translates directly into describing the temperature dependence of diffusion (Eq. 3.6) where D_{app} is the apparent diffusion coefficient for the solid and D_o is D_{app} when the activation energy is zero [108].

$$D_{app} = D_o \exp\left(\frac{-E_a}{RT}\right) \tag{3.6}$$

Thus, fixation by diffusion into spherical solid particles can be described by equations of the form:

$$Pf_t = Pf_o + 6\sqrt{\left(\frac{D_{app}\ t}{\pi\ r^2}\right)} \tag{3.7}$$

Where Pf_o and Pf_t are the proportions of added metal ions fixed at time zero and time 't'.

The linear dependence of metal fixation on $\sqrt{t}$ is often presented as strong evidence for a diffusion-controlled process and most studies appear to conclude that a higher temperature will increase the rate of fixation in soils. Thus, Ma et al. [72] used a combination of Eqs. 3.6 and 3.7 to model the decline in isotopic exchangeability of Cu added to soils and incubated at three temperatures for 30 days. A similar response has been observed for Cd adsorption on goethite [81], Pb reaction with carbonate hydroxyl apatite [128] and several other studies. In addition, the relative affinity of different metals may change with temperature and differences in activation energy may indicate the underlying fixation process, such as diffusion [43] or reflect the nature (e.g., porosity) of the soil adsorption surfaces [11].

3.4 Modelling Metal and Metalloid Adsorption

In the soil chemistry literature many of the early empirical approaches to modelling trace metal equilibria, intended mainly for predictive purposes, can still be found published alongside the very latest developments in 'mechanistic' models of metal adsorption.

Adsorption of metals by soil, and soil constituents, is often expressed as the mathematical relationship between the concentrations of metal in the solid phase (M_{ads}) and in an equilibrated solution (M_{soln}). However, both M_{ads} and M_{soln} may represent several alternative variables. The variable M_{ads} may be the total concentration of metal in the soil solid phase, or it may be a specific fraction such as 'extractable' or 'isotopically exchangeable' metal [40]. Similarly, M_{soln} can represent either the ‘total’ or the ‘non-complexed’ concentrations of metal ions in solution, or their free ion activity [117].

The two most common objectives of characterising the solid-solution equilibration of metals are:

(i) to predict concentration (or activity) of metal species in solution, perhaps under changing circumstances, to address questions of plant availability, ecotoxicological risk to water systems etc.;
(ii) to assess alternative adsorption mechanisms and (ideally) gain greater understanding of the adsorption process itself.

3.4.1 Simple Adsorption Isotherm Equations

The simplest expression of the strength of metal adsorption by soil is the ‘distribution coefficient’ (k_d): the ratio of M_{ads} to M_{soln} (Eq. 3.8).

$$k_d = \frac{M_{ads}}{M_{soln}}; \quad M_{ads} = k_d(M_{soln}) \tag{3.8}$$

The most obvious shortcomings of this approach to describing metal equilibria are the implied assumptions of (i) infinite adsorption capacity, (ii) homogeneity of adsorption site type, (iii) no effect of site occupancy on the free energy of (further) adsorption and (iv) no effect of competitor ions (e.g., H^+ or other metals). Clearly for sorption of metal ions on to charged humus and oxide surfaces, in the chemical cocktail of a soil environment, ***all*** of these assumptions are invalid. Nevertheless, the simple distribution coefficient has found widespread application in risk assessment approaches which characterise sorption of radionuclides and pesticides. For metals also, if we assume that the characteristics (pH, humus content, texture, metal content) of individual soils are fairly conservative, then metal k_d values could provide a reasonable assessment of adsorption strength for comparative purposes. Sheppard et al. [102] measured kd values for 54 elements in Canadian soils intended as an aid to critical load assessment. Covelo et al. [28] suggested a standard comparative index (k_{d100}) which is the value of k_d measured following adsorption by 12 g soil from 200 mL of an initial solution concentration of 100 mg L^{-1} after 24 h equilibration. They also proposed extending this to a general index of metal adsorption strength ($k_{d\Sigma100}$) for a suite of different metals.

Nevertheless, in most studies of metal adsorption, the non-linearity of the relationship between M_{ads} and M_{soln} is acknowledged and a wide range of equations have been deployed to describe metal adsorption isotherms in Soil Science. Giles et al. [44] classified adsorption isotherms on the basis of their ‘shape’ (initial slope and curvature). Their basic classification includes constant partition (C), high affinity (H), Langmuir (L) and sigmoidal (S) forms. The choice of which adsorption equation to use is discussed in several publications [50, 59]. Traditionally, however, the two most widely used functions are the well known Langmuir and Freundlich adsorption equations.

$$\text{Langmuir:}\quad K_L = \frac{M_{ads}}{M_{soln}(N_s - M_{ads})};\quad M_{ads} = \frac{K_L N_s M_{soln}}{1 + K_L M_{soln}} \tag{3.9}$$

$$\text{Freundlich:}\quad k_F = \frac{M_{ads}}{(M_{soln})^n};\quad M_{ads} = k_F (M_{soln})^n \tag{3.10}$$

The Langmuir equation (LE, Eq. 3.9) is attractive because it is asymptotic [50] and therefore 'provides' an important soil characteristic – the maximum adsorption capacity or 'number of sites' (N_s). Its failings include an assumption that the standard free energy of adsorption is constant, regardless of 'site coverage' which, for ion adsorption on to charged surfaces, is incorrect. Although the single LE also ignores competition from other ions and assumes a single type of adsorption site, these can easily be included in extended forms of the equation [129].

The Freundlich equation (FE, Eq. 3.10) is an empirical relation that is consistent with an exponential distribution of binding energies [12]. Strobel et al. [110] demonstrated that the k_d values for Cd and Cu in arable soils increased with depletion of the metal; therefore a measured k_d value may overestimate the solubility of the majority of the soil metal content. Thus the FE addresses the issue of site heterogeneity, to some degree, and it is probably fair to say that it is considerably more useful than the LE for trace metal studies [12]. Although the FE ignores the notion of an adsorption maximum it could be argued that this is seldom an issue because the concentration of adsorbed metal present is normally much less than the metal-adsorption capacity of the soil.

Both equations are still used to describe metal adsorption for comparative purposes. This approach is perhaps most valid when the soils being studied have a restricted range of conditions (especially pH) or when single soils or pure mineral substrates are being assessed. Sako et al. [96] used the FE to compare adsorption of platinum group elements (Pd, Rh and Pt) on a single kaolinitic soil. Jalali and Moharrami [55] tested both the FE and LE as descriptions of metal adsorption in calcareous soils from Western Iran with a narrow pH range (c. pH 7.0–7.5). Markiewicz-Patkowska et al. [75] used the simple LE to estimate the adsorption capacities of (urban) brownfield soil material at just two (controlled) pH values (pH 2 and pH 7).

The simple LE and FE models are often applied when the adsorption of metals is only a part of the overall reaction process being studied and it is convenient to adopt a simple description of metal equilibrium. Thus, Őren and Kaya [85] applied the FE to Zn adsorption on zeolite. Shirvani et al. [104] described adsorption of Cd on pure clays (Sepiolite and Palygorskite) and calcite using the FE. Ahmed et al. [2] used the FE to describe Cd adsorption on zeolite. In all these studies the primary objective was not to derive a definitive description of adsorption *per se* but to integrate a convenient adsorption equation into a wider study of adsorption kinetics, desorption hysteresis and/or reaction mechanisms.

There have been several attempts to develop more flexible forms of the FE and LE which address the problems such as site heterogeneity and competition from other ions. Temminghoff et al. [111] tested a ‘two species Freundlich’ (TSF) model alongside the more mechanistic NICA model (Sect. 3.4.3) to describe Cu^{2+}-H^+ competition for adsorption on humus in a sandy soil. Barrow et al. [12] used a modification of the FE, in which the exponent (n) varied with solution concentration (M_{soln}), to explain competition between selenite and phosphate in a Chilean Andosol. Xue et al. [129] adapted the LE to include competition and non-integer reaction stoichiometry to describe Cd and Zn adsorption on a yellow cinnamon soil from China.

3.4.2 Relating Adsorption Equations to Soil Properties

It is inevitable that ‘single component’ (i.e., M_{soln}) forms of the LE and FE provide only ‘soil-specific’ parameters at best and, for the same reasons, they will fail if the characteristics (such as pH) of a single soil are changed. The recognition of correlations between soil properties (e.g., pH) and metal adsorption strength has therefore encouraged the development of regression approaches so that metal adsorption may be empirically predicted for soils with differing characteristics. The soil properties chosen for regression are usually those known to have direct, or indirect, effects on metal binding strength and are normally fairly ‘accessible’ soil variables. Typically they include various combinations of pH, cation exchange capacity (CEC), humus content (%C or %LOI), Fe or Mn oxide content, clay content, concentration of the major cations or competing trace metals etc.

In fact, such regression equations are essentially an extended form of the FE if it is assumed that $\log k_F$ is a linear function of multiple soil properties (P_i), while the Freundlich exponent (n) remains constant across all soils, (Eqs. 3.11 and 3.12):

$$\log(M_{ads}) = \log k_F + n\log(M_{soln}); \quad \log(k_F) = k_o + \sum_{i=1}^{m} k_i \log(P_i) \tag{3.11}$$

$$\log(M_{ads}) = k_o + \sum_{i=1}^{m} k_i \log(P_i) + n\log(M_{soln}) \tag{3.12}$$

This has been called the ‘general purpose Freundlich’ model (GPF) [35]. Sauve et al. [98] reviewed over 70 studies and optimised GPF expressions for Cd, Cu, Pb, Ni and Zn with pH and SOM content as the predictive soil properties (Pi, Eq. 3.12). This approach explained 61 – 88% of the variation in dissolved metal concentration; for Pb the fit was considerably poorer. Gray and McLaren [45] included the predictive properties pH, %C and amorphous Fe/Al oxide content in a study of 200 New Zealand soils contaminated from a wide range of sources. Their optimised equations were able to predict between 50% and 85% of the variation in M_{soln} for six metals across the range of soils studied. Horn et al. [52] parameterised GPF equations for Cd with a dataset of nearly 500 soils from Germany; they included pH, clay, soil organic carbon, CEC and Fe/Mn oxides as predictive soil properties. Similar dependencies on soil properties were found by Lair et al. [64] for long term field experiment soils from Austria. Tipping et al. [114] included just pH and %LOI as predictive properties in a study of metal solubility in 98 upland soils from the UK and achieved results which were only slightly inferior to a more complex mechanistic model (Sect. 3.4.3). Gandois et al. [41] found that the solubility of eight trace metals, in a range of soils, could be predicted from soil organic carbon content, pH value, total Fe content and DOC.

Attempts have also been made to improve the basis of expression for the two metal variables (M_{ads} and M_{soln}) in order to describe metal equilibria on a more mechanistic basis. Thus, Elzinga et al. [35] used 92 published sources to collect 2,000, 700 and 1,500 data for Cd, Cu and Zn adsorption respectively. They tested for improvements in the fit of a GPF model by varying the definition of M_{soln} as total concentration or corrected for ionic strength, inorganic complexation and organic complexation. Overall these refinements to M_{soln} produced fairly small improvements. Model predictions of M_{ads} from field datasets under-estimated by a factor of 5–10. This was thought to be due to overestimation of 'adsorbed reactive' metal by acid digestion of field soils and partly because of metal competition effects which are not included in the adsorption studies but limit metal adsorption in field soils. Trancoso et al. [115] tried to improve the fit of a GPF description of Pb equilibria in a study of Portuguese soils (P_i = pH, Fe/Al oxides) by measuring labile forms of Pb_{soln} using differential pulse polarography. Tye et al. [117] used what was effectively a GPF approach, applied to UK soils incubated with added Cd (Pi = %LOI, pH, Zn_{soln}, ionic strength). They defined Cd_{soln} as the free ion activity (Cd^{2+}), calculated from a solution speciation model (WHAM-VI; Sect. 3.4.3) and Cd_{ads} was measured as the isotopically exchangeable (labile) soil Cd concentration. Groenenberg et al. [46] used a similar approach, but with nitric acid extractable metal as a proxy for the 'reactive' metal pool (M_{ads}). They confirmed the controlling influence of humus content and pH value on free ion activity of Cd, Cu, Pb, Ni and Zn in over 200 soil solutions from the Netherlands and UK. Broadly speaking, in most applications of the GPF to large multi-soil datasets, the resulting 'models' are able to predict M_{soln} from soil properties (P_i) to within approximately 0.5–1.0 $\log_{10}$ units.

3.4.3 Mechanistic Models of Metal Adsorption

A wholly rigorous treatment of adsorption reactions is simply not possible because of the inherent complexity of soils. Thus, when models of metal adsorption are described as 'mechanistic' this normally means that (i) defined adsorption mechanisms form the operational basis of the model and (ii) the model is thermodynamically consistent in that the masses of all defined species and their associated charges are conserved and balanced respectively.

Several geochemical models describing metal bonding to organic matter, Fe/Mn/Al oxides and alumina-silicate clays have been combined to predict equilibrium speciation and fractionation in 'whole soils' (see for example the Visual MINTEQ site managed by Jon Petter Gustafson [48]). Perhaps the two models which have been most widely applied are the 'extended versions' of the Windermere Humic Acid Model (WHAM-VI) and the Non-Ideal Competitive Adsorption model (NICA-Donnan). Both these models started life as descriptions of metal binding to humic and fulvic acid in solution and have been extended to include surface complexation models dealing with exchange reactions on clays and specific adsorption on Fe/Mn/Al oxides to form the 'assemblage' models 'SCAMP' (e.g., [68]) and 'ECOSAT' (e.g., [124]) respectively. Crucially, this progression enables a complete audit of metal speciation in solution and fractionation in the solid phase. However, the description of metal binding to humus acids probably remains the most important component of both extended models and, in this function, they have elements in common. They both recognise that: (i) HA and FA have two types of group; (ii) there is heterogeneity within each type of group; (iii) metals may bond to HA and FA through multiple linkages; (iv) HA and FA are charged molecules, partitioned between solid and solution phases, with non-specifically adsorbed counter ions. The basic approach of both models is briefly outlined below.

3.4.3.1 WHAM-VI Model

WHAM-VI [112, 113] has its origins in 'conventional' descriptions of equilibria between metals and anionic molecules in solution but extended to allow for build up of electrostatic charge on macromolecules with multiple functional groups. In WHAM-VI, humic and fulvic acids are assumed to be impenetrable spheres (radii 1.72 and 0.8 nm) with the functional groups (Hu-COOH and Hu-OH; Sect. 3.2.1) confined to the surface of an otherwise hydrophobic molecule.

The existence of negative surface charge (Z) on humic acid molecules (Hu-COO$^-$) weakens proton dissociation constants and so the apparent acidity constant at a given humic charge (K_Z) is calculated from an 'intrinsic' dissociation constant (K_i), which would apply if the humic molecule carried zero surface charge, modified by an electrostatic interaction factor (w) and the surface charge (Z). The electrostatic interaction factor (w) is an empirical function (P) of ionic strength to reflect suppression of the electrostatic field around the charged humic molecule or colloid at high salt concentrations.

$$\mathrm{K_Z} = \frac{[Hu - COO^-](H^+)}{[Hu - COOH]} = \mathrm{K_i}\exp(2wZ); \quad w = P\log(I)$$

Group heterogeneity is incorporated by assuming two types of group (A and B) which probably, but not explicitly, represent carboxyl and phenolic-hydroxyl groups. Each group type is subdivided into four and it is assumed that (i) the ratio of Type A: Type B groups is 2:1 and (ii) each of the four subgroups are equally represented on the humic molecule. The resulting eight subgroups all have individual 'intrinsic' pK_i values. These are calculated from the average intrinsic pK (pK_A or pK_B) and a 'spreading factor' to provide 'group heterogeneity' within type A and B groups, For example, for carboxyl (A) groups:

$$pK_i = pK_A + \left(\frac{2i - 5}{6}\right)\Delta pK_A$$

Typical parameter values for humic acid are $pK_A = 4.0$ and $\Delta pK_A = 1.8$ which would give four carboxyl groups with intrinsic pK_i values of 3.1, 3.7, 4.3, 4.9.

Specific sorption of metals is described with analogous intrinsic equilibrium constants and allowance for electrostatic effects. Metal-specific spreading factors provide heterogeneity and there is also allowance for mono-, bi- and tri-dentate bonding between metals and functional groups. Values of intrinsic stability constants for bidentate (log(Ki,j) and tridentate (logKi,j,k) bonding are expressed as the sum of the component monodentate constants but with additional terms (x ΔLK_2 and y ΔLK_2) which extend the heterogeneity caused by multi-site bonding to allow for high affinity chelate sites. Thus, for tridentate bonding, y is set to 0, 1 or 2 for 90.1%, 9% and 0.9% of the adsorption sites. Considering the large number of possible sites arising from combinations of groups (e.g., 120 tridentate sites), the number of sites used in the model is rationalised by restricting bi- and tri-dentate sites to combinations of dissimilar groups types and utilizing a representative subset (80 sites in total, of which 8 are monodentate).

Finally, metal ions are also bound (weakly) as non-specific counter-ions within the diffuse double layer around the charged humic molecule. In the WHAM model this zone is simply described as a discrete Donnan layer, calculated from ionic strength, and the amount of electrostatically bound trace metals reflects their relative abundance in the bulk solution and their valence. Normally the ratio of chemically bound to electrostatically bound trace metals would be high.

3.4.3.2 NICA-Donnan Model

The origins of the NICA-Donnan model are closer to the mathematical descriptions of adsorption isotherms; the model was derived originally from the Langmuir-Freundlich equation (LFE). The NICA model also recognises (two) discrete classes of group on humic acid but within each class assumes a continuous 'affinity distribution' of functional groups rather than trying to subdivide into individually identified groups. The LFE includes provision for site heterogeneity and can be extended to describe adsorption of multiple species (protons and metal ions). However, in order to describe the specific adsorption affinity shown by individual metal ions, a further term was introduced. The equation below describes adsorption of a divalent metal ion (M_{ads}) by humic acid, again with two types of group (A and B) in which T represents the total concentration of group A or B. The exponent (n) primarily reflects metal-specific stoichiometry; the ratio n_M/n_H may be seen as the average binding stoichiometry of metals to individual groups and so should be <1 although this is not always true for optimised values. The parameter 'P' (0–1) describes the heterogeneity of ion affinity and is a characteristic of the molecule rather than individual metal ions; (M^{2+}) is the free ion activity of the adsorbing metal species and K is the average affinity constant. The compound term $Tj(n_{M,j})/(n_{H,j})$ reflects the different binding maximum, to group A or B, for individual ions.

$$M_{ads} = \sum_{j=A}^{B} \left(Tj \times \frac{n_{M,j}}{n_{H,j}} \times \frac{\left[K_{M,j}(M^{2+})\right]^{n_{M,j}}}{\sum \left[K_{M,j}(M^{2+})\right]^{n_{M,j}}} \times \frac{\left\{\sum \left[K_{M,j}(M^{2+})\right]^{n_{M,j}}\right\}^{P_j}}{1 + \left\{\sum \left[K_{M,j}(M^{2+})\right]^{n_{M,j}}\right\}^{P_j}} \right)$$

The NICA-Donnan model again includes provision for non-specific metal adsorption within a diffuse double layer of the charged humic acid molecule. More detailed descriptions of this widely used model, its applications, and its extension to (whole soil) assemblage models incorporating the metal oxide binding model 'CD-MUSIC' can be found in many publications, e.g., [62, 119].

3.4.3.3 Applications of WHAM and NICA-Donnan Models

An obvious, and probably unfair, criticism of these models is that they are 'data-hungry'. To work effectively, as a means of predicting speciation in solution and fractionation in the solid phase, they should ideally be useable in 'default mode' with input of data from straightforward soil chemical analysis. If users have to measure or infer a large number of unique soil parameters (specific surface areas, active humus fractions, intrinsic stability constants etc.) for each application then their value diminishes. However, when such models are applied to whole soils it is often found that some 'fine tuning' of model parameters is required. Furthermore, in comparison with empirical approaches, such as the GPF or regression equations, mechanistic models may sometimes provide only marginal advantages.

Thus Tipping et al. [114] applied WHAM-VI to 98 upland soils from the UK and improved the fit by using (optimised) soil-specific values for the active organic matter (AOM) fraction. Shi et al. [103] also had to optimise the proportion of AOM when using WHAM-VI to predict Cd adsorption by 14 non-calcareous soils from the USA. Amery et al. [5] used WHAM as an assemblage model to predict metal speciation in an arable field site in Belgium and tried to improve estimates of 'active fulvic acid' in solution by UV-spectroscopic measurement. Ålmas et al. [4] applied WHAM to Norwegian arable soils contaminated with smelter output and had to optimise the active fraction of metals in the soil; for arable soils they found that the results were sensitive to the 'active' Ca concentration in particular. Buekers et al.

[18, 19] applied WHAM-VI to 28 soils with widely varying characteristics. Their prediction of solution speciation was good and the distribution of Cd, Ni, Zn and Cu in the solid phase showed the expected pH-trend across the range of soils with Fe oxides deposing organic matter as the principal metal adsorbent at $pH > 6$. However, they identified several complications to the application of the model including possible irreversible ‘fixation’ of Cu within organic matter, the need to refine the estimate of ‘reactive’ metal (using isotopic exchange) and some uncertainty in the specific surface area used for Fe oxides.

Benedetti [14] applied the NICA-Donnan (with CD-MUSIC) model to a woodland soil from France affected by Pb/Zn smelting activity and found good agreement with measured solubility of Cd, Zn, Cu and Pb, following minor changes to humic-Pb binding parameters. MacDonald and Hendershot [74] applied the NICA-Donnan model to a study of Canadian forest soils contaminated with smelter output and had to optimise the ‘active organic matter’ fraction and the ratio of HA to FA for each soil. Bonten et al. [17] applied the NICA-Donnan model to a large dataset from the Netherlands and found disparities in Zn-contaminated soils where the simple measure of ‘active Zn’ (0.43 M HNO_3 extraction) failed. They also identified possible problems with the description of Zn binding to metal oxides, Cd binding constants to humus acids and overestimation of reactive Pb. They suggested that there may be a possible problem with the ‘additivity’ principle of assemblage models where adsorption surfaces (humus, oxides, clays) are considered only as discrete entities and interactions between them are not considered.

3.4.4 Conclusions

Ultimately, mechanistic models of metal adsorption will probably supersede the simpler approaches outlined in Sects. 3.4.1 and 3.4.2. This will arise partly because of an increasing awareness of the importance of both fractionation in the solid phase and speciation in solution to accurately assess mobility, bioavailability and ecotoxicological risk of heavy metals in soil. In future, it will not be sufficient to predict M_{soln} to within an order of magnitude from broad empirical relationships, nor, as at present, to rely on measurement of total soil metal content in risk assessments. However, key to providing more effective mechanistic ‘assemblage’ models will be resolving some important underpinning processes.

3.4.4.1 Single Adsorbents

Aspects still requiring improvement include:

(i) better characterisation of adsorption surface capacity – predicting or measuring the reactive surface area of Fe/Mn/Al oxides and the proportion of ‘active organic matter’ in both the solid and solution phases;

(ii) developing better descriptions of adsorption on alumina-silicate clay edges and within ‘pillared’ clays;

(iii) allowing for more complex ion-surface associations within existing surface-complexation models, such as ternary complexes in which specifically adsorbed anions bridge heavy metal associations with (Fe)oxides.

3.4.4.2 Multi-Phase Adsorbents

There is also a need for greater understanding of colloidal-molecular interactions between the individual metal adsorbents (FA/HA, Fe/Mn/Al oxides and silicate clays). There is evidence that the aggregate behaviour of organic-mineral assemblages is not simply additive, due partly to interacting electric field effects [122]; modelling the resulting effects on metal adsorption is an active research area [125, 126].

3.4.4.3 Reduction and Oxidation Processes

The integration of changing redox conditions into adsorption models has been neglected in the past, despite a clear qualitative understanding of its importance, and is likely to feature in future developments [100].

3.4.4.4 The ‘Slow Reaction’

Following early work integrating solid phase diffusion processes with surface complexation models [10] there is now the emergence of coupled ‘kinetic-adsorption’ models [18, 19, 37, 123].

3.4.4.5 Solution Speciation

Finally, in the solution phase, a greater appreciation of more complex metal speciation is emerging with evidence of slowly reactive metal in sub-micron sized particulates [69, 71] which might require a re-assessment of consequences for mobility and ecotoxicology.

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Chapter 4
Methods for the Determination of Heavy Metals and Metalloids in Soils

Christine M. Davidson

Abstract This chapter explores the analytical methods currently available for the measurement of heavy metal content in soils, ranging from well-established techniques routinely applied in laboratories worldwide, to newly emerging approaches, and with emphasis on the need to select strategies that are 'fit-for-purpose' in terms of the information required. Included are guidelines for field sampling and for the storage of samples and avoidance of contamination. Brief information is provided on analytical techniques directly applicable to solid samples including neutron activation analysis, laser-induced breakdown spectrometry and X-ray-based methods. Suitable approaches to sample extraction for different situations are summarised (total digestion, pseudototal digestion, single and sequential extraction) together with examples of procedures involving hot-plate, block, bomb, and microwave apparatus. The use of extractants to assess (plant) bioavailability or (human) bioaccessibility of heavy metals in soils is discussed. Details are provided of the various types of atomic spectrometry that nowadays serve as 'workhorses' for trace metal determination in environmental chemistry, with particular emphasis on their principles, strengths, limitations and applicability. Included are flame and electrothermal atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry. The chapter also provides a brief introduction to the vast topic of speciation analysis, an area of particular interest for metals that can occur in different oxidation states e.g. Cr, or that have environmentally important organometallic forms e.g. Hg. Finally, some recommendations are given on strategies that researchers should adopt whenever possible to improve the quality of their analytical data.

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4.1 Introduction

The determination of heavy metals and metalloids in soil may be carried out for a variety of reasons. The total element content provides base-line knowledge of soil composition, with respect to which changes due to natural or anthropogenic processes can be assessed. Soils from metal-contaminated industrial sites may be analysed for legislative purposes, to assess risk to human health or the environment, or to monitor the success of remediation strategies. Agricultural chemists may wish to assess the availability of metals in soils, either as an indicator of potential plant deficiency or toxicity, or to determine the likelihood of metals' entry into the food chain of animals and man.

A potentially bewildering range of analytical techniques and methods now exist for the determination of heavy metals in soils. However, the most important factor to consider when deciding which approach to use is "What is the purpose of the study?" Knowing the type of information that needs to be obtained, or environmental question(s) to be answered, will guide the soil analyst towards analytical methods that are fit-for-purpose. For example, a portable, X-ray based spectrometer that measures total metal concentrations may be preferred for field analysis of metal-rich soil affected by mining waste, but a multi-step chemical extraction procedure, combined with advanced laboratory instrumentation, is likely to be more suitable for estimating the fraction of the metal content that will be bioaccessible in the human gastro-intestinal tract following accidental ingestion of a typical soil.

Many other factors may need to be considered when planning an analytical strategy including, but not necessarily limited to:

- sampling logistics (e.g. site access, sampling regime, safety)
- sample preservation, storage and preparation
- number(s) of analytes to be measured
- concentrations of analytes to be measured
- precision and accuracy required
- availability of laboratory apparatus and instrumentation
- cost of analysis
- time required to generate results.

This chapter describes current approaches to the determination of heavy metals in soils: it outlines their principles; discusses their strengths and limitations; provides information on their scope and applicability, and highlights some recent developments and applications.

Information on general [33, 75, 83, 98] and environmental [61, 96, 169] analytical chemistry can be found in several textbooks whilst detailed guidelines for handling analytical data are provided in [130]. It is particularly important to distinguish between accuracy and precision in analysis. Accuracy – the closeness of a measurement to the true value – indicates whether there is any systematic error ('bias') in a measurement.

It cannot be assessed for a sample where the analyte concentration is unknown. However, soil certified reference materials (CRM) of known composition are available commercially. Experienced laboratories will analyse these regularly to ensure that analytical methods remain under control (see Sect. 4.9).

Precision – the closeness of a set of measurements to one another – is a measure of the repeatability of an analysis. It indicates the magnitude of random error associated with the measurement, and is often expressed as the relative standard deviation (RSD) of n replicate measurements.

$$RSD = \frac{\sigma}{\bar{x}} \times 100$$

where σ is the standard deviation and $\bar{x}$ is the mean value.

The existence of random error means that the average of a set of analytical measurements is unlikely to be exactly equal to the true value. For this reason, experienced analysts rarely quote a mean value alone. Instead, it is usual to report a range within which the true value is likely to lie. This is termed the *analytical uncertainty* (some texts use the term *error*). It can be expressed as a confidence interval or by quoting the mean value ± the standard deviation.

Analytical techniques also suffer from background ‘noise’ from various sources. These can make a signal from the analyte difficult to distinguish from the blank. The limit of detection (LOD) below which concentrations cannot reliably be measured (and hence never should be reported) is often estimated by replicate analysis of a blank or low concentration standard and can be calculated from:

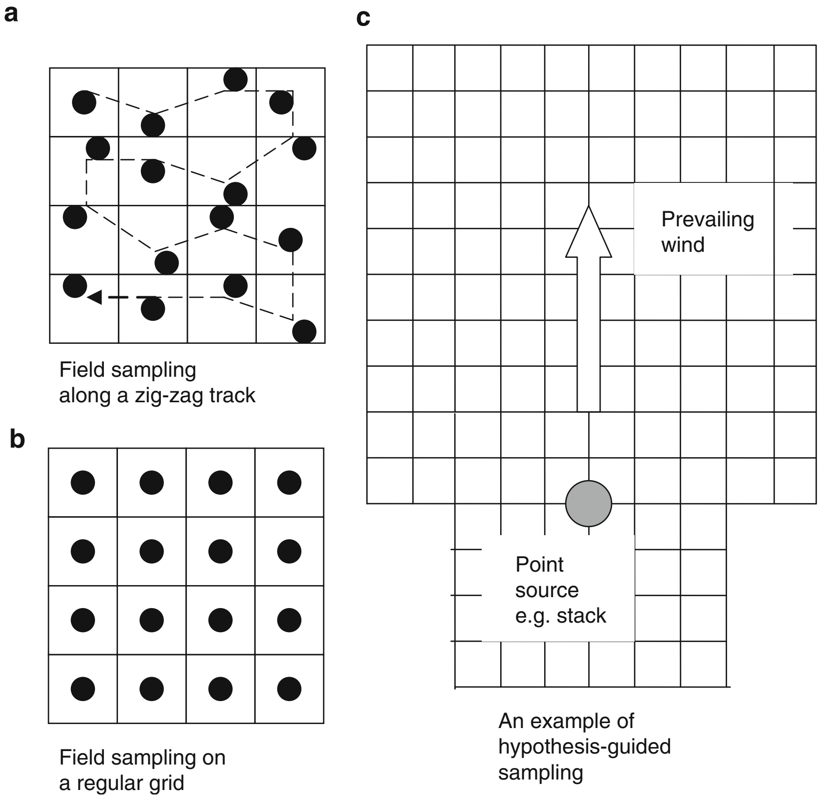
$$LOD = \frac{3\sigma_{BLANK}}{s}$$

where σ is the standard deviation of 10 replicate measurements
s is the slope of the calibration curve.

Analysts distinguish between the instrumental LOD, the lowest concentration that can be measured by a technique when the analyte in the required form (usually in solution) is presented to the instrument, and the procedural LOD, which takes account of any digestion and dilution steps required to prepare the test portion for analysis. The $\text{LOD}_{\text{PROCEDURE}}$ can easily be 100× or even 1,000× poorer (i.e. higher in concentration) than the $\text{LOD}_{\text{INSTRUMENT}}$.

4.2 Field Sampling

The first stage in the determination of heavy metals in soils is the collection of samples for analysis. The samples must be representative and collected using a suitable sampling regime i.e. one designed to match the purpose of the study. Even where this is the case, sampling can make a large contribution to the overall measurement uncertainty [69, 104, 163].



Field sampling along a zig-zag track

Field sampling on a regular grid

An example of hypothesis-guided sampling

Fig. 4.1 Examples of sampling grids. (**a**) Field sampling along a zig-zag track. (**b**) Field sampling on a regular grid. (**c**) An example of hypothesis-guided sampling

If the goal is to obtain an average metal concentration, it is common to subdivide the field or plot (either notionally or physically with marker flags and twine) into segments (perhaps 20–25 segments for an area of 1–2 ha). A regular grid or herring-bone pattern may be used. The vertices of the grid and locations of the sampling points may be obtained from a map or, nowadays, by use of a hand-held GPS, which has the advantage that the same sites may be easily revisited and sampled several times. Sample units are then collected, along a zig-zag path, either from a sampling point in each of the segments (Fig. 4.1a) or from a selection thereof (e.g. in the UK, arable soils are typically sampled by taking 25 cores per 5 ha, at 0–15 cm depth, in a W-pattern, avoiding any obvious ‘anomalous’ areas). These are combined to form a bulk sample, usually containing about 1 kg of field moist soil, although larger samples may be required for peaty or highly organic soils. Other studies aim to assess the spatial distribution of metals. In this case a grid may still be used, but one (or more) sample will usually be taken in each segment (Fig. 4.1b) and analysed individually, with associated increase in analytical workload and cost. Kriging [123] may be performed on the data to interpolate concentrations between sampling points.

In other situations, prior knowledge about the site under investigation, or the likely distribution of analytes therein, can be used to inform the sampling strategy. This is called *hypothesis-guided* soil sampling [186]. For example, if the aim of a study was to assess metal deposition onto soil from a point source such as a stack (or chimney), the sampling grid might be altered or extended to take account of prevailing wind direction, since contamination may reasonably be expected to be greater, and more extensive, in the downwind direction (Fig. 4.1c). A particularly challenge exists in designing sampling strategies appropriate for recently-derelict industrial sites. Detailed knowledge about the site history may be required e.g. previous locations of buildings, nature of processes carried out in various areas, types of compounds used etc.

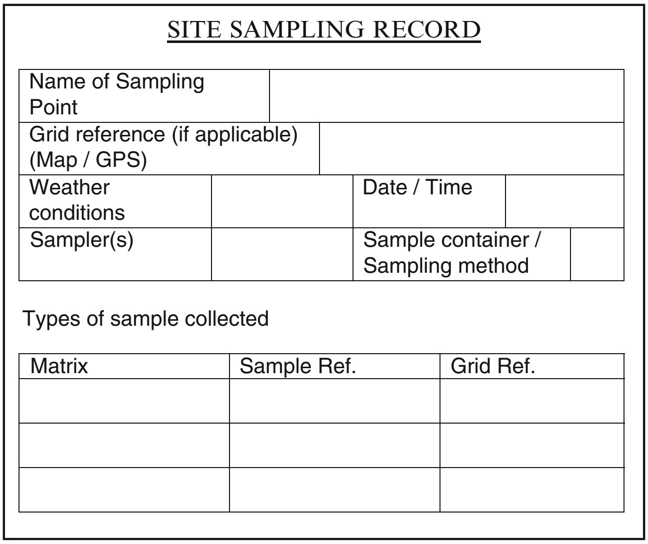
Sample units are taken to a uniform depth using an auger or corer (or, if these are unavailable, a spade or trowel). Arable land is usually sampled to the plough depth (typically 15 or 20 cm) whereas soil under grassland is sampled to a depth of only 7.5 or 10 cm [14]. A variety of sampling depths may be used at contaminated sites: sometimes surface soils are taken; sometimes trial pits are excavated to >1 m depth and material – which may be ‘made-up ground’ containing substantial quantities of materials such as brick, ash and clinker rather than true soil – removed from specific depths or visible layers for analysis.

Samples must be placed in proper containers. Polyethylene bags are suitable for the determination of most heavy metals, but should not be used if Hg is amongst the analytes because elemental mercury can pass through polyethylene and be lost or contaminate nearby samples. Glass bottles with screw-top lids are preferred in this case. Care must be taken to avoid all sources of contamination [173]. Carbon steel or aluminium sampling tools are generally preferred to stainless steel since the latter may incorporate large quantities of metals such as Cr, Mn, Mo and Ni; some plastics, notably PVC, should be avoided since they may contain trace metals; even paper towels may cause difficulties if they have been whitened with TiO_2 or dyed with a metal-containing compound. Tools should be rinsed with distilled water, or wiped clean, between samples.

Each sample must be labelled with a unique sample number, using a permanent marker, on the outside of the sampling bag (to avoid contamination of the soil with metal-containing inks). Other relevant details, such as sampling date and location (obtained from a map or GPS) should be recorded on site. Many organisations use a standard sampling pro-forma, an example of which is shown in Fig. 4.2. Sampling soils for trace analysis remains an active topic of research (see e.g. [217]).

4.3 Sample Preservation, Storage and Preparation

On arriving at the laboratory, soil samples are spread out (e.g. on polyethylene sheets in aluminium trays), aggregates are broken down, and the samples are dried. Air-drying, or drying at slightly elevated temperature (25°C) is usual. Higher temperatures may be used in the preparation of reference soils to improve their long-term stability. The dried soil is then passed through an aluminium or nylon



SITE SAMPLING RECORD

Name of Sampling Point			
Grid reference (if applicable) (Map / GPS)			
Weather conditions		Date / Time	
Sampler(s)		Sample container / Sampling method	

Types of sample collected

Matrix	Sample Ref.	Grid Ref.

Fig. 4.2 An example of a sampling pro-forma

sieve, usually of 2 mm mesh. Stones and other material >2 mm in diameter are discarded. The <2 mm ('fine earth') fraction is re-bagged and stored until required. Sub-samples may be ground or milled to smaller particle size (e.g. <150 μm) to ensure a more homogeneous test portion for direct methods of analysis, or expose a larger surface area for acid digestion. Representative sub-sampling of the dried soil can be carried out by coning and quartering or a mechanical riffler may be used. There is a minimum weight of soil, depending on the heterogeneity and grain size, that will be representative of the whole sample. Jackson [86] recommended that the test portion should contain at least 1,000 particles of the sieve opening size. Assuming a soil density of 1.3 g cm^{-3}, this corresponds to about 5 g for samples passed through a 2 mm sieve or about 0.7 g for samples passed through a 1 mm sieve. In practice, analysis of a larger test portion, say 20 g for soil sieved to 2 mm and 2–3 g for soil sieved to 1 mm, is desirable. Particular care is required when handling soils intended for speciation analysis to preserve the intrinsic form(s) of the analyte elements [50, 173, 209].

Contamination with analytes not originally present in the sample is a constant threat and can occur at any point in the analytical process [82]. The risk becomes more critical as the concentration to be measured decreases. The laboratory itself can be a source of heavy metals (used, for example, in some paints and plastics). Instrumentation for (ultra)trace element analysis such as inductively coupled plasma mass spectrometry (ICP-MS, see Sect. 4.7.5) should ideally be housed in a separate laboratory, remote from areas used to handle or digest soil samples. Avoiding the sample coming into contact with apparatus during processing is clearly impossible, but care should be taken to choose materials unlikely to cause problems in the particular analysis being undertaken e.g. avoid stainless steel when measuring Cr. Milling and grinding can be sources of various trace elements [58]. All glassware should be soaked, preferably overnight, in 5% HNO_3 and then rinsed with distilled water before use. High purity water (at least distilled or deionised) should be used at all times. Reagents should generally also be of high purity and should be run as blanks to check for contamination. Different chemical suppliers use different terms (e.g. Analytical Reagent, AnalaR etc.) for purified reagents and it is advisable to check the specification in the catalogue to choose the option with lowest concentrations of the analytes of interest.

4.4 Direct Methods of Analysis

Most methods for heavy metal determination in soils require the analytes to be presented to the instrument in solution. However there is growing interest in methods that can be applied directly to solid substrates, especially if these can be used in the field.

4.4.1 Instrumental Neutron Activation Analysis (INAA)

A sample is placed in a nuclear reactor by a remote-handling system and irradiated with a known flux of thermal neutrons. Stable isotopes can capture these neutrons and be transformed into radionuclides. The sample is then removed and the activation products are quantified, usually by γ-spectrometry. INAA was the first technique able to perform non-destructive, multi-element analysis on small (50–100 mg) solid samples with detection limits < 1 mg kg^{-1} (parts-per-million). Its applications include ‘high-value’ samples such as the soils recovered by Apollo astronauts from the lunar surface [91]. Disadvantages are the requirements for specialist irradiation facilities and highly-trained personnel, which limit the availability of the technique to national facilities or workers with access to a local research reactor. Recent applications include a study of the accumulation of Cr, Fe, Mn and Zn in arable soils amended with chemical fertiliser and animal manure [143], an investigation of soils affected by sulphides exploitation [113] and measurement of 16 trace elements to assess anthropogenic influence on agricultural soils in Argentina [142]. However, the scarcity of facilities, concerns over nuclear radiation, and improvements in other analytical techniques mean that the use of INAA is becoming less common.

4.4.2 X-ray Based Techniques

X-ray fluorescence spectrometry (XRF) is a powerful technique for multi-element analysis. It is relatively insensitive to sample form, essentially non-destructive, and able to detect elements with atomic numbers greater than about 8. In XRF, samples are irradiated with primary X-rays, usually from an X-ray tube or radioactive source. These eject inner electrons from atoms. The energy released when outer electrons ‘fall’ into these vacancies is observed as an X-ray fluorescence spectrum; the wavelengths observed are characteristic of the element(s) present. Two types of instrument are used: wavelength-dispersive X-ray fluorescence (WDXRF) [102, 192] and energy-dispersive X-ray fluorescence (EDXRF) [178, 214]. In WDXRF, the radiation emitted by the sample is diffracted in different directions and a (Si(Li)) detector is moved to detect X-rays with different wavelengths (alternatively, several detectors at fixed angles may be used). In EDXRF, a single detector is used in combination with a multi-channel analyser. EDXRF instruments have no moving parts and hence are cheaper than WDXRF, but WDXRF generally offers superior resolution. Samples for XRF analysis are ground finely and then either subjected to fusion, producing a glass for analysis [141], or compressed into pressed powder pellets [36, 192]. Matrix effects occur in XRF and mathematical corrections must be applied if accurate results are to be obtained [172].

A key advantage of XRF for measuring heavy metals in soils is the availability of instruments suitable for use in the field [92]. Portable XRF instruments have been used to measure As, Cu, Pb and Zn at a former waste site (now a sports ground used by children) [28] and in soils affected by mining [162]; As, Cu and Cr in soil polluted by chromated copper arsenate wood preservatives [118], and Cr, Cu, Mn, Ni, Pb, V and Zn in industrial soil [7]. Results obtained by portable XRF were found to be broadly similar to those of laboratory-based techniques, but the detection limits are poorer. The method is therefore most suited for rapid screening of contaminated sites to identify samples of interest that can then be taken back to the laboratory for more detailed or confirmatory analysis.

Recent developments in X-ray analysis [220] include total reflection-XRF in which the incident X-ray beam is directed at the sample surface at such an acute angle that it is reflected, thus reducing background interference problems caused by penetration into the bulk [224] and the advent of powerful, synchrotron-based techniques – reviewed recently by Lombi and Susini [112] – suitable for direct measurement, mapping and speciation of heavy metals in soils. Indeed, one of the first environmental science experiments performed using the new ‘Diamond’ light source in the UK was a study of the speciation of Pb and Zn in soil undergoing remediation with bone meal [136].

4.4.3 Laser-Induced Breakdown Spectroscopy (LIBS)

This is an emerging form of atomic emission spectrometry (see Sect. 4.7.1) applicable to a wide variety of sample types, including solids such as dusts and soils, with minimal sample preparation [108]. A high powered, pulsed laser (typically a Nd:YAG at either 1,064 nm or frequency-doubled to 532 nm) is used to ablate the surface of the sample. This forms a high temperature microplasma in which the

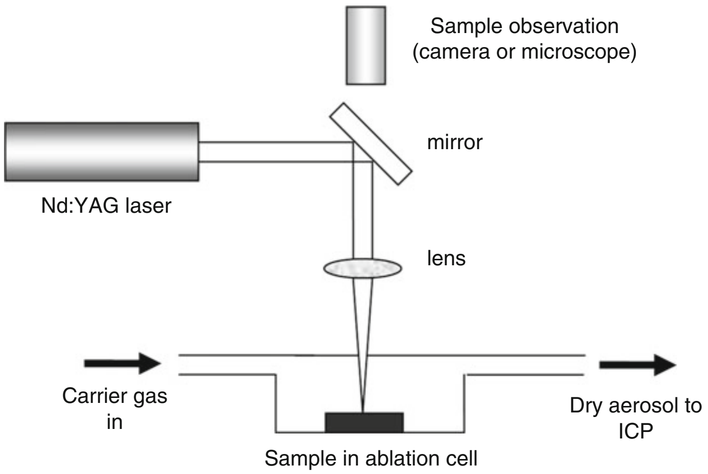


Fig. 4.3 Laser ablation inductively coupled plasma mass spectrometry

constituents of the ablation plume are atomised, ionised, excited, and then emit light of characteristic wavelengths. This light is measured after a short delay (around 500 ns) during which the intense broadband emission from the plasma decays. Comparisons between soil heavy metal concentrations obtained by LIBS and by other methods suggest that the technique shows promise [27, 188] but further optimisation and a better understanding of the behaviour of analytes in the plasma [60], together with improvements in accuracy and LOD [54, 80] are required. A particular advantage of LIBS, in common with XRF, is the potential to develop field-portable instruments [34, 73].

4.4.4 *Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)*

Conventional (solution sample) ICP-MS is described in Sect. 4.7.5. However there is also considerable current interest in the use of lasers to generate ions for introduction to the plasma. This allows the technique to be applied to a wide variety of solid samples, including soils, plants and related materials, yielding important information on, for example, the distribution of heavy metals in response to pedogenic processes [183]. As in XRF, the sample must be finely ground before analysis. The particle size has a strong influence on the quality of the measurement [88] and use of <1 μm diameter particles is recommended [9]. The powdered sample is pressed into a pellet, sometimes with the addition of a binder, and placed in an ablation chamber (Fig. 4.3). Early workers [11, 16] used aqueous calibrants for LA-ICP-MS. However, nowadays, it is common to prepare matrix-matched standards by spiking soils with appropriate analytes and internal standards [88, 107].

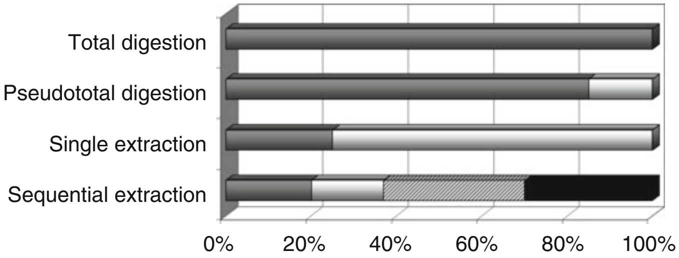


Fig. 4.4 Some approaches to the determination of heavy metals in soils (After [210])

4.4.5 *Slurry Sampling*

This is an approach that allows solid samples to be analysed by techniques such as atomic spectrometry that usually require solution samples. In essence, the sample is ground finely, suspended in a suitable medium, and the resulting slurry is introduced into the instrument in a similar fashion to solution samples. The method is particularly useful for refractory samples that are difficult to digest, but great care must be taken to optimise the sample particle size distribution, stablise the slurry, and properly calibrate the instrument response [52]. Recent reviews are available discussing the use of slurry sampling with electrothermal atomic absorption spectrometry (ETAAS) [26], with ICP-based techniques [52, 180], and with hydride generation [125].

4.5 Sample Digestion and Analyte Extraction

Digestion or leaching to transfer the analytes into solution is a necessity for most instrumental methods of analysis. The nature of the extractant used to release the metals from the soil matrix is of vital importance: different reagents liberate metals from different soil components and hence provide different types of information. Some approaches to the measurement of heavy metals in soils are summarised in Fig. 4.4 and discussed in the following sections.

4.5.1 *Total Digestion*

Total element contents are of interest, for example, in geochemical surveying [135] and to assess geogenic metal concentrations [97]. Hydrofluoric acid is used for total digestion of soil samples because it can dissolve silicates. The entire sample is solubilised and the total metal content released for measurement. Special precautions are required when handling HF: it cannot be stored or used in glass vessels; fume hoods may have to be specially adapted to avoid corrosive vapours attacking the components of the ventilation system, and use of appropriate personal protective equipment (including the provision of calcium gluconate HF antidote gel) is vital due to the serious nature of HF burns. An oxidising acid such as nitric or perchloric is often used in combination with HF to aid dissolution of organic matter and sulphides.

Another approach for total dissolution of soil samples is fusion. Typically, a small sample (e.g. 0.1–0.2 g) of ground (<100 μm particle diameter) soil is placed in a platinum crucible with ~0.8 g of lithium metaborate and heated to around 1,000°C. The sample dissolves in the molten flux. This may be quenched (with care!) by pouring it into a solution of nitric acid, or the flux may be allowed to cool and the resultant glass later dissolved in nitric acid. The acid solution is then made up to a set volume for analysis. The method tends to be reserved for samples containing refractory minerals e.g. chromite [135] that are difficult to bring into solution by other means.

4.5.2 Pseudototal Digestion

In pollution studies the goal is often to assess anthropogenic input, or estimate the maximum amounts of metals that could hypothetically be mobilized and transported in the environment and affect a receptor. Pseudototal (PT) digestion with mixtures of hydrochloric acid, nitric acid or hydrogen peroxide is widely used for this purpose. Although primary silicates are not dissolved, metals associated with most other major soil components are liberated.

In a typical PT digestion, a few grams of soil are weighed into a vessel. The soil is moistened with water and then *aqua regia* (a mixture of 3 parts HCl to 1 part HNO_3) added. The vessel is allowed to stand overnight, then the temperature is raised and the contents maintained under reflux for 2 h. After being allowed to cool, the digest is filtered into a volumetric flask, the residue washed with dilute nitric acid and the washings combined with the filtrate. Finally, the digest is made up to the mark with distilled water or dilute HNO_3 ready for analysis.

Both total and PT digestions may simply be carried out using beakers topped with watch glasses (made of PTFE in the case of HF) on a hot-plate placed in a fume cupboard. The digestion needs to be monitored and extra acid added to compensate for losses due to evaporation. Further additions of, for example, HNO_3 might also be necessary if the soil had a high organic content. However, many soil laboratories use more sophisticated apparatus, such as block or bomb digestors, and laboratory microwave ovens

Aluminium and graphite block digestors are able to extract metals from soils at controlled temperature. The digestion may be performed in disposable calibrated vessels that can be placed directly onto the autosampler of, for example, an ICP instrument, or the sample may be filtered prior to analysis. These digestors offer savings in time and increased sample throughput for laboratories handling large numbers of soil samples, although the fact that each digestion tube can hold only a few grams of soil may be a limitation for some applications. Tubes are usually topped with disposable watch glasses. However, specialised, non-disposable tops can be used to minimise loss of volatile species, for example in the measurement of Hg.

Bomb digestion, in which a soil sample and appropriate acid mixture are placed in a sealed vessel made from PTFE, stainless steel or aluminium and heated on a hotplate or in an oven, is also still popular. Because the vessel is sealed, loss of volatile species is minimised and there is less opportunity for the sample to become contaminated. An obvious danger is that, if the vessel exceeds its maximum operating pressure, it may explode. Bomb digestors should therefore always be operated exactly according to the manufacturer's recommendations.

The use of microwave-assisted sample digestion is now widespread. Microwave energy is absorbed directly by the solution, rather than there being a delay whilst heat is transmitted from an external source. Hence, it offers the advantages of speed, uniform heating of the sample, and contamination avoidance (provided closed vessels are used). Initially, many soil laboratories used domestic i.e. kitchen microwave ovens and home-made PTFE digestion vessels. Nowadays, commercial laboratory microwave apparatus is available. In a typically microwave-assisted PT digestion, 1 g of soil would be placed in a PTFE digestion vessel, 20 mL *of aqua regia* added and, after any initial vigorous reaction has subsided, the vessel would be placed in the microwave cavity and heated for, perhaps, 20 min. The vessel would then be removed, allowed to cool, and the contents filtered into a volumetric flask. Modern commercial microwave digestion systems can digest up to 40 samples simultaneously. The power is controlled by a temperature sensor that monitors all of the vessels in the cavity. The heating program and acid mixture can be optimised, for example by analysis of suitable CRM [15, 77, 179].

Several authors have compared digestion methods to determine those most suited to particular applications e.g. [103, 222]. For calcareous soils, Mico et al. [129] obtained higher extraction efficiencies, but poorer precision, using an open-vessel block digestor than closed-vessels in a microwave system, whilst Marin et al. [122] discovered significant underestimation of Al in the presence of HF when comparing microwave digestions with various acid mixtures. For Florida soils, Chen and Ma [32] obtained recoveries in the order: microwave (*aqua regia* + HF) > microwave (*aqua regia*) > hotplate (*aqua regia*). Useful general guidelines on preferred digestion approaches for soils of different composition (organic matter, carbonate content and closeness of metal concentrations to legislative limits) are provided by Sastre et al. [182].

4.5.3 Single and Sequential Extraction

There is considerable interest in assessing the fractions of the total metal content associated with specific soil mineral phases. This information is now beginning to be available through application of direct methods of speciation analysis (see Sect. 4.8). However, for many years, soil scientists have tried to infer it by application of selective chemical extractants. Although this approach has produced much useful information, it is important to be aware that the reagents used are rarely completely specific. It is therefore often beneficial to consider extractants as targeting not precise mineral phases, but specific ‘pools’ or ‘reservoirs’ of heavy metals in the soil, each of which will have different solubility, mobility and potential environmental impact. A selection of approaches and reagents that have been used to isolate heavy metals associated with different soil phases are discussed below. Further details and numerous additional examples are available in Ure and Davidson [210] and in the recent, comprehensive, review by Rao et al. [165].

The soil solution contains the most mobile and readily plant-available species, including free ions and metals complexed with soluble organic matter and other ligands. It can be isolated by filtration [156], dialysis [90, 115], centrifugation [197] or displacement [114]. Metal concentrations are generally low and sensitive analytical techniques such as ICP-MS may be required for quantification. Water-soluble species may be isolated by water extraction [196] (hot water for boron [41]) or treatment with a dilute salt solution e.g. 0.01 mol L^{-1} $CaCl_2$ [115].

Exchangeable metals – those held by electrostatic interactions on both inorganic and organic soil components – can be liberated by treatment with cations. A variety of extractants have been recommended, including 0.1 mol L^{-1} $Ca(NO_3)_2$ [17], 0.1 mol L^{-1} $CaCl_2$ [187], 1.0 mol L^{-1} NH_4NO_3 [68] and 1.0 mol L^{-1} $Mg(NO_3)_2$ [149]. Use of an acetate salt e.g. 1.0 mol L^{-1} ammonium acetate at pH 7 [12] is advantageous since acetate can complex the liberated analytes and prevent re-adsorption [46] but may not be applicable in all soils [164].

Organic matter can be destroyed by treatment with hydrogen peroxide/nitric acid [149] or sodium pyrophosphate [159], thus liberating any associated heavy metals into solution for quantification. Alternatively, metals can be extracted by a chelating agent such as ethylenediaminetetraacetic acid (EDTA) [159] or diethylenetriaminepentaacetic acid (DTPA) [164] although neither reagent is entirely phase-specific. Carbonates are susceptible to dissolution in acid e.g. 1.0 mol L^{-1} acetic acid [12]. Hydroxylammonium chloride can release metals sorbed on manganese and iron (hydr)oxides, with different concentrations used to target separately the amorphous and crystalline forms [47]. Tamm’s reagent (acidified ammonium oxalate) has, for almost a century, been applied to dissolve iron (hydr)oxides [215], although some heavy metals, notably lead and cadmium, form insoluble oxalate species and so may precipitate from solution after extraction [38].

One way to improve the selectivity of soil extraction is to apply not one, but a series of reagents, in order of increasing ‘vigour’. Metals released early in the series are those more weakly bound to the soil and so have greatest potential mobility. Sequential chemical extraction can sub-divide the soil metal content into pools, nominally associated with different mineral phases and which are likely to respond in different ways to changes in environmental conditions such as pH or redox potential. A wide variety of sequential extraction procedures have been proposed since the early work of Tessier et al. [202]. These are summarised in detail in recent

Table 4.1 The revised BCR sequential extraction scheme[a]

	Reagent	Fraction	Nominal target phase(s)
Step 1	0.11 mol L^{-1} acetic acid	Exchangeable, water and acid soluble	Soluble and exchangeable cations, and carbonates
Step 2	0.5 mol L^{-1} hydroxylammonium chloride at pH 1.5	Reducible	Iron and manganese oxides
Step 3	H_2O_2 (85°C) then 1.0 mol L^{-1} ammonium acetate	Oxidisable	Organic matter and sulphides
(Step 4)[b]	*Aqua regia*	Residual	

[a] For the full protocol, see [167]

[b] Although not officially a step in the extraction, it is recommended that the residue from step 3 be digested with *aqua regia* and the sum of the fractions compared with results obtained from *aqua regia* digestion of a separate test portion of the sample

reviews [63, 165, 177]. Difficulties in comparing results obtained by different protocols led to the development, under the auspices of the Commission of the European Communities Community Bureau of Reference (BCR), of a harmonised three stage extraction [212] which was later modified to improve the dissolution of iron oxides in step 3 [176]. The revised BCR sequential extraction [167] is outlined in Table 4.1. A reference material, lake sediment BCR 701, certified for metals extractable by the procedure, is available.

Sequential extraction has provided considerable insight into the behaviour of heavy metals in soils. For example, the BCR scheme has recently been applied to assess potential mobility of Cd, Cr, Cu, Ni, Pb and Zn in agricultural soils from Greece [67]; to investigate the influence of parent material and pedogenic processes on distribution of heavy metals in soils from Iran [139]; to study temporal changes in soils contaminated with pyritic sludge and acidic wastewater released by an opencast mine in Spain [158], and to explore interactions between soil, meltwater and lakes in Antarctica [119]. The procedure has improved understanding of urban geochemistry [39, 94] and, when combined with isotopic analysis, shed light on the transport and mobility of depleted uranium (DU) at weapons testing sites [145]. In the field of soil remediation, the influence of EDTA on uptake of Ca, Cu, Fe, Mn, Pb and Zn by *Taraxacum officinale* (dandelion) [137] and the potential of the iron reducing microorganism *Desulfuromonas palmitatis* as a biostabilisation agent for chromate contamination [148] have been investigated.

The user of sequential extraction must always be aware of the inherent limitations of the approach, including potential redistribution of analytes, non-selectivity of reagents, incomplete extraction and formation of artefacts. A critical review of the field has recently been published [10] that includes the following general recommendations for use of sequential extraction procedures:

(i) use standard protocols e.g. the BCR extraction, precisely as recommended
(ii) use available quality control measures e.g. mass balance calculations and CRM
(iii) report results in terms of operationally-defined fractions e.g. ‘reducible phase’ and not specific minerals e.g. ‘iron oxide bound’

(iv) present data as absolute concentrations because fractionation patterns can be misleading

(v) use the approach in comparative studies e.g. soil before and after amendment

(vi) be cautious in drawing inferences about bioavailability in the absence of corroboratory evidence e.g. results of pot cultivation experiments etc.

4.5.4 Bioavailability and Bioaccessibility

There is increasing interest in the determination of the bioavailable metal content in soils because, when assessing risk, it is the fraction able to enter and affect the biological systems of an organism that is of concern, not the total metal content [150, 184]. Unfortunately, the term *bioavailable* has different meanings in different disciplines and, perhaps as a result, it is sometimes used rather non-specifically in soil literature. It is vital that workers investigating bioavailability should always make clear the target organism(s), chemical species and exposure route(s) being considered.

In agriculture, a high proportion of soil analyses are conducted for the purpose of estimating the levels of essential trace elements that are currently plant-available. This allows appropriate nutrient management decisions to be made concerning, for example, whether a particular crop can be grown or whether trace element deficiencies are likely to occur, in which case soil amendment with chemical fertilisers may be required. A variety of empirically-derived extraction procedures have been developed to estimate plant availability of heavy metals (Table 4.2) using similar reagents to those discussed in Sect. 4.5.3. These can also be used to assess the suitability, or monitor the progress, of phytoremediation strategies applied to contaminated land.

Numerous studies have demonstrated that the optimal extraction procedures (i.e. those providing data most closely correlated to that obtained in pot cultivation experiments) are specific to particular elements, crops, and even soils types [6, 13, 89, 133, 219]. Takeda et al. [198] compared metal uptake in plants with results of soil extraction using acids (1.0, 0.1 and 0.01 mol L^{-1} HNO_3), a chelating agent (0.05 mol L^{-1} EDTA), neutral salt solutions (1.0 mol L^{-1} NH_4OAc, 1.0 mol L^{-1} NH_4NO_3, 0.01 mol L^{-1} $CaCl_2$) and water. They found strong correlations only for a few elements, and only for some of the neutral salt extractions. Both McBride et al. [127] and Menzies et al. [128] also recommended neutral salt solutions as the best 'general purpose' soil extractant for the estimation of phytoavailability. Other workers proposed the Mehlich 3 reagent (a mixture of 0.2 mol L^{-1} acetic acid, 0.25 mol L^{-1} NH_4NO_3, 0.013 mol L^{-1} HNO_3, 0.015 mol L^{-1} NH_4F and 0.001 mol L^{-1} EDTA) [132], or a rhizosphere-based method involving extraction with a mixture of low molecular weight organic acids (acetic, lactic, citric, malic and formic acids in the molar ratio 4:2:1:1:1 at a combined concentration of 0.01 mol L^{-1}) [59]. There is also recent interest in the use of passive sampling devices based on diffusive gradients in thin films to predict plant uptake [29, 153].

Table 4.2 Examples of extractants used to estimate plant-available heavy metals

Extractant	Elements	Plant	Reference
Water	B	*Brassica chinensis, Agropyron elongatum*	[225]
Water	Cd, Cu, Mn, Zn	Native plants	[218]
Water	As, Cd, Cr, Cu, Ni, Pb, Zn	Maize	[87]
0.005 M DTPA[a]	Cd, Cu, Mn, Ni, Pb, Zn	*Brassica chinensis, Agropyron elongatum*	[225]
0.005 M DTPA	Cd, Cu, Fe, Pb, Zn	Tomato	[99]
0.005 M DTPA	Cu, Zn	Rice	[228]
0.005 M DTPA	Hg	Rice – cabbage – radish	[89]
0.005 M DTPA	Cd, Cu, Mn, Zn	Native plants	[218]
0.005 M DTPA	Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Wheat	[18]
0.01 M acetic acid	Cu, Ni	Wheat	[219]
0.01 M citric acid	Cu, Ni	Wheat	[219]
0.01 M oxalic acid	Cu, Ni	Wheat	[219]
0.01 M tartaric acid	Cu, Ni	Wheat	[219]
0.01 M organic acid mixture	Cu, Pb, Zn	Barley	[117]
0.01 M $CaCl_2$	As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn	Potential bioavailability	[207]
0.01 M $CaCl_2$	Cd	Oats	[71]
0.01 M $CaCl_2$	Cu, Pb, Zn	Barley	[117]
0.01 M $CaCl_2$	Cu, Pb, Zn	Ryegrass	[4]
0.01 M $CaCl_2$	As, Cd, Cr, Cu, Ni, Pb, Zn	Maize	[87]
0.05 M EDTA	Cu, Ni	Wheat	[219]
0.05 M EDTA	Cu, Pb, Zn	Barley	[117]
0.05 M EDTA	As, Ni, Pb	*Rubus ulmifolius*	[124]
0.1 M $CaCl_2$	Hg	Rice – cabbage – radish	[89]
0.1 M HCl	Hg	Rice – cabbage – radish	[89]
0.4 M LiCl	Cd, Cr, Cu, Ni, Pb	Various food crops	[53]
0.5 M $Ca(NO_3)_2$	Cd, Cu, Fe, Pb, Zn	Tomato	[99]
0.5 M NH_4Ac, 0.5 M acetic acid 0.02 M EDTA	Cu, Pb, Zn	Ryegrass	[4]
1.0 M $MgCl_2$	Cu, Ni	Wheat	[219]
1.0 M NH_4OAc	Cu, Ni	Wheat	[219]
1.0 M NH_4OAc	Hg	Rice – cabbage – radish	[89]
1.0 M NH_4HCO_3	Cd, Cu, Mn, Ni, Pb, Zn	*Brassica chinensis, Agropyron elongatum*	[225]
1.0 M NH_4NO_3	Cu, Ni	Wheat	[219]
1.0 M NH_4NO_3	Cd, Cu, Pb, Zn	Potential bioavailability	[100]

[a] Actually a 0.005 M DTPA, 0.01 M $CaCl_2$ and 0.1 M triethanolamine buffered (pH 7.3) solution [111]

Table 4.3 Examples of physiologically-based extractions used to assess the human bioaccessibility of heavy metals in soils

Procedure	Mouth	Stomach	Intestine
1 [116, 134]	n/a	0.4 M glycine at pH 1.5; 1 h	n/a
2 [19, 147, 174, 221]	n/a	Pepsin, citrate, malate, lactic acid, acetic acid; pH 1.5; 1 h	Stomach + pancreatin, bile salts; pH 7; 2–4 h
3 [25]	KCl, NaH_2PO_4, KSCN, Na_2SO_4, NaCl, NaOH, urea, amylase, mucin, uric acid; pH 6.5; 15 min	NaCl, NaH_2PO_4, KCl, $CaCl_2$, NH_4Cl, HCl, glucose, gluouronic acid, urea, glucosaminehydrochloride, bovine serum albumin, mucin, pepsin; pH 0.9–1.0; 1 h	NaCl, $NaHCO_3$, KH_2PO_4, KCl, $MgCl_2$, HCl, urea, $CaCl_2$, bovine serum albumin, pancreatin, lipase; pH 7.4; 4 h

Of increasing recent interest is the estimation of human oral uptake of heavy metals following ingestion of soil. Ingestion may occur either accidentally, due to poor hygiene and consumption of inadequately washed foodstuffs, or deliberately due to geophagia (soil consumption for medicinal or religious purposes) and pica (an eating disorder in which the sufferer consumes non-food substances). It is important to distinguish between *bioavailability* (the fraction of the oral dose that is absorbed into the systemic circulation [171]) which can only be measured by blood metal analysis, and *bioaccessibility* (the fraction that is soluble in the gastrointestinal environment and thus available for absorption) which can be estimated *in vitro*.

A variety of extraction procedures have been developed to simulate conditions in the human gastro-intestinal tract and thus assess human oral bioaccessibility of heavy metals in soils [85, 146, 226]. These are performed at 37°C with stirring or shaking, but differ in complexity, reagents used, duration and number of compartments simulated. Procedure 1 in Table 4.3, sometimes called the simplified bioaccessibility extraction test (SBET) method has recently been applied to urban soils in Sevilla and Torino [116] and to soils from a transect across the United States and Canada [134]. Procedure 2, derived from the physiologically-based extraction test (PBET) of Ruby et al. [174] has been used to assess human bioaccesibility of As in soil with high geogenic concentrations [147] and of As [221] and Pb [19] at sites affected by mining and ore processing. Procedure 3 is the emerging unified BARGE (Bioaccessibility Research Group of Europe) method, results of which have recently been compared with both total As concentrations and As concentrations in earthworms at sites in the UK [25].

Unfortunately, rather few of the physiologically-based extractions have so far been validated by comparison with *in vivo* studies and then only for a limited range of analytes e.g. the PBET of Ruby et al. has shown correlations with animal models for As and Pb [174]. Also, similar to sequential chemical extraction in the 1990s, the approach suffers from limitations, including needs for harmonisation of analytical methods, development of standard protocols and CRMs. These topics are currently being addressed, for example by the EU BARGE consortium [227].

4.6 Analyte Preconcentration and Separation

Matrix components may interfere with the determination of heavy metals in soils, in which case it may be necessary to separate the analyte(s) from potential interferents prior to measurement. There are also situations where analytes are present at concentrations too close to (or below) the LOD of available instrumental techniques. Preconcentration methods can increase the concentration of analyte in the solution presented to the instrument, allowing accurate quantification. It is of course necessary to know the preconcentration factor achieved, so that the original analyte concentrations can be calculated.

Procedures for the preconcentration of heavy metals in soil extracts and digests tend to be based on solid phase extraction, co-precipitation, or cloud-point extraction (for recent examples see [23]). In solid phase extraction, a selective sorbent is prepared by functionalising a supporting medium with chemical moieties able to complex selectively the metal(s) of interest. The sorbent is packed into a column and the soil extract passed through. Analytes are retained but interferents are not. The analytes can then be eluted for analysis. If the volume of eluant used is smaller than the volume of extract originally loaded, then preconcentration will be achieved. An alternative approach is to add the complexing agent to the soil extract, rather than functionalise the sorbent. Co-precipitation procedures involve the trapping of analytes (or interferents) on a solid carrier. In cloud point extraction a surfactant is added to the soil extract, together with a selective chelating agent. Under appropriate conditions, the mixture partitions into a surfactant-rich phase, in which the metal complexes are concentrated, and a dilute aqueous phase [42].

4.7 Instrumental Techniques for Measurement of Heavy Metals

Most techniques for measuring heavy metals in soils require the sample to be dissolved or leached to produce a solution for analysis and the instrument to be calibrated with a series of standard solutions of known concentration. These often can be prepared in dilute acid solution e.g. 5% HNO_3. However, in some analyses, the presence of extractant reagents alters the response of the instrument (Fig. 4.5a). In this case, calibrants must be reagent-matched. In other situations, components of the soil matrix, co-extracted with the analytes, may interfere in the analysis. Reagent-matching will not overcome this type of interference; instead it is necessary to matrix-match the standard solutions (i.e. they should contain all the same components as the soil extract, but no analyte). Since this is rarely possible, analysis is instead performed by the method of standard addition (Fig. 4.5b). Known concentrations of analyte are added to aliquots of the soil extract. The graph obtained is extrapolated and the (positive value of the) point where it crosses the x-axis is the analyte concentration in the extract.

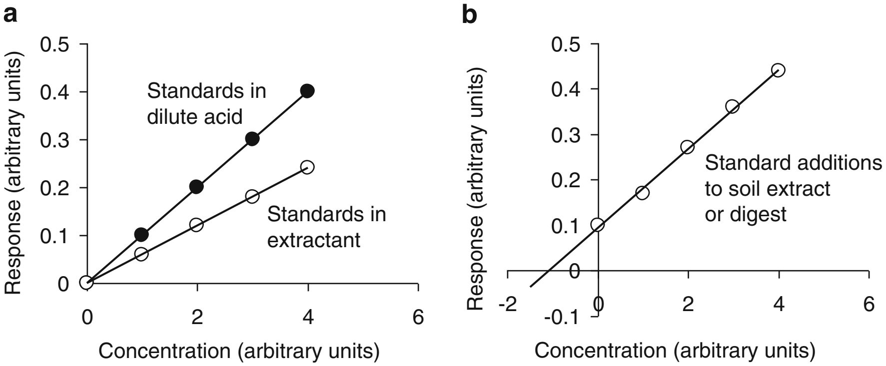


Fig. 4.5 Calibration in atomic spectrometry (**a**) a suppressive interference caused by the extractant matrix (**b**) calibration by standard addition

4.7.1 Atomic Spectrometry

Atomic spectrometry involves measurement of the electromagnetic radiation absorbed or emitted by free atoms when their valence electrons undergo transitions between atomic energy levels [45, 106]. In atomic absorption, energy is transferred from a photon to an atom, causing an electron to be promoted to an excited state. In atomic emission, electrons in an excited state de-excite and their excess energy is emitted as photons. The number of atoms with electrons in higher energy levels increases with temperature, and so spectroscopic techniques involving atomic absorption tend to be conducted in the (relatively) low temperature environment of a combustion flame, whereas emission techniques require higher temperatures such as those available in plasmas. Because different types of atom have different electronic configurations, each element absorbs and emits light at characteristic wavelengths. The amount of light absorbed or emitted is proportional to the concentration of analyte present.

4.7.2 Flame Atomic Absorption Spectrometry (FAAS)

A typical atomic absorption spectrometer consists of a light source to supply photons, an atom cell to create free analyte atoms, a monochromator to isolate the wavelength of interest, and a photo-multiplier tube detector (Fig. 4.6). The light source is usually a hollow cathode lamp (HCL) (Fig. 4.7) although electrodeless discharge lamps (EDL) are also used. In an HCL, the cathode is made from, or coated with, the analyte element. A voltage is applied between anode and cathode, producing an electrical discharge in the fill gas (typically neon or argon at 1–5 torr). Noble gas ions are accelerated towards the cathode where they cause sputtering. When excited atoms removed from the surface de-excite, a line emission spectrum

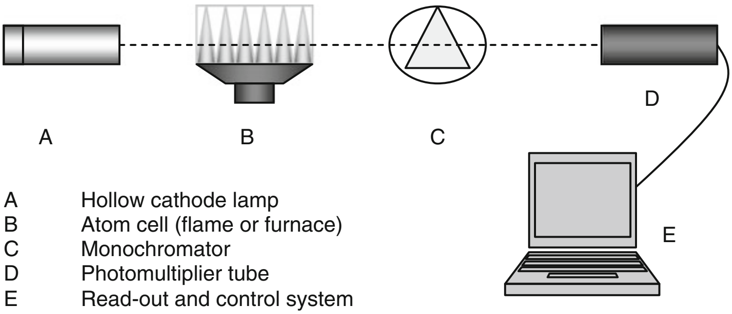
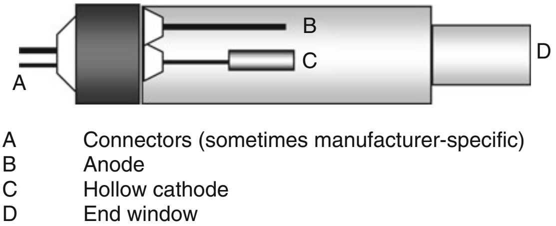


Fig. 4.6 Schematic diagram of an atomic absorption spectrometer

Fig. 4.7 Schematic diagram of a hollow cathode lamp



characteristic of the cathode element is produced. This light is directed through the atom cell, where it can be absorbed by analyte atoms. Spectral lines are broadened relative to natural widths by the Doppler effect (related to temperature) and collisional effects (related to temperature and pressure). Since the hollow cathode lamp operates at lower pressure and temperature than typical atomisers, the emission linewidth from the lamp is narrower than the analyte absorption profile in the atom cell. Hence, all of the light can be absorbed.

FAAS is widely used for determining heavy metals in soils. The atom cell is a combustion flame. The most common type is the air-acetylene flame (T ~2,200°C). Air and fuel are pre-mixed in a spray chamber and then flow past a nebuliser (a narrow metal tube connected to a plastic tube, which draws the sample up at a rate of about 5 mL min^{-1}). A proportion ($<10\%$) of the aerosol generated – that part containing the smallest, most uniformly-sized droplets – is swept into the base of the burner and aspirated into the flame. At least a few milliliter of sample solution are required to perform a measurement, although this can be reduced by the use of pulse nebulisation.

An alternative flame uses nitrous oxide-acetylene (T ~ 2,900°C). This provides better atomisation efficiencies but is less safe because of the higher burning velocity – hence a shorter burner head is used (5 cm *cf.* 10 cm for air-acetylene) – and also gives out a more intense background emission spectrum. Its use tends to be reserved for elements that are difficult to atomise with air-acetylene due to formation of thermally stable oxides, such as Al and Mo. Whichever flame is used, the conditions (fuel flow and burner height) have to be optimised for each analyte (and for different reagent matrices) to maximise the atomisation efficiency.

FAAS is subject to spectral, physical and chemical interference effects that can lead to inaccurate results being obtained. Spectral line overlap occurs if matrix components such as other metals absorb light at the same wavelength as the analyte. Fortunately this type of interference is rare because HCL line widths are narrow. If necessary, it can be overcome be chemical separation of analyte and interferent prior to analysis (although this may be time-consuming) or by conducting the measurement at a different analyte wavelength (although this may reduce sensitivity). Interference due to flame emission – the release of light over a range of wavelengths by the hot gases present – can be overcome by modulating the light from the HCL and using a detector that can discriminate between a steady-state and a pulsed signal. Molecular absorption and scattering of light by particles in the flame also occur. These are overcome in commercial AAS instruments by incorporating a background correction system, based on the Zeeman effect or, more usually, a continuum light source such as a deuterium lamp. If the light beams from the D_2 source and the HCL follow exactly the same path through the flame, and each is modulated at a different frequency so that they can be detected individually, then the signal from the HCL represents atomic absorption plus non-specific absorption, whilst the signal from the continuum lamp effectively represents only non-specific absorption. By subtracting one from the other, the corrected absorbance is obtained.

Physical interference effects can arise if the sample and standard solutions are dissimilar in their viscosity or surface tension, and hence are aspirated at different rates. This can usually be overcome by reagent-matching. Chemical interferences can disturb equilibria between analyte molecules and atoms, or between atoms and ions, altering the atomisation efficiency in the sample solution relative to the standard solution (where no matrix is present). Where matrix components form stable compounds with the analyte, fewer atoms are produced (a suppressive interference effect). This may be overcome by addition of a reagent that preferentially binds to the interferent, leaving the analyte free to atomise. The atomisation of Group 1 and Group 2 metals can be affected by the presence of other easily-ionised elements in the sample matrix. If the equilibrium between interferent atoms and ions is strongly in favour of ions, the electrons liberated during ionisation of the interferents will suppress ionisation of the analyte (an enhancing interference effect). Addition of a large excess of a very easily ionised element such as caesium (Cs) to both samples and standards usually overcomes this problem. The analyte can also become physically trapped within particles. Reagents are available, e.g. ammonium chloride and EDTA, that can combat this type of interference effect.

FAAS is a mature analytical technique but still widely applied. It has recently been used to assess the uptake of heavy metals from soil into coffee [49], corn [95], medicinal plants [168] and grapes [204]. The environmental impact of a tannery [200] and a Zn smelter [203] have been assessed, and general differences in metal concentrations in industrial, rural and urban soils studied [229]. One notable recent analytical development is high resolution continuum source FAAS. Although not yet widely used, the technique has provided promising results for the measurement of Cu, Fe, Mn and Zn in 0.005 mol L^{-1} DTPA extracts of agricultural and reference soils [166].

Table 4.4 Typical ETAAS heating programmes[a]

Stage	Temp. (°C) Cd	Temp. (°C) Cr	Duration (s)	Ramp rate (°C s^{-1})	Purpose
Dry	110	110	30	20	Remove solvent e.g. water
Pyrolyse	700	1,650	20	2,000	Remove matrix
Atomise	1,600	2,500	3	>2,000	Generate free analyte atoms
Clean	2,650	2,650	2	>2,000	Remove residue ready for next sample injection

[a] Adapted from [168]

Limits of detection in FAAS are limited to the region of parts-per-million because of the relative inefficiency of sample introduction by pneumatic nebulisation, combined with the short residence time of analyte atoms in the HCL beam and their dilution by the large excess of flame gases present.

4.7.3 Electrothermal Atomic Absorption Spectrometry (ETAAS)

In ETAAS the flame is replaced by an electrically-heated graphite tube atomiser, roughly 3 cm in length and <1 cm in diameter. A small aliquot of analyte solution e.g. 20 μL is pipetted into the tube through a dosing hole in the top and a step-wise heating programme is applied to create analyte atoms. The HCL beam passes along the axis of the tube. Limits of detection are improved greatly relative to FAAS (to around parts-per-billion levels) because the atoms are confined, but chemical interferences are severe, as are memory effects, although the latter can be reduced by use of low permeability, chemically resistant pyrolytic graphite.

The heating programme has to be optimised for each analysis, the goal being to remove as much as possible of the (potentially interfering) sample matrix, but retain the analyte until atomisation.

Examples of furnace programs for measurement of contrasting elements (Cd and Cr) in acid digests are shown in Table 4.4. An inert gas such as N_2 is flowed around and through the furnace, except during atomisation, to protect the tube from combustion and help carry away volatile material. A typical graphite tube might endure several hundred ‘firings’ before it has to be replaced, but tube lifetime will be reduced substantially if high temperatures are used, or if the sample matrix is corrosive.

Even with an optimised heating cycle, interferences may still persist, notably the formation of volatile analyte species that can be lost during ashing, or of refractory analyte species that do not atomise efficiently. ETAAS is particularly prone to chloride interferences, and these commonly occur when analysing HCl soil digest or $CaCl_2$ soil extracts. A large variety of ‘matrix modifiers’ – reagents that are added to the furnace together with the sample to improve atomisation – have been developed to overcome interferences in ETAAS. Examples include ammonium nitrate, magnesium nitrate, and palladium nitrate. Another common approach is to delay the atomisation of the sample until the gas within the tube has reached a higher temperature by depositing it not on the tube wall but onto a small graphite platform (called a L'vov platform after its inventor). Further details of interference effects in ETAAS and methods by which these may be overcome can be found in [106].

Nowadays, ETAAS tends to be used in studies where a single element, present at relatively low concentration in soil, is of interest because of its toxicity (recent examples have focussed on Cd [154], Cr [62] and Sb [43]); for the detection of specific chemical species [37], or where ICP-MS is unavailable [31]. A key limitation of both ETAAS and FAAS is that the vast majority of HCLs commercially available contain a single element. This means that atomic absorption spectrometry can measure only one analyte at a time. Whilst there are many situations where only one (or few) heavy metals are of interest, many studies require multi-element analysis.

4.7.4 Inductively-Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Flame atomic emission spectrometry is still used for some specific applications, notably the determination of major cations in soils [168]. The instrumentation is similar to FAAS, except than no HCL is required. However, for most analyses, it has been supplanted by ICP-AES.

Plasma is gas in which a high proportion of the atoms and molecules present have been ionised. Most commercial ICP-AES instrument use an argon plasma operating at a power of 0.5–1.5 kW and a frequency of 27 or 40 MHz. The temperature in the plasma is in the range 7,000–10,000 K (different regions have different temperatures). Hence, there is ample energy available to atomise, excite and even ionise most heavy metals. The argon ICP is formed in a specially designed torch, made of three concentric quartz tubes surrounded by a water-cooled, copper, radio frequency coil (Fig. 4.8). Three streams of argon are supplied. The inner or carrier gas transports the sample aerosol to the ICP, whilst the outer gas helps shape the plasma and prevents it from melting the torch. When radiofrequency energy is supplied to the coil an intense magnetic field is created. Seed electrons generated by a spark from a Tesla coil are accelerated by the field and collide with argon atoms, producing a self-sustaining plasma. The carrier gas punches a hole through the centre of the plasma, giving it a characteristic toroidal shape. Because of the intensity of background spectral emission from the core of the plasma, analytical measurements are usually made in the tail plume, 1–2 cm above the load coil. Even so, significant levels of background emission can reach the detector and so there are significant advantages in viewing the plasma axially, rather than from the side [20].

Soil digests and extracts are introduced to the ICP in a similar way to FAAS. Hence similar physical interference effects can occur. Also as in FAAS, the majority of the sample goes to waste, with just a few percent reaching the plasma. A variety of designs of spray chamber and nebuliser are available [189, 190]. Most routine analysis uses pneumatic or cross-flow nebulisers, but there are also ultrasonic nebulisers (which can increase the proportion of sample entering the

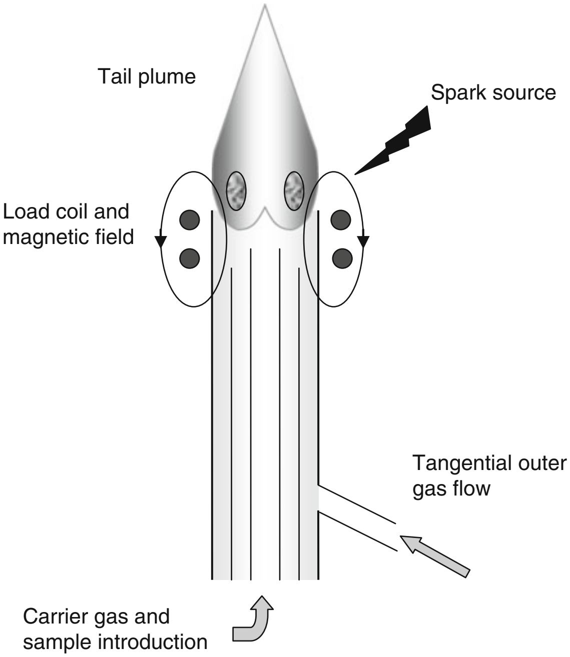


Fig. 4.8 Schematic diagram of an inductively coupled plasma torch

plasma, and hence the sensitivity) and 'high-solids' nebulisers. Chemical interferences are effectively eliminated because the energy of the plasma is so much greater than that of a flame that even elements forming refractory oxides are atomised efficiently. In contrast, spectral line overlap is a considerably bigger problem in ICP-AES than in FAAS because the higher temperature environment means that virtually all the elements present in the plasma will have atoms (and ions) in several excited states. When these de-excite a complex spectrum, rich in emission lines, is produced. Separation of the wavelength(s) of interest requires a higher resolution monochromator than in AAS. Echelle spectrometers are most common. These contain two dispersive elements, a grating and a prism. The echelle grating separates light in one direction and the prism in a perpendicular direction. The two-dimensional spectrum produced i.e. a series of short regions of the spectrum, stacked above on another, is focussed onto a charge-coupled device (CCD) detector.

Key advantages of ICP-AES over atomic absorption techniques are the wide dynamic range (several orders of magnitude) and ability to perform multi-element analysis. This means that it is often feasible simultaneously to measure major and trace elements. Since the last edition of this book [3] ICP-AES has become probably the most widely used spectroscopic technique for measuring heavy metals in soils, plants and related materials. Examples of recent applications include the measurement of Ba, Cd, Cu, Fe, Mn, Ni, Pb, V and Ti in urban topsoils [144]; of As, Cd, Cu, Fe, Ni, Pb and Zn in roadside soils [55]; of As, Cd, Cu, Pb and Zn in soils affected by nonferrous metal mining [109] and of Al, Ba, Cr, Cu, Fe, Mn, Ni, Pb, Sr, Ti, V and Zn in peat cores [84]. The technique has also been used to provide insight into phytoremediation of heavy metal contaminated soil using, for example, vetiver grass (*Chrysopogon zizanoides*) [8] and to study the input of heavy metals to soil from application of fertilizers [131].

The main limitation of ICP-AES is that the LOD achievable – typically parts-per-million levels or a little lower – are insufficient for some applications. For example, when measuring phytoavailability by application of a neutral salt solution to a relatively uncontaminated soil, the concentrations of heavy metal released may be too low for accurate measurement. This problem can be overcome by coupling the ICP to a mass spectrometer.

4.7.5 Inductively-Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS is the newest atomic spectrometry technique to become widely applied in soil analysis. Relatively rare 20 years ago because of high instrument cost and the need for a specialist, skilled operator, it is now frequently used in multi-element studies of heavy metal distribution in relation to potential pollution sources e.g. [121, 151, 233] and in work focused on trace element uptake by plants [181] or biogeochemical cycling [194].

The ICP is the same as that in AES but, instead of measuring light emitted, the ions generated in the plasma are directed into a quadrupole mass analyser (typically capable of unit mass resolution i.e. discrimination of m from $m - 1$ or $m + 1$). One of the major challenges in developing ICP-MS was extracting ions from the hot, dense plasma into the high vacuum environment of the mass analyser. Modern instrument interfaces use two, water-cooled nickel or platinum cones for this purpose (Fig. 4.9). The first cone is positioned in the tail plume of the plasma and allows an expanding jet of material to pass through its ~1.0 mm orifice into an intermediate vacuum region. The second, 'skimmer', cone sub-samples this jet, allowing a small proportion of the ions into a higher vacuum region where they are accelerated into the quadrupole.

ICP-MS has LOD similar to those of ETAAS (parts-per-billion or lower) but the capability to perform multi-element and isotopic analysis. Common interferences include deposition of solid material at the tip of the cones, especially when analysing sample solutions containing high concentrations of dissolved solids. This can be overcome by sample dilution, but with a concomitant reduction in LOD. More important are the occurrence of isobaric interference (e.g. that of ^{40}Ar on the measurement of ^{40}Ca) and of polyatomic ions from the plasma or sample matrix at the same mass to charge ratio as the analyte ion. These can sometimes be removed by changing the sample preparation procedure e.g. the interference of $ArCl^+$ on As^+ at m/z 75 may be avoided by use of nitric acid rather than *aqua regia* in soil digestion, but interferences arising from the plasma itself are more difficult to overcome e.g. that of Ar_2^+ on Se^+ at m/z 80. One option is to use a different analyte isotope for quantification, but this will lead to a reduction in sensitivity if the relative abundance is lower than that of the original isotope, and it is impossible for mono-isotopic elements such as As. The newest generation of commercial ICP-MS instruments incorporate devices to overcome polyatomic ion interference. Different manufacturers approach

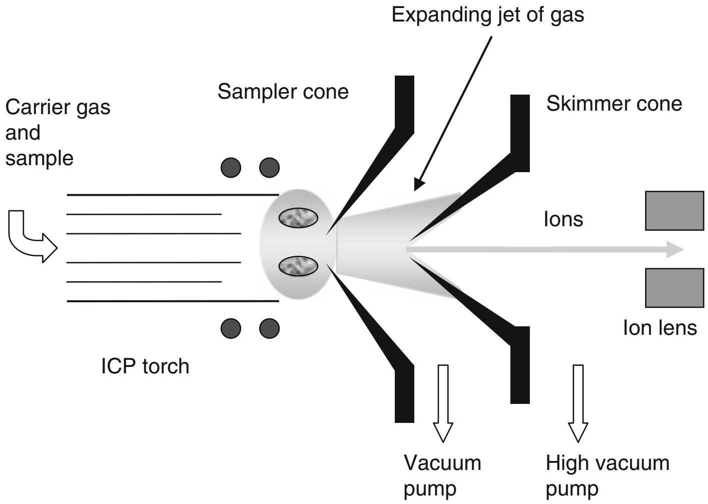


Fig. 4.9 Schematic diagram of an ICP-MS interface

the problem slightly differently. Options include the breaking-up of the interfering ions into their component atoms, altering their mass through reaction with reagent gas (e.g. H_2) or changing their energy through collisions with inert species (e.g. He). The overall effect is to free the analyte ion for detection.

An alternative approach is to replace the quadrupole mass analyser with a magnetic sector. Sector field-ICP-MS offers many analytical advantages, including excellent mass resolution [101] – indeed the technique is sometimes called high resolution-ICP-MS – but significantly increases the cost of the instrument. It tends therefore to be used for rather specialist applications such as the accurate measurement of stable isotope ratios [157, 193].

There is considerable interest in the development and use of various sample introduction systems for ICP-MS and/or ICP-AES. Approaches currently being explored include electrothermal vaporisation [79, 170, 206], laser ablation (see Sect. 4.4.4) and the direct coupling of chromatography with ICP-MS [81] for speciation analysis (see Sect. 4.8).

4.7.6 Other Types of Atomic Spectrometry

Hydride generation atomic absorption spectrometry (HGAAS) is applicable to the elements As, Bi, Ge, Pb, Sb, Se, Sn and Te, all of which form volatile hydrides on reduction with sodium borohydride in acid media. The hydrides are swept into an atom cell where they are decomposed to atomic vapour. The cell is usually a quartz glass tube. It may be electrically heated or placed in the flame of an FAAS instrument. The main advantage of hydride generation methods is increased sensitivity relative to conventional solution nebulisation. A limitation is that the technique suffers from chemical interference effects, especially due to the presence of transition metals such as nickel, which can affect the hydride generation efficiency in solution. Recent applications include the measurement of Pb in soil digests [120] and several studies involving sequential extraction of Se [21, 110]. Petrov et al. [155] recently described an optimised method for As speciation in EDTA extracts of soil and sediment by continuous flow-HGAAS.

Cold vapour atomic absorption spectrometry (CVAAS) is used to measure Hg in soil [211]. Monatomic elemental Hg vapour is generated from sample extracts or digests by reduction, usually with tin(II) chloride, and swept into the light beam from a hollow cathode lamp. No heating of the atom cell is required. Sensitivity can be improved by preconcentration on gold amalgam [70]. CVAAS methods are available to allow separate measurement of inorganic and organic Hg species [205].

In atomic fluorescence electrons are promoted by photons and the light emitted when they return to their ground states (‘fluoresce’) is measured. In atomic fluorescence spectrometry (AFS) a plasma source may be used to atomise the sample, but excitation of the atoms is brought about by an element-specific EDL or by a tunable laser [64, 223]. AFS is potentially a powerful analytical technique, combining some of the advantages of AAS and AES. However, current applications are relatively limited, tending to focus on the measurement or speciation of hydride-forming elements such as As [48, 175, 231], Sb [43] and Se [232] or on the determination of Hg by cold vapour AFS [66, 78].

4.7.7 Other Analytical Techniques

Although the measurement of heavy metals in soils is dominated by atomic (and elemental mass) spectrometry, other techniques are used. There are developments and applications of capillary electrophoresis [2, 65, 213], ion chromatography [191], ion-selective electrodes [44] and stripping voltammetry [1]. Electroanalytical instruments can be made that are capable of rapid, sensitive, selective analysis [56, 72] and there is strong interest in developing hand-held systems e.g. for field speciation of As [126].

4.8 Speciation and Speciation Analysis

Speciation refers to the chemical ‘form’ of an analyte e.g., its oxidations state, the atoms or molecules it is bound to, or mineral phases with which it is associated. Ure [208] subdivided speciation into three classes:

(i) classical speciation, where a specified chemical form is considered e.g., $\mathrm{Cr}^{\mathrm{III}}$ *vs*. $\mathrm{Cr}^{\mathrm{VI}}$ or inorganic mercury *vs*. monomethylmercury

(ii) functional speciation, where species are defined by their role e.g., plant-available species

(iii) operational speciation, where species are defined by the reagents used to extract them e.g., 0.05 mol L^{-1} EDTA-soluble species, or metals released by a sequential extraction.

More recently, IUPAC adopted a narrower definition [201] similar to the ‘classical’ speciation of Ure. This latter definition is the one used in this chapter.

Speciation is a key factor influencing the mobility, fate, bioavailability and toxicity of heavy metals in soils. Potentially toxic elements for which speciation is currently of particular interest include As, Cr, Hg, Pb, Sb, Se and Sn, many of which form environmentally-important organometallic species. Speciation analysis (measurement of the kinds and amount of heavy metal species present) is an extremely challenging, but rapidly expanding, area of analytical science [35, 57, 74].

As noted in 4.4.2, direct speciation analysis of metals and metalloids in soils is now possible with synchrotron-based X-ray techniques. In recent examples, extended X-ray absorption fine structure (EXAFS) spectroscopy has been used to measure Pb species in soil and assess the effectiveness of phosphate-induced immobilisation [76], whilst X-ray absorption near edge structure (XANES) revealed information on the mechanism of transport of Cu and Mn across the soil/root interface [140] and on transformation of Cr^{VI} to Cr^{III} in soil [93]. Voegelin et al. [216] used several X-ray techniques to study As in riparian floodplan soils. Synchrotron micro-XRF showed the distribution of As closely matched that of Fe in the vicinity of plant roots; XANES showed the As was mainly present as As^{V}, and EXAFS confirmed an association between As and iron (oxy)hydroxide species. A similar association of Sb^{V} with iron minerals was found in soil from a shooting range in Switzerland [185].

Other approaches for speciation of heavy metals in soils are based around the coupling of chromatographic separation methods to element-specific detectors such as ICP-MS. Great care must be taken during sample pretreatment since there is considerable danger of altering the original speciation, in which case the results obtained will lose their environmental relevance.

Size exclusion chromatography-ICP-MS has revealed associations between heavy metals and different forms of dissolved organic matter in soil solution [199] and leachates [105]. Analysis by high performance liquid chromatography-ICP-MS showed that little of the Hg present in a contaminated soil was present in the soil solution and available for plant uptake [30]. Measurement of methylated species of As, Sb and Sn in urban soils by hydride generation gas chromatography followed by ICP-MS has improved understanding of the biogeochemical cycling of these elements [51].

4.9 Quality Assurance

Laboratories involved in the determination of heavy metals in soils, whether for regulatory or research purposes, should regularly monitor the quality of their analyses [5]. A range of approaches are available. At the very least, appropriate blanks should be analysed (both reagent and procedural blanks) to check for contamination, whilst analysis of replicate test portions will provide an indication of the repeatability and precisions of measurement.

A Certified Reference Material (CRM) is a soil or other material in which one or more metal concentrations have been firmly established, through analysis by several laboratories using a range of analytical techniques. Results are subject to keen scrutiny and only those in which there is a high degree of confidence are accepted as certified values [160, 161]. CRMs are prepared and issued by agencies such as NIST in the USA and JRC-Ispra in Europe [138]. They are available for a variety of soil types and analytes (see Table 4.5). When using a CRM, it is important to select one as similar as possible in composition to the samples and certified for the type of extraction being performed. CRMs can be used to assess the accuracy of a new analytical method or instrument, to establish whether results of an established method are under control, and as an aid in training or monitoring the competence of staff. Limitations of CRMs include their high cost and the fact that they are available for a restricted range of soil types, analytes and extraction procedures. As a consequence, many laboratories prepare their own, in-house, reference materials (RM). These are soils, often with characteristics relevant to a particular study (e.g. urban soils [40]) which are obtained, homogenised, stabilised (e.g. by heat treatment) and their heavy metal contents established by analysis of replicate test-portions in parallel with CRM and, if possible, by more than one laboratory. The RM can then be incorporated into all batches of analysis and control charts plotted to monitor the long-term reproducibility of the analytical method, whilst the CRM is included only periodically to ensure accuracy is maintained.

Another way in which trace metal laboratories can assess their competence is to participate in inter-comparison exercises (also called proficiency tests) [152, 230]. These are organised by various national and international bodies and involve the distribution for analysis of test samples whose composition is usually known to the organisers but not to the recipients. Alternatively, laboratories working together may elect to exchange check-samples for analysis [40]. Proficiency tests are particularly useful in identifying bias in particular laboratories or methods.

Inter-laboratory harmonisation can also be enhanced by using standard analytical methods [22], especially those recommended by national bodies such as the USEPA (United States), BSI (UK) and DIN (Germany), and by the International Organisation for Standardisation (ISO). Advantages of these are that they are well-established and thoroughly tested methods, and hence results obtained by different laboratories should be comparable. A disadvantage is that it takes a considerable amount of time and discussion for the international soil science community to agree on a standard method. Hence, their availability tends to lag behind advances in analytical science. A selection of current ISO methods relevant to the measurement of heavy metals in soils is provided in Table 4.6. However, new guidelines are continually being produced. For the most up-to-date list, the reader is directed to the ISO website, www.iso.org/iso/home.htm

Table 4.5 A selection of soil certified reference materials

CRM	Material	Extraction	Analytes[a]
SRM 2709a	San Joaquin soil (uncontaminated)	Total	Al, Ba, Ca, Cd, Cr, Co, Fe, K, Mg, Mn, Na, P, Pb, Sb, Si, Sr, Ti, V, Zn
SRM 2710a	Montana I Soil (highly contaminated)	Total	Al, As, Ba, Ca, Cd, Co, Cu, Fe, Hg, K, La, Mg, Mn, Na, P, Pb, Sb, Si, Sr, Ti, U, Zn
SRM 2711a	Montana II Soil (slightly contaminated)	Total	Al, As, Ba, Ca, Cd, Cr, Co, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, Si, Sb, Sm, Sr, Ti, U, V, Zn
SRM 2586	Soil contaminated with Pb from paint	Total	As, Cd, Cr, Pb (nominally 500 mg kg^{-1} Pb)
SRM 2587	Soil contaminated with Pb from paint	Total	As, Cd, Cr, Pb (nominally 3,000 mg kg^{-1} Pb)
SRM 2701	Hexavalent chromium in soil	Total and EPA method 3060A	Total Cr, Fe, Mn; method 3060 extractable Cr(VI);
SRM 4353	Rocky Flats soil number 2	Total	Radionuclides
BCR-142R	Light sandy soil	Total	Cd, Co, Cu, Hg, Mn, Ni, Pb, Zn
		Aqua regia	Cd, Co, Cu, Mn, Ni, Pb, Zn
BCR-143R	Sewage sludge amended soil	Total	Cd, Co, Cu, Hg, Mn, Ni, Pb, Zn
		Aqua regia	Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn
ERM-CC690	Calcareous soil	Total	Ce, Dy, Gd, La, Nd, Sc, Sm, Tb, Th, Tm, U, Yb
BCR-483	Sewage sludge amended soil	EDTA, acetic acid, calcium chloride, sodium nitrate, ammonium nitrate	Cd, Cr, Cu, Ni, Pb, Zn
BCR-484	Sewage sludge amended (terra rossa) soil	EDTA, acetic acid	Cd, Cu, Ni, Pb, Zn
BCR-700	Organic-rich soil	EDTA, acetic acid	Cd, Cr, Cu, Ni, Pb, Zn
BCR-701[b]	Lake sediment	BCR sequential extraction	Cd, Cr, Cu, Ni, Pb, Zn

[a] Not all analytes are certified – some may have indicative values only – and so it is advisable to check with the supplier before purchasing a CRM

[b] Although not a soil, this is the only CRM available certified for metals extractable by sequential extraction and so is often used by soil trace metal laboratories

Table 4.6 A selection of ISO methods relevant to heavy metals in soil

Method	Title
ISO 10381–1:2002	Soil quality – Sampling – Part 1: Guidance on the design of sampling programmes
ISO 10381–2:2002	Soil quality – Sampling – Part 2: Guidance on sampling techniques
ISO 10381–3:2001	Soil quality – Sampling – Part 3: Guidance on safety
ISO 10381–4:2003	Soil quality – Sampling – Part 4: Guidance on the procedure for the investigation of natural, near-natural and cultivated sites
ISO 10381–5:2005	Soil quality – Sampling – Part 5: Guidance on the procedure for the investigation of urban and industrial sites with regard to soil contamination
ISO 11047:1998	Soil quality – Determination of Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn – Flame and electrothermal atomic absorption spectrometric methods
ISO 11464:2006	Soil quality – Pretreatment of samples for physico-chemical analysis
ISO 11466:1995	Soil quality – Extraction of trace elements soluble in aqua regia
ISO 14869–1:2001	Soil quality – Dissolution for the determination of total element content – Part 1: Dissolution with hydrofluoric and perchloric acids
ISO 14869–2:2002	Soil quality – Dissolution for the determination of total element content – Part 2: Dissolution by alkaline fusion
ISO 14870:2001	Soil quality – Extraction of trace elements by buffered DTPA solution
ISO 15903:2002	Soil quality – Format for recording soil and site information
ISO 16772:2004	Soil quality – Determination of Hg in aqua regia soil extracts with cold-vapour atomic spectrometry or cold-vapour atomic fluorescence spectrometry
ISO/TS 17924:2007	Soil quality – Assessment of human exposure from ingestion of soil and soil material – Guidance on the application and selection of physiologically based extraction methods for the estimation of the human bioaccessibility/bioavailability of metals in soils
ISO 18512:2007	Soil quality – Guidance on long and short term storage of soil samples
ISO 19730:2008	Soil quality – Extraction of trace elements from soil using ammonium nitrate solution
ISO 20279:2005	Soil quality – Extraction of Tl and determination by electrothermal atomic absorption spectrometry
ISO 20280:2007	Soil quality – Determination of As, Sb and Se in aqua regia soil extracts with electrothermal or hydride generation atomic absorption spectrometry
ISO 22036:2008	Soil quality – Determination of trace elements in extracts of soil by inductively coupled plasma atomic emission spectrometry (ICP-AES)
ISO 23909:2008	Soil quality – Preparation of laboratory samples from larger samples
ISO 25177:2008	Soil quality – Field soil description

Finally, laboratories conducting commercial soil analysis for regulatory, legislative or forensic purposes may seek accreditation of their analytical procedures from relevant national bodies e.g. the United Kingdom Accreditation Service (UKAS) for British laboratories. UKAS accredited laboratories must demonstrate high levels of analytical traceability and pass rigorous inspection visits by teams of expert assessors.

Table 4.7 Key characteristics of some atomic spectrometry techniques

Technique	Single or multi-element analysis	Sample form	Portable version available	Relative cost to purchase
INAA	Multi	Any	No	–
XRF	Multi	Solid	Yes	High (for a lab based instrument)
LIBS	Multi	Solid	Yes	–
LA-ICP-MS	Multi	Solid	No	Very high
FAAS	Single	Liquid	No	Low
ETAAS	Single	Liquid	No	Moderate
ICP-AES	Multi	Liquid	No	Moderate
ICP-MS[a]	Multi	Liquid	No	High
ICP-MS[b]	Multi	Liquid	No	Very high

[a] Quadrupole mass analyser
[b] Magnetic sector mass analyser

4.10 Concluding Comments

Although a variety of other approaches are used, the determination of heavy metals in soils is still performed chiefly by spectrometry, with different techniques used, depending on their capabilities (Table 4.7). As was predicted a decade ago [195] multi-element methods based on ICP-AES and ICP-MS are now predominant, although FAAS (often with analyte preconcentration) is still widely used, as is ETAAS for specific applications. Techniques formerly the exclusive provenance of research laboratories e.g. LA-ICP-MS and LIBS, are now finding wider application. Speciation analysis remains of interest, with applications of direct methods for the determination and speciation of heavy metals in soils increasing. To keep up with current developments in spectroscopic methods for measurement of heavy metals in soils, the reader is directed to the Atomic Spectrometry Update on Environmental Analysis, published annually in the *Journal of Analytical Atomic Spectrometry* e.g. see [23, 24].

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Chapter 5
Effects of Heavy Metals and Metalloids on Soil Organisms

Mark E. Hodson

Abstract At the molecular level metals and metalloids cause organisms to produce chemicals such as metallothioneins to bind metals and reduce their toxicity and/or chemicals such as heat shock proteins that repair any damage done. On a cellular scale metal-rich P and S "granules" are often produced, particularly in cells that line the digestive organs, which concentrate and detoxify the contaminants. Granules either accumulate or are excreted. If metals accumulate, the location of accumulation varies between species though is often either in an organ analogous to the liver or at sites which are shed during moulting. Countless studies document effects on weight, reproduction and mortality of organisms. Variation in results are due to a complex combination of contaminant bioavailability, uptake pathways, exposure duration and soil properties. At the field scale metal and metalloid contaminants usually result in either population decline due to toxic effects/loss of prey or population growth due to the removal of predators or competition. Populations of different species are affected in different ways, modifying community structure and ecosystems. Organisms found in contaminated soils in which naïve introduced individuals of the same species can not survive exhibit either acclimation/tolerance (reversible changes in physiology) or adaptation/resistance (a change in genetic structure). A large number of toxicity tests exist to investigate and demonstrate the impact of metals and metalloids on organisms. Omic technologies offer great potential to help develop our level of understanding of these effects but are not yet a mature technology.

Keywords Cells • Organisms • Populations • Communities • Ecosystems • Evolution • Tolerance • Adaptation • Ecotoxicology • Testing

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5.1 Introduction and Scope of Chapter

Pollutants may affect organisms at a number of levels. In this chapter effects are discussed at the molecular, physiological, population and ecosystem level. The impact that metals have on evolution of organisms together with methods to determine effects of contaminants in the field, i.e. toxicity tests, are also reviewed. The chapter focuses on soil invertebrates, but soil microbiota are also covered. To have an effect on an organism, a metal must first be available to it. Metal availability is discussed in Chap. 6. Details of specific metal chemistry and behaviour are given in Chap. 3 and Part II of this volume.

5.2 Effects of Metals and Metalloids on the Molecular Scale

When metals interact with organisms they may generate a variety of effects. Two common molecular level effects, well documented in the literature, are the production of chemicals to bind with the metals to reduce their bioavailability and thus their toxicity and the production of chemicals to repair damage done to proteins by bioavailable metals. Metallothioneins are examples of the first group of these chemicals and heat shock proteins (HSP) of the second.

Metallothioneins are proteins that have a high binding capacity for metals (4–12 atoms per molecule) which are bound via thiolate bonds. The dominant amino acid in the protein is cysteine but metallothioneins from some species also contain histidines. Metallothioneins typically have a molecular weight of $<$10,000 amu [59, 70]. One role of metallothioneins is thought to be the binding of metals to prevent metal-induced damage to organisms. Studies have found metallothioneins produced by bacteria in response to Cd and Zn [21], by earthworms [23, 140, 143] and nematodes [89, 143, 147] in response to Cd, Cu and Zn, by snails in response to Cd [28, 37–39] and Springtails in response to Cd [60, 76, 148]. Metallothionein-like proteins have also been reported for isopods produced in response to Zn [162]. Metallothionein proteins appear to be concentrated in the intestine or hind-gut of organisms e.g. [82, 144, 162]. Despite the ability of metallothioneins to bind so many different metals, they are mainly produced in response to Cd with lower levels of production occurring in response to other metals. It has been speculated that as well as acting as a detoxifying agent they are also involved in homeostatic regulation, the scavenging of free radicals, control of intracellular redox potential and sulphur metabolism [59].

Heat shock proteins are less well studied in soil organisms than metallothioneins but have been recorded as being produced following metal-induced stress in nematodes in response to Ag, Cr, Cu, Cd, Pb, Hg, Zn and Mn [128], in earthworms in response to Cd, Cu, Pb and Zn [66] and in isopods in response to Pb [80]. Heat shock proteins are within-cell chaperones for other proteins, they assist in the repair of cell damage and protect other proteins from disruption.

5.3 Effects on the Cellular to Organism Scale

Above the biochemical level, effects of metals on organisms may be considered in terms of their effects on organism physiology, that is the functioning of the organism and the processes and functions of all or part of an organism [157]. Effects can be seen from the cellular to organism level.

A well documented effect of metals and metalloids on organisms is the formation of metal-rich "granules" within cells, in particular cells that line the digestive organs as these are often the first cells that metals reach following digestion of metal-rich material. These micron-scale granules have been divided into three classes [67, 68, 157]. Type A granules are Ca- and P-rich granules, typically with a concentric structure, that can contain metals such as Pb and Zn e.g. [32]. Type B granules are S-rich heterogeneous granules that contain metals with a high affinity for S such as Cd and Cu e.g. [32, 69, 97] the granules probably contain cysteine residues derived from metallothioneins. Type C granules contain Fe, probably in the form of hemosiderin, a breakdown product of ferritin. Type A granules have also been called chloragosomes [120] and Type B granules cadmosomes [97]. Type A granules have been reported in earthworms, snails, collembolans, nematodes, millipedes and spiders, Type B in earthworms, isopods and spiders [67, 81]. Whilst the different granule types are common amongst different organisms, the fate of the granules, once formed can differ. For example isopods accumulate Type B and C granules in their hepatopancreas over their lifetimes and as such develop high metal body loads when living on metal contaminated soils. In contrast spiders accumulate these granules in digestive cells which break down at the end of each digestive cycle with the granules being excreted in the spiders faeces so that metal concentrations remain relatively low [67]. As far as the author is aware Type A and Type B granules have not been reported in soil micro-organisms but accumulation of metals as precipitates, often associated with P have been reported for bacteria, algae and fungi and it is possible that further investigation would reveal these to be Type A granules [50, 70].

On a larger scale many studies have investigated effects of metals on organisms in terms of accumulation of metals in particular organs or body regions. In micro-organisms such as bacteria and fungi, metals have been shown to accumulate on cell surfaces as precipitates and also to be complexed to extracellular polysaccharides that coat cell surfaces e.g. [50, 70, 122]. In isopods metals preferentially accumulate in the hepatopancreas, an organ of the digestive tract analogous to a combined liver and pancreas. In some species these metals are transferred to the cuticle for excretion during moulting [69, 81]. In earthworms the site of preferential metal accumulation is the posterior alimentary canal and more specifically the chloragogenous tissue, which surrounds the digestive tract and has a similar function to a liver e.g. [7, 96, 98]. In millipedes the main site of metal accumulation is the midgut for Cd and the cuticle for Zn, for Collembolans it is the midgut epithelium which is also excreted during moulting [81]. Using the chemical digestion and separation methodology of Wallace et al. [160] accumulation of metals in the “C fraction” (considered to be biologically active, including the cytosol, metallothioneins, heat shock proteins), “D fraction” (metal rich granules) and “E fraction” (metabolically inert material such as cell tissue fragments and membranes) of earthworms [3, 5, 7, 157, 158] and snails [52] have also been considered. Typically Pb, Zn, and Ni accumulate in the D and E fractions whilst Cd and Cu accumulate in the C fraction.

On the scale of the whole organism there are countless studies that report the effect of metals on soil organisms in terms of accumulation of metals expressed as bulk tissue concentrations and effects on mortality, reproduction, growth rate and avoidance e.g. [8, 15, 19, 36, 53, 61, 68, 92, 101, 104, 117, 119, 134]. In all cases when organisms are exposed to too high a concentration of metal the life cycle stage under investigation is detrimentally affected. The concentration of metal at which this occurs is a complex combination of the bioavailability of the metal, the exposure pathway, duration of exposure and soil chemical and physical properties.

5.4 Effects on the Population, Community and Ecosystem Scale

Perhaps more important than the effects of metals on individual organisms is their effects on populations of soil organisms and indeed on soil ecosystems themselves. Broadly, populations of species may respond in one of two ways [157]: (i) populations may decline, sometimes down to zero, due to toxic effects or a loss of prey though they may survive at lower levels than at uncontaminated sites due to a loss of predators e.g. [15, 16, 18, 20, 31, 49, 57, 103, 104, 113, 115, 133, 134, 155], (ii) populations may increase due to the removal of predators/competitors e.g. [53, 58, 95, 103, 125, 142]. Populations of different species will be affected differently and thus relative numbers of different species will change; so soil organism communities are also affected by metals. Changes in soil (or any) communities can be viewed either structurally, that is simply by determining changes in numbers of species and size of population, or functionally, for example determining whether the C or N cycle has been impacted. Although many studies determine population and community changes at contaminated sites, the majority simply infer that the contaminants are “to blame”. It is vital to remember that correlation does not equal causation.

There is a vast tract of ecological literature concerned with documenting population and community changes and the interested reader is referred to such standard texts as [14, 84, 149]. A large number of different indices and parameters have been used to quantify the abundance and diversity of soil organisms at contaminated sites, for example Simpson’s diversity index which takes into account both numbers of species and abundance or biomass of individual species and Shannon’s diversity index which is similar to Simpson’s, but is weighted towards rarer species (see references above and also [55, 104, 113, 134]. Multivariate statistical methods such as classification and ordination using for example canonical correspondence analysis (CCA), and redundancy analysis (RDA) have also been used to determine community changes e.g. [95, 103, 104]. Functional approaches to investigating community and ecological changes have focussed on measuring soil respiration rates, nitrogen mineralisation rates and organic matter decomposition rates e.g. [141, 142, 155]; many examples are given in the reviews of [12, 51, 94, 151].

Typically studies on metal contaminated sites have recorded decreases in species numbers and population sizes of soil organisms with increasing metal concentrations (Table 5.1).

5.5 Evolutionary Effects? Acclimation and Adaptation

Metals exert an environmental stress on organisms. The presence of organisms in metal-rich soils suggests that it is possible for those organisms to develop mechanisms by which they can tolerate or resist the effects of metal-induced stress. Tolerance or resistance to the direct effects of stress may be acquired either through reversible changes in an organisms' physiology (termed acclimation; this is reliant on plasticity within the organisms' phenotype and leads to changes in the response of an organism known as tolerance) or through a variation in the genetic structure of the organism (termed adaptation and which leads to changes in an organisms response known as resistance). Hoffman and Parsons [65] suggest that the response of organisms following exposure to environmental stress may follow the temporal sequence of: detection, behavioural response, hormone change, physiological change and genetic change. The first four of these (behavioural response to physiological change) represent acclimation whilst genetic change is adaptation. There are many examples of soil organisms exhibiting acclimation in the scientific literature, but relatively few demonstrating adaptation. Lack of adaptation may be due to phenotypic plasticity, continuous recruitment of "normal" individuals from uncontaminated areas and/or heterogeneity of metal concentrations in the soil [99]. To demonstrate adaptation, five lines of evidence are required [22, 116]. In several studies focussing on the presence of organisms at metal contaminated sites no differences in the metal tolerance of exposed and naïve (i.e. not exposed to above background concentration of contaminant) populations have been found, e.g. [11, 13]. In studies where the concentrations of metals at the contaminated site are sufficiently high to kill naïve populations, the most significant missing piece of evidence to demonstrate adaptation is usually studies demonstrating the heritability of tolerance once the stress source (i.e. the metals) has been removed e.g. in the studies showing differences in survival, growth and reproduction of the earthworms *Dendrodrilus rubidus* [8], *Dendrobaena octaedra* [17] and *Lumbricus rubellus* [135], differences in genes in the earthworm *Lumbricus rubellus* [4] and differences in physiological responses of the isopods *Oniscuc asellus* and *Porcelluio scaber* [9]. In laboratory studies designed to investigate adaptation, e.g. for the standard ecotoxicological test earthworm *Eisenia fetida* [121, 136], whilst offspring of metal exposed earthworms have demonstrated tolerance relative to naïve populations the metal stress was always present during the culturing of the tolerant offspring. In contrast to the above studies,

Table 5.1 Examples of studies recording changes in populations and communities of soil organisms in soils contaminated with metals and metalloids

Metal source	Metals	Organisms/process	Impact of increasing metal concentration	Reference
Sewage sludge	Cd	Bacteria	Loss of gram positive bacteria but no change in Shannon's diversity index	[13]
Brass mill	Cu, Zn, Pb	Enchytraeids	Reduced number of species and individuals	[15]
		Earthworms	Decreased density and biomass, reduced ratio of juveniles to adults	[18]
		Collembola	Reduction in total numbers, change in dominant species	[16]
Secondary Pb smelter	Pb, As, Cd, Cu	Earthworms, bacteria, nematodes	Decreased numbers, relative numbers change	[20]
Metal-rich sewage sludge	Cd, Cu and Zn	*Rhizobium leguminosarum* biovar *trifolii*	Reduced numbers in response to Zn but not to Cd or Cu	[31]
Cu fungicide	Cu	Bacteria	Increase ratio of gram negative to gram positive bacteria; changes in community structure but no change in diversity levels	[42]
Cu-Ni smelter	Cu, Ni	Bacteria, respiration	Reduced bacterial numbers, changes in proportions of different functional groups, reduced respiration	[49]
Pb and Zn smelter	Cd, Pb, Zn	Myriapods, isopods	Absent at most contaminated sites	[53]
Pb and Zn smelter	Cd, Pb, Zn	Collembolans	Largest saprophagous organisms at most contaminated sites	
Geogenic site	Pb	Microarthropods	Decreased number of species, abundance of individuals unaffected. Prostigmata dominate, *Isotoma olivacea* Tullberg (a collembolan) and Nanorchestes sp. (a mite) favoured at highly contaminated sites	[57]

Cu-Ni smelter	Cu, Ni	Enchytraeids, nematodes, tardigrades, rotifers	Generally decreased numbers. Collembolans *Folsomia fimetarioides*, *F. dovrensis* and *Isotoma notabilis* increased in number.	[58]
Shooting range	Pb, Sb	Collembola, Protura, Diplura	Increased numbers	[95]
		Symphyla	Decreased numbers	
		Overall	Number and abundance of taxa unaffected	
Zn smelter waste	Zn	Macrofauna	Density of earthworms reduced, increased density of some Coleoptera and arachanids possible due to increased litter layer thickness	[103]
Zn smelter	Zn	Earthworms	Reduced density and species numbers	[104]
Industrial effluent	As, Hg, Pb, Zn	Bacteria	Reduced biomass, asymbiotic nitrogen-fixers and heterothrophs particularly sensitive	[110]
Agrochemicals	Cu	Microarthropods	Decreased species diversity	[113]
Urbanisation	Cd, Cu, Pb, Zn	Earthworms	Decreased biomass	[115]
Geogenic	Cd, Pb, Zn	Microarthropods, organic matter	Increased density, more organic matter in mineral horizons. Collembolan densities unaffected but species composition changes.	[125]
Zn smelter	Zn (Cu, Cd, Pb)	Earthworms	Reductions in numbers of species and individuals	[133, 134]
Zn smelter	Cd, Cu, Pb, Zn	Arthropods, leaf litter	Decrease in abundance of all taxa but an increase in the relative proportion of Collembola. Reduced litter decomposition	[141, 142]
Smelters and pigment manufacture	Cd, Cu, Ni, Pb, Zn	Respiration, ATP content	Decreased respiration and ATP content	[155]

adaptation to metals in unexposed offspring have been demonstrated for the earthworms *Lumbricus rubellus* and As [87] and *Dendrobaena octaedra* and Cd [124], the isopod *Porcellio scaber* and Cd and Cu [44], and the springtails *Orchesella cincta* and Cd [117–119, 148] and *Onychiurus armatus* (Tullb.) and *Isotoma notabilis* Schäffer and Cu and Zn [150]. The phenomenon of the acquisition of mobile genetic elements via horizontal gene transfer makes it difficult to differentiate between acclimation and adaptation in soil micro-organisms. Several studies identify metal-tolerant bacteria e.g. [13, 27, 42, 43, 70, 111, 114, 122] with metal tolerance either being associated with specific plasmids or chromosomes. It appears however, that metal-tolerance may be present in many bacteria, even in the absence of metals.

5.6 Methods for Quantifying Effects

One method of determining the impact of metals on soil organisms is to expose the organisms to a particular metal or metals under controlled conditions and observe a specific response. A wide range of standardised, internationally accepted toxicity tests exist which do just this e.g. [10, 71–75, 106–109]. Typically such tests were developed for the testing of agricultural products but are now routinely used to assess the toxicity of metals. The advantages of such tests lie mainly in the controlled conditions that laboratory work permits. Often an unambiguous response of the test organism to a particular metal can be determined. The major disadvantage or problem with such tests lies in relating controlled laboratory results to more variable field conditions e.g. [6, 40, 41, 132, 138]. The problems include: relating the effects of a single contaminant in the laboratory to effects in contaminated field soil where multiple contaminants are present, relating the effects on a single species in the laboratory to an ecosystem in the field, the differing bioavailabilities of contaminants between laboratory and field soils (see Chap. 6, [64]) and, potential acclimation or adaptation of field exposed populations (see above). None-the-less, toxicity tests represent a useful tool for determining the effect of metals on soil organisms and can be used to determine the effects of mixtures of contaminants on organisms. Also many studies have sought to modify laboratory tests so that they are applicable in the field. In most cases this means that, rather than determining the concentration of a chemical which causes 50% mortality (LC50), a reduction of 50% in growth or reproduction (EC50s) or the highest concentrations at which no effect on these parameters are observed (no observed effect concentrations or NOECs) the response of the test organism exposed to the contaminated soil is compared to the response in a control soil. Alternatively serial dilutions of the test soil or an extract from that soil are used to determine LC50, EC50 or NOEC values. By modifying such tests for use with field soils, the clarity of identifying a toxic effect of a specific contaminant is lost, however the tests allow the effects of the soil (and the metals within it) to be assessed in a holistic fashion. Depending on the answers sought by the investigator this is either an advantage or disadvantage.

5.6.1 Application of Toxicity Tests to Field Soils

A range of criteria have been identified that toxicity tests should satisfy [88]; these fall under the categories of practical arguments (e.g. level of technical expertise required to carry out the test), acceptability of tests (dealing with standardization, reproducibility, statistical validity etc.) and ecological significance (concerned with test sensitivity, ecological realism and biological validity) [152]. Four toxicity tests are described below which have been successfully applied to contaminated soils and which also have agreed international standards associated with them [123]. Additional tests that have been applied to field contaminated soils include those for which no international standards exist or for which international standards exist but which don't appear to be sensitive or lack a clear response to metals. Examples of the former are bait lamina test strips which are used to monitor the feeding activity of soil organisms e.g. [2, 62] and the neutral red bioassay in which the integrity of lysosome membranes are assessed e.g. [127, 146, 154]. An example of the latter is the C mineralisation test (OECD [107]) in which the rate of CO_2 production is monitored following addition of a carbon source to the test soil e.g. [1, 85, 100]. A range of molecular based techniques, and particularly gene-based biomarker studies and the "-omic" technologies have great potential for assessing the impact of metals on organisms. Details of these methods are beyond the scope of this chapter but can be obtained from articles such as [24, 25, 90, 112]. The challenge for these technologies lies in relating biochemical/genetic responses to a meaningful effect at organism to ecosystem level [26, 54, 105, 145, 157].

5.6.1.1 Earthworm Tests

There are several well established earthworm toxicity tests e.g. [71, 73, 106, 109]. The earthworm *Eisenia fetida* is exposed to increasing concentrations of a chemical under controlled soil moisture and temperature conditions and impacts on mortality and reproduction are assessed. Applications of these tests to field soils involve comparing the response of the earthworm to the contaminated soil to that of a control, uncontaminated soil which is otherwise as close as possible in terms of its properties to the test soil e.g. [8, 102, 132]. Whilst *Eisenia fetida* is not typically found at contaminated sites (at least not in temperate climates where it lives primarily in organic-rich material such as compost heaps, manure etc.) and contaminant sensitivities vary between earthworm species e.g. [46, 86, 137], the use of *E. fetida* as a standard organism has continued due to its ease of use in the laboratory and the large amount of existing data on single contaminant toxicity to this species. None the less a further modification of the standard laboratory tests has been the use of more environmentally relevant species e.g. [86, 139].

5.6.1.2 Springtail Reproduction

Like earthworms, springtails are a key component of the soil fauna. An ISO protocol exists [75] in which the springtail *Folsomia candida* is exposed to a chemical at increasing concentrations and effects on growth and reproduction are assessed. For application to contaminated field soils growth and reproduction are compared to an uncontaminated control soil e.g. [48, 126, 130, 131] or the contaminated soil is mixed with uncontaminated soil in order to create a dilution series for the calculation of toxicity parameters e.g. [33]. The standard test duration is 4 weeks, but the test has been successfully modified to allow assessment of growth and reproduction (and mortality) at more frequent intervals [47].

5.6.1.3 Nitrogen Mineralisation

This test is not species-specific but rather assesses the rate of nitrate production as a general measure of soil health. In the standardised laboratory test [72, 108] field moist soils are amended with the chemical of interest and after 0, 7, 14 and 28 days the amount of nitrate extractable by a weak ionic solvent such as 0.01 M KCl or $CuSO_4$ is determined. Rate of nitrate production is compared to that in a control. In its application to field-contaminated sites, rate of nitrate production is compared between soils e.g. [34, 156]. Despite its recommendation in a recent English Environment Agency review as a useful test for contaminated soils [123], the majority of studies applying this test to the effects of metals on soil organisms have been carried out with metal-amended soils e.g. [29, 45] and the test has been shown to produce results that have no good correlation between mineralisation rate and metal concentrations e.g. [161].

5.6.1.4 Microtox™

This test was originally developed for assessing water quality and as such several standardised protocols exist e.g. [10, 74]. In this test a luminescent marine bacteria (Vibrio fischeri NRRL B-11177) is exposed to a solution or solutions. In laboratory testing of single chemicals the concentration of that chemical required to reduce the luminescence of the bacteria by 50% is the parameter determined. For assessing contaminated environments either the luminescence of exposed bacteria is compared to a control or dilutions are used and the dilution that results in a 50% reduction in luminescence is determined e.g. [35, 79, 129]. Clearly as a marine organism *Vibrio fischeri* is not ideal for assessing the impacts of contaminated soil on soil organisms. Additionally, because a solution is required as the test media results are biased by the extraction method used to obtain this from the soil. However, the method is relatively rapid, reproducible and gives a good indication of whether metals (and other contaminants in soils) will have a detrimental effect or not on soil organisms.

5.6.2 Dealing with Mixtures of Metals or Metalloids

Perhaps the most useful role for toxicity tests in determining the effects of metals on soil organisms lies in their ability to determine the effects of mixtures. Whilst the majority of toxicity tests are performed on single contaminants, most contaminated sites contain many different potential sources of toxicity. It is generally assumed that toxic effects will be additive, that is the toxicity of a combination of two contaminants will be equal to that of the sum of the toxicities of the individual contaminants. However synergistic (or potentiation) effects may occur where the combined toxicity of the two contaminants is either greater or less than the sum of the individual toxicities e.g. Cd and Zn and the springtail *Folsomia candida* [153], Cd, Cu and Pb and soil enzyme activity [30] and Cu and Zn and nematodes [83]. In broad terms reasons for potentiation may be either one contaminant inhibiting the detoxification mechanism for another or one contaminant stimulating production of chemicals which react with the second contaminant to have a toxic effect. Readers are directed to e.g. [63, 93, 157] for more detail. In recent years much progress has been made in understanding the effects of mixtures of contaminants (including metals) on soil organisms through the use of toxicity tests and the application of modelling techniques e.g. [56, 77, 78, 91].

5.7 Concluding Comments

Metals and metalloids impact on soil organisms in a variety of ways. Exposure to metals and metalloids stimulate the production of chemicals to protect organisms from damage (metallothioneins) or to repair damage once it occurs (heat shock proteins). Within cells changes occur related to detoxification of metals (production of granules) and at a larger scale different parts of organisms accumulate metals. The metals, when present at high enough concentrations, will impact on all key life-cycle stages of soil organisms such as growth, reproduction and life span. Metals can act as evolutionary drivers. This in turn will impact on population and community structures of soil organisms and the soil ecosystem as a whole. Laboratory methods exist for determining the effects of chemicals on soil organisms but relevance of these to the field is confounded by factors such as bioavailability and interference with other contaminants. Progress is being made in adopting these laboratory test methods for field testing but in doing so the resolution of the tests in terms of identifying key contaminants responsible for specific responses is lost. Particular progress is being made in modelling the effects of mixtures of contaminants on soil organisms. The “omic” technologies offer great potential for determining effects of contaminants on soil organisms but much more work is required to relate biochemical responses to those at organism or community level.

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Chapter 6
Soil-Plant Relationships of Heavy Metals and Metalloids

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Abstract Nutrient uptake by plants is essential for their development and for the passage of minerals into the food chain, but it also faces several limitations. Whereas soil physicochemical characteristics impose limiting factors on element availability for plants, excess of non-essential metals and metalloids pose a threat for plant health and the environment. To improve nutrient uptake, the plant possesses several mechanisms to explore the soil for minerals such as root development, but the symbiosis with microorganisms clearly improves the ability of plants to overcome these limitations. After metal uptake by the plants, plants make use of different strategies to maintain the metal homeostasis and to limit the metal-induced cellular damage. Also in the research on metal phytotoxicity, microorganisms are shown to be important players in the protection of the plant to excess metal exposure.

Keywords Metal uptake • Metal homeostasis • Toxicity • Deficiency • Metal tolerance • Plant-associated bacteria • Mycorrhiza • Oxidative stress • Anti-oxidative defence

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6.1 Introduction

As important suppliers of dietary minerals for humans and animals, plants form a bridge between the soil elemental composition and the food chain. Consequently, plant nutrient uptake is essential for its central role in element cycling, but also for the growth and development of plants. Soil physicochemical characteristics often impose limiting factors on the bioavailability of elements and mineral deficiencies are often experienced in crop production. Moreover, many regions in the world are unsuitable for growing crops due to contamination with potentially toxic elements such as metals and metalloids. The uptake and transport mechanisms crucial for essential elements also form an entrance for non-essential elements that pose a threat to the plant's fitness and the food chain [166].

In this chapter the focus is on (1) nutritional exploration of the soil by plants and their associated micro-organisms (2) protection by these micro-organisms against excess amounts of (non-)essential elements and (3) the ability of plant cells to cope with metal stress.

6.2 The Soil-Plant Interface: Microbial and Molecular Interactions Define Plant Elemental Uptake

6.2.1 Molecular Interactions Defining Plant Elemental Uptake

Plants obtain essential metals and metalloids (micronutrients) primarily from the soil, so appropriate systems must be in place to ensure adequate uptake of these elements (B, Cu, Fe, Mn, Mo, Ni, and Zn). These elements are heterogeneously distributed in the soil, so exploration of the soil by the root system is the first important parameter to optimize nutrient uptake. Whereas root growth responses to macronutrient deficiencies, especially phosphorus (P) and nitrogen (N), have been intensively studied, responses to micronutrient deficiencies largely remain to be determined. Responses to nutrient deprivation often result in an increased surface area of the root system in a localized part of the soil. Some reports of root developmental responses to Fe deficiency show a stimulatory effect on root hair production in dicotyledonous and non-grass monocotyledonous species [149, 188]. Some plant species that are adapted to growth on very nutrient-poor soils are able to develop cluster roots, which are bottlebrush-like in shape due to dense formation of short lateral roots on the primary root axis. These structures occur in a subset of species of the *Casuarinaceae*, *Leguminosae* and *Proteaceae* families [195] and have been described under iron (Fe)-deficiency [9, 116, 139, 189].

Another parameter determining plant metal uptake is the bioavailability of the elements, which is defined by the chemical properties of the metal cations and by the physicochemical characteristics of the soil [161]. Metals in soil are often adsorbed to soil particles or present in an insoluble form (for example Fe hydroxides in alkaline soil types [134, 159]). Plant roots can interact with the rhizosphere to increase the bioavailability of minerals and turn them into a form appropriate for uptake by transporters. Roots extrude protons via plasma membrane H^+-ATPases to acidify the rhizosphere. This creates a large membrane potential (-100 to -250 mV), which is the main driving force for cation uptake [160]. Furthermore, the protons can participate in cation exchange, releasing divalent metal ions that are tightly bound to soil particles, and the resulting acidification of the rhizosphere can release metals from their hydroxides [159, 160].

Regarding Fe-uptake, plants have been divided into two groups according to the strategy they use in the interaction with the rhizosphere to solubilize Fe: (1) reduction based or (2) production of chelating molecules. Non-graminaceous plant transport systems take up Fe in the form of Fe^{2+}, whereas Fe in the soil is mostly present as Fe^{3+}. These plants have a reduction-based system in which Fe^{3+} is reduced to Fe^{2+} by the ferric chelate reductase FRO2 [180]. Ferrous ions (Fe^{2+}) are subsequently translocated into the cytoplasm by the high-affinity transporter IRT1 [172]. Graminaceous plants, on the other hand, use a chelation-based strategy. Roots actively secrete compounds, known as phytosiderophores that can function as metal chelators in the soil. Phytosiderophores belong to the mugineic acid family (MAs) and expression of the genes involved in MA biosynthesis is upregulated under Fe-deficiency [159]. Maize roots take up MA-Fe^{3+} complexes through a specific transporter named YS1 [50]. Other species take up the metal-chelator complexes by Yellow stripe-like (YSL) transporter proteins. In barley, phytosiderophores can also assist in the uptake of zinc (Zn) [217] but a role for phytosiderophores in copper (Cu) uptake has not been revealed. The categorisation in graminaceous and non-graminaceous plants regarding reduction-based or chelation-based uptake strategy is not so clear since rice plants have been shown to take up not only Fe^{3+}-chelates, but also Fe^{2+} via OsIRT1 and OsIRT2 transporters (orthologues to Arabidopsis IRT transporters) [91]. There may be an evolutionary aspect to this as rice has been grown and selected on paddy soils where Fe^{2+} is abundant.

After uptake, minerals can migrate into the root apoplastic space, but the impermeable Casparian strip in the endodermal cell layer ultimately blocks this route. Here metals have to be actively transported across the plasmamembrane into the symplast. Ferrous ions (Fe^{2+}) and Cu^+ (after reduction, both by FRO2) are taken up by their respective transporters IRT1 and COPT1 [172]. However, Cu may also enter the plant as Cu^{2+} via a member of the ZIP (ZRT, IRT-related protein) family, a transporter family known to preferentially transport divalent cations. Zinc (Zn^{2+}) is also believed to be transported by ZIP transporters or by the Fe transporter IRT, which can also transport divalent metals other than Fe^{2+} [159].

Metal uptake systems are highly regulated at transcriptional and posttranscriptional levels. Copper is transported as Cu^+ by the COPT1 transporter and COPT1 expression is upregulated under Cu-deficiency [186]. Also ZIP2 and ZIP4 are upregulated by Cu-deficiency, but their functional role as Cu^{2+} transporters remains to be established [159]. IRT1 and FRO2 are co-ordinately regulated at the transcriptional and posttranscriptional level. FRO2 and IRT1 are induced together under Fe-deficiency and repressed under sufficient Fe-supply [45]. In transgenic plants that overexpress IRT1, increased mRNA accumulation was only translated to increased IRT1 protein in Fe-deficient plants, suggesting posttranscriptional control [44]. Protein levels of IRT1 are tightly controlled via ubiquitination at lysine residues, which leads to proteasome-mediated degradation [101].

High affinity transport systems are indispensable for plants to acquire essential micronutrients, but unspecific metal uptake from the soil seems unavoidable under metal-excess as transporters for essential nutrients also take up non-essential elements. Examples are the metalloid arsenic (As) and the heavy metal cadmium (Cd), which have no demonstrated biological function in higher plants, and for which plants are not expected to have specific uptake mechanisms. Instead, the uptake of Cd seems to occur primarily via calcium (Ca^{2+}), Fe^{2+}, manganese (Mn^{2+}) and Zn^{2+} uptake systems [37, 167]. For example, the Fe^{2+} transporter IRT1 contributes significantly to the uptake of Cd [244]. Arsenate [As(V)] is taken up by the high affinity phosphate transporter system and rapidly reduced to arsenite [As(III)] [141]. In reducing environments, As(III) can be taken up by aquaporin nodulin 26-like intrinsic proteins [21, 90] for example the rice OsNIP2;1/Lsi1, which also transports silicon (Si), a beneficial element for rice [125].

6.2.2 Microbial Interactions Defining Plant Elemental Uptake

Nutrient uptake in plants is in no way a monopoly of the plant itself. From the early days that plants started to colonise the terrestrial environment, microorganisms turned out to be essential partners for the colonisation of the land [26]. Their major task was/is the scavenging for essential elements that are scarce, poorly soluble or immobile in the solid substrates. Both fungi and prokaryotes provide services to plants in terms of nutrient acquisition and protection against biotic and abiotic stresses. This interdependency of plants and microorganisms was shaped by evolution, new symbioses arose in particular plant families – e.g. N-fixing Rhizobia in legumes –, other symbioses were replaced by new innovations on the same theme, such as the ectomycorrhizal fungi that since the Cretaceous replaced the arbuscular mycorrhizal fungi in some woody plant lineages. The evolutionary persistence and ubiquity of the plant-microbe interactions illustrates the positive cost-benefit balance and the synergistic nature of the interactions.

6.2.2.1 The Mycorrhizal Symbiosis

Amongst the plant-microbe interactions, the mycorrhizal symbiosis is the most widespread intimate interaction between plants and fungi. Between 80% and 90% of all seed plant species harbour fungi in their roots, forming structures known as mycorrhizas. Mycorrhizas are a functional part of plant roots where the fungal hyphae of the external mycelia might be considered as a very fine extension of the absorption roots that provides a cost-effective increase of the absorptive interface between roots and soil [211]. Most mycorrhizal fungi are strict biotrophs, they are morphologically and metabolically very well equipped for mobilising, assimilating and transporting plant nutrients, including essential metals.

Over evolutionary times, different mycorrhizal types and many different fungal species have evolved, showing broad functional diversity and adaptation towards different soil conditions and (or) host plants. And although the functionality of only a limited number of these mycorrhizal interactions has been studied in detail, there is consensus that host plants in a greater or lesser extent experience positive nutritional effects. In general, the nutritional benefit for a host plant seems to be greatest in nutrient poor soils, a condition which is also characteristic for most metal-contaminated soils [140]. Nevertheless, plants differ greatly in their dependence on mycorrhizal fungi, a major aspect being the size and architecture of their root system. Roots with a thick cortex and exodermis suberisation make a fungal symbiont essential, whereas extensive much-branched root systems with very fine elongated fine roots can make the fungal symbioses more futile [26]. Amongst mycorrhizal fungi the efficiency of nutrient uptake and transfer to a host varies significantly both at the intra- and interspecific level [152]. This means that not all fungi are equally effective in plant growth promotion. Mycorrhizal fungi have high nutritional needs themselves and keep significant amounts of assimilated nutrients for their own metabolism and structures. The nutrition of the fungi themselves may also depend on interactions with microbes associated with the hyphae (the mycorrhizosphere) [73, 157]. Recent studies indicate the presence of specific endocellular bacteria in arbuscular mycorrhizal fungi [7], endosymbionts that may have a role in fungal nutrition.

The key role of mycorrhizal fungi in P and N nutrition in plants has been demonstrated in many investigations. Both arbuscular and ectomycorrhizal fungi possess an elaborate set of transporter genes for uptake of a whole range of nutrient sources present in soil solution [135, 136]. There is increasing evidence that both symbiotic partners affect the specific transporter gene or protein expression of each other [80]. Although most mycorrhiza research focuses on the improved macronutrient acquisition in plants, the contribution of mycorrhizal fungi in mobilisation, uptake and transfer of micronutrients has been recognised as well [28]. Weathering of minerals through ectomycorrhizal fungi has been observed *in situ* [24, 86] and is supposed to improve cation uptake in fungi and host plants. Under experimental conditions deficiencies of essential metals in plants can be overcome through inoculation with specific mycorrhizal fungi [105].

6.2.2.2 Plant-Bacteria Partnerships

Beside mycorrhizal symbiosis, plant-associated bacteria can also enhance biomass production and tolerance of plants to trace elements in environments with increased levels of these elements [57, 95, 126, 154, 199, 245]. Some details of chemical communication between plant roots and their associated bacteria in the rhizosphere were covered in a recent review by Bardi et al. [12]. Endophytic bacteria and their interaction with host plants have also attracted attention [15, 88, 89, 216, 251, 252].

Plant-bacterium partnerships provide a wide range of benefits to the host plants, such as promoting plant growth and development. Plant-associated bacteria can promote plant growth and development (1) directly, by (1a) fixating nitrogen, (1b) increasing the supply of unavailable nutrients such as P, Fe and other mineral nutrients, (1c) producing plant growth regulators such as auxins, cytokinins and gibberilines; and (2) indirectly, by preventing the growth or activity of pathogenic organisms through (2a) competition for space and nutrients, (2b) antibiosis, (2c) production of hydrolytic enzymes, (2d) inhibition of pathogen-produced enzymes or toxins and through (2f) induction of plant defence mechanisms [13, 46, 72, 94, 97, 103, 137, 142, 218, 226, 243, 251, 252, 255, 259].

A number of mineral nutrients in soils, including N, P and Fe, can frequently be limiting and thus restricting the growth of terrestrial plants. Requirements for adding these nutrients accounts for the major portion of fossil fuels used in agricultural systems and minimal application of fertilisers is therefore desirable in order to make feedstock production economically and energetically viable and sustainable. For this reason, strategies to minimize fertiliser inputs by promoting uptake of nitrate or ammonium of biological nitrogen fixation, as well as acquisition of P, Fe and other essential elements are of great interest.

For plants, N needs to be in the form of either ammonia or nitrate before it can be utilized. Plant-associated diazotrophic bacteria possess the enzyme nitrogenase, an O_2-sensitive enzyme that catalyzes the reduction of atmospheric nitrogen to ammonia. The plant growth promoting activity of diazotrophic endophytes has been demonstrated in several greenhouse and field studies of different plant species; for example, sugarcane [23], soybean [147] and rice [23, 132].

Beside N, P is a common limiting mineral nutrient affecting terrestrial plant growth. Phosphate solubilising and phosphate mineralizing bacteria are present in the rhizosphere and inside the plant [181, 243]. These bacteria can either solubilise inorganic phosphates by releasing organic acids, such as gluconic acid and 2-ketogluconic acid, or mineralize organic phosphates by secreting extracellular phosphatases [102].

Iron in the aerobic environment is often present in the highly insoluble forms of ferric hydroxides and oxyhydroxides, making it largely unavailable to plants and microorganisms. To acquire sufficient Fe, many bacteria developed strategies to solubilize this element for a more efficient uptake. One of the most commonly found strategies evolved by bacteria is the production of siderophores, low-molecular-mass Fe chelators with high association constants for complexing Fe. These siderophores are able to bind Fe^{3+} and render it available for reduction into the Fe^{2+} form, which is preferred by plants. As described above, also so-called graminaceous plants release siderophores (*e.g.* mugineic acid in barley and avenic acid in oat) to enhance their Fe uptake, but these phytosiderophores typically have a lower affinity for Fe than microbial siderophores. Plant–microbe interactions involved in the regulation of siderophore production and their role in mediating competition for iron in the rhizosphere have been the subject of comprehensive reviews by Crowley et al. [49] and Rajkumar et al. [174]. Furthermore, there is evidence that several plant species can also recognize and take up bacterial Fe^{3+}–siderophore complexes. In this way, bacterial Fe^{3+}–siderophore complexes might facilitate uptake of Fe not only into bacteria, but also into plants and this process is considered as crucial for plant Fe uptake, particularly in calcareous soils [100, 197, 198].

Beside these nutrient mobilizing bacteria, phytohormone (such as auxins, cytokinins and gibberellins) producing bacteria can also be applied to increase nutrient uptake. Phytohormones that are produced by plant-associated bacteria can frequently stimulate growth and indeed have been considered the causal agents for altered plant growth and development [218, 220]. The extended root system that is achieved in this way, can contribute to an increased nutrient uptake.

In addition to the above-mentioned beneficial effects on plant growth, both rhizosphere bacteria and endophytes can also contribute to enhanced trace element availability and uptake [111, 112, 127].

Bacteria possessing metabolic pathways for the synthesis of natural chelators (*e.g.* organic acids and siderophores) can mobilize trace elements. As certain plants make use of microbial chelators to increase their Fe uptake (see above), it has been hypothesized that bacterial Fe chelators can eventually also enhance the uptake of other trace elements by plants [25, 187]. The production of these bacterial chelators is in tight equilibrium with plant activity, meaning that trace element mobilization only takes place when plants are active and by consequence can take up the elements. In this way, the risk for leaching of trace elements to the groundwater is limited.

6.3 Plant-Associated Microorganisms: Protection Against Metal Stress

Apart from the nutritional effect, plant-associated micro-organisms may also protect their host plants against various stress factors, including soil toxic compounds and soil-borne pathogens [111, 112, 127, 191]. Such plant protection might be achieved by acting directly on aggressive factors (mainly pathogens and herbivores) or by enhancing plant responses. Plant protective microbial symbionts determine the ecological success of plants; they modify plant communities and related trophic webs.

6.3.1 Mycorrhizal Fungi

There is no doubt that in many metal-polluted environments, mycorrhizal fungi ameliorate metal stress in their host plants [4, 93, 110, 176]. However, the mechanisms involved are not always clear. Nutritional and hormonal effects often improve plant fitness and thus indirectly stress tolerance. For example, excess metals become more diluted in plant tissues when plants grow better. However, more direct processes that affect the transfer of a metal from soil into the plant may further strengthen such indirect ways of plant protection. In a number of experiments particular mycorrhizal fungi collected from polluted soils, could reduce the accumulation of metals in the shoots of their host plants [3, 110]. Mycorrhizal fungi possess mechanisms involved in metal homeostasis and detoxification of essential and non-essential metals; mechanisms that are probably not different from those present in other eukaryotes [18, 47]. Under high selection pressure these metabolic networks might become more efficient in coping with metal stress and toxicity.

For a long time researchers suggested that soil microorganisms in general exhibit higher tolerance against metal toxicity than plants [83]. They expected little evolutionary adaptation towards elevated tolerance in mycorrhizal fungal communities, as there are sufficient fungi with a high constitutive tolerance that are selected for and thus become dominant in metal-contaminated environments [22, 140].

However, on severely metal contaminated sites, the development of metal tolerant ecotypes in both plant and fungal species has now been demonstrated. For plants, such an influence of soil metal toxicity can easily be demonstrated and there is a lot of evidence for the evolution of adaptive metal tolerance in higher plants. Such evidence is only recently coming up for mycorrhizal fungi. Metal-tolerant arbuscular and ericoid mycorrhizal fungi have been isolated from naturally and anthropogenically polluted sites [6, 117, 138]. The same is true for some higher fungi that form ectomycorrhizas, including *Pisolithus tinctorius* and *P. albus* [67, 96], *Suillus* species [3, 41, 42, 109] and *Cenococcum geophilum* [78]. These fungal ecotypes are mostly adapted towards those specific metals (Al, Ni, Zn, Cu, Cd, . . .) that are in excess in their soil of origin.

Mechanisms involved in metal tolerance in fungi include extracellular processes such as precipitation (e.g. secretion of oxalic acid), chelation and cell-wall binding. Intracellular mechanisms include chelation with organic acids, phytochelatins and other S-compounds, polyphosphates, peptides and transport into intracellular compartments (vacuole) [18]. Some of these mechanisms are constitutively present, whereas others are more activated when excess metals show up in the cytoplasm. Additional antioxidative detoxification systems, which allow the fungus to counteract the accumulation of reactive oxygen species (ROS), directly or indirectly are part of the detoxification response. It is likely that one or more of these mechanisms are modified in the evolution towards adaptive true tolerance in ECM fungi. Homeostasis of essential transition metals such as Cu and Zn requires balanced activities of transporters that mediate import into the cell, distribution to organelles and export from the cell [169]. Transcriptional control is important for the regulation of this cellular homeostasis. Nevertheless, when metals are present in very high concentrations in the environment, the regulatory mechanisms may fail and selection pressure for a more robust homeostasis will increase. In *Suillus* species (Basidiomycete), a strong differential net uptake of Zn is observed among Zn-tolerant and Zn-sensitive ecotypes when the fungi are exposed to elevated Zn [43].

Zinc-tolerant ecotypes accumulate less metal per unit biomass, indicating a metal exclusion system. In sensitive strains, excess Zn is transferred to vacuoles, with little efflux over the plasma membrane. In tolerant strains Zn efflux is much higher and less Zn accumulates in vacuoles.

Metal exclusion mechanisms in mycorrhizal fungi prevent metal stress in fungal cells, but are also of ecological importance for a host plant on metalliferous soil. Tolerant ecotypes are probably better filters than non-tolerant ecotypes because the former more strongly prevent metal transfer to their host. Ashford and Allaway [10] suggest that motile tubular vacuoles are an important vector in the transport chain of mineral nutrients from the site of uptake at hyphal tips to the exchange region in the mycorrhizal root. The observation that Zn-tolerant *Suillus* ecotypes do not store large amounts of Zn into their vacuoles may thus prevent a massive transport of Zn towards the mycorrhizas. Pine seedlings inoculated with metal-tolerant *Suillus* ecotypes in most cases have lower metal concentrations in their needles than seedlings inoculated with sensitive strains [110] confirming that metal-tolerant isolates restrict metal transfer more effectively and thus lead to a more efficient partnership with host plants thriving on metal-polluted soil.

6.3.2 Plant-Associated Bacteria

Under stress conditions including trace element stress, the synthesis of ethylene is increased which negatively affects plant growth [79, 145, 250]. Many plant-associated bacteria are equipped with the enzyme 1-aminocyclopropane-1-carboxylic acid deaminase (ACCD). This enzyme has no known function in bacteria, but antagonizes ethylene release in plants by cleaving the ethylene precursor 1-aminocyclopropane-1-carboxylic acid (ACC). ACCD-producing bacteria therefore can reduce production of stress ethylene and in this way protect plants against trace element toxicity when growing on contaminated soils [77].

For survival in metal-enriched environments, plant-associated bacteria have developed diverse mechanisms to tolerate the uptake of these ions by which they can immobilize or transform the trace elements rendering them inactive. These mechanisms include physical sequestration, exclusion, and complexation or detoxification, etc. Certain efflux-based systems involved in bacterial trace element resistance include post-efflux sequestration of these elements. Extruded trace element ions are prevented from re-entering the cell by precipitation, chelation or by binding to exopolymers [60, 185]. The above-mentioned mechanisms immobilize the trace elements in the rhizosphere and reduce their uptake into the plant root, resulting in a reduced phytotoxicity. For instance, Madhaiyan et al. [127] found that inoculation with *Magnaporthe oryzae* and *Burkholderia* sp. reduces the Ni and Cd uptake in roots and shoots of tomato and also their availability in soil. This effect was attributed to the increased trace element biosorption and bioaccumulation by bacterial strains. Endophytes living in xylem vessels and possessing such systems may contribute to metal detoxification inside their host plants resulting in lowered phytotoxicity and an increased trace element translocation to the above-ground plant parts [123, 251].

Bacteria equipped with the above characteristics are frequently naturally occurring and even abundant on metal contaminated sites [194]. Hyperaccumulator plants, such as *Thlaspi goesingense*, *Alyssum bertolonii* and *Thlaspi caerulescens*, are able to accumulate large amounts of metals and metalloids in their shoots and provide a specific niche for resistant endophytes [15, 88, 89, 124, 143, 144].

Lodewyckx et al. [124] characterized the cultivable Zn- and Cd-resistant endophytes in the Zn hyperaccumulator *T. caerulescens* subsp. *calaminaria*. Interestingly, shoot and root possessed different microbial communities and among shoot endophytes, *Methylobacterium* strains showed to be highly resistant to Zn, Cd, Co and Ni. Likewise, Barzanti et al. [15] isolated and characterized 83 endophytic strains from the Ni hyperaccumulator *A. bertolonii* endemic to the serpentine outcrops of Central Italy. Most of the isolates showed coresistance to more than one trace element and coresistance to Ni, Cr, Zn and Cu was the most frequent, whereas coresistance to Ni and Co was found less frequently. Idris et al. (2004) identified a wide range of bacteria showing high Ni resistance in the rhizosphere and shoots of the Ni-hyperaccumulator *Thlaspi goesingense*. Among the different bacterial isolates 36% of the endophytes showed ACC deaminase activity.

Recently, Kuffner et al. [112] isolated different rhizospheric and endophytic strains associated with Zn/Cd-accumulating *Salix caprea* ecotypes and investigated their potential to enhance phytoextraction of trace elements. Five of the endophytic strains were further tested for their production of trace element-mobilizing metabolites. Four of the *Actinobacteria* were shown able to mobilize Zn and/or Cd.

To improve phytoextraction efficiency, these naturally abundant strains equipped with the appropriate characteristics can be enriched by means of inoculation. In case these bacteria are not naturally colonizing the plant after isolation, bacteria can also be equipped with metabolic pathways for the synthesis of natural chelators and with trace element sequestration systems [222]. Proof of this concept was provided by Lodewyckx et al. [123] who inoculated Ni-exposed yellow lupine plants with a constructed Ni-resistant endophyte. They introduced the *ncc-nre* nickel-resistance system of *Ralstonia metallidurans* 31 A in the lupin endophytes *Burkholderia cepacia* L.S.2.4 and *Herbaspirillum seropdicae* LMG2284. Inoculation of lupin plants grown on a Ni-enriched substrate with the engineered endophytes, resulted in a 30% increased Ni concentration in the root tissue, whereas, the Ni concentration in the shoots remained comparable with that of the control plants.

Sun et al. [216] isolated and characterized 32 endophytic strains with respect to trace element resistance and production of plant growth promoting factors. In experiments using rape (*Brassica napus*) grown in vermiculite containing 4 mg kg^{-1} of Cu, inoculation with endophytic isolates was found to increase dry weights of roots and aerial tissues when compared to the non-inoculated control. Furthermore, increase in the Cu-content of aerial tissue varied from 63% to 125% in inoculated rape cultivated in the Cu-enriched substrate compared to the non-inoculated control. In another study, trace element resistant endophytic bacteria (*P. fluorescens* G10 and *Microbacterium sp.* G16) colonizing rape roots were investigated for their potential to increase Pb uptake and accumulation [200].

6.4 Plant Metal Stress Responses

6.4.1 Metal Homeostasis: Chelation and Sequestration

After plants take up metals, it is important to keep the free metal concentration under tight control in order to prevent metal-induced cellular damage. Passage across the plasma membrane by metals is enhanced by intracellular binding and sequestration. Once across the plasma membrane, metal ions are either bound to chelators or chaperones. Chelators contribute to metal detoxification by buffering cytosolic free metal concentrations. Chaperones specifically deliver metal ions to organelles and metal-requiring proteins. It is well described that Cu is a cofactor for plastocyanin, Cu/Zn-superoxide dismutase (CuZnSOD), etc. and it is required in different subcellular locations [171, 256]. Several chaperones are identified that deliver Cu to a specific protein in their specific location, such as CCS (Copper Chaperone for SOD) [17, 27, 168]. Phytochelatins, metallothioneins, organic acids and amino acids are well-described metal ion ligands with metal-specific properties [241]. Mugineic acid, nicotianamine, organic acids, histidine and phytate and their role as metal ion ligands for Fe, Zn, Cu, Mn and Ni for metal homeostasis in plants were reviewed by Haydon and Cobbett [84]. Whereas phytochelatins are clear chelators for Cd and As [38, 257], recently Tensteddt et al. [221] observed that phytochelatins function as important chelators of excess Zn^{2+}.

The activities of metal-sequestering pathways in root cells are crucial in determining the rate of metal translocation to the aerial parts. Beside Fe-nicotianamine transport for Fe translocation, this could also be an important mechanism for Mn translocation [92]. The role and characterization of membrane transporters in xylem loading of metal ions/ligands is currently under intense study. Ferric reductase defective 3 (FRD3), a member of the multidrug and toxin extrusion (MATE) family of transporters, is shown to be a citrate transporter involved in the loading of iron into the xylem [66]. A role is attributed to the membrane transporter HMA4 (Heavy metal ATPase 4) in Cd/Zn tolerance more specific in the root-to-shoot translocation of Cd and Zn [48, 82, 253].

6.4.2 Physiological Responses

Generally, plants can withstand metal accumulation until the metal reaches the toxic threshold level in the tissue, leading to growth retardation and toxicity at higher levels. As usual, metal-exposed plants develop reduced, compact roots system and smaller leaf area [193]. Furthermore, weaker growth is often accompanied by different toxicity symptoms such as root browning [170, 239], foliar chlorosis [151, 240], necrotic spots [215, 234], etc. The symptoms may appear in single or complex manner depending on numerous factors including species tolerance, external metal concentration, duration of exposure, etc. As a rule, chlorosis is stronger in the younger leaves [29], while necrotic spots appear mostly on older leaves, where metal concentrations are higher [232]. The observed root browning most probably is due to enhanced lignifications processes [5]. At low levels of metal contamination, visual phytotoxicity symptoms may be less pronounced or even absent, but an enhanced activity of enzymes involved in plant cellular defense against metal induced oxidative stress, e. g. peroxidases, catalases, superoxide dismutases, as well as $NAD(P)^+$ reducing enzymes may be detected (cfr. Infra) [227, 239].

Due to similar phytotoxicity symptoms, there is an assumption that different metals have similar modes of toxic action. However, Cd, Pb and several other problematic metals have no biological function, while Zn, Cu and Mn are essential micronutrients, which become phytotoxic at supra optimal concentrations [39, 59]. Presumably, as the role of these metals in plant cell metabolism is completely different, their impact on plant performance can be also expected to differ. Some proofs in this aspect have been recently obtained when Cd and Zn were applied in concentrations producing similar (near 50%) inhibition of relative growth rate of durum wheat plants [104]. Briefly, Cd induced classic xeromorphic changes in leaf structure, which were not presented in Zn-exposed plants. In addition, Cd exposure strongly modulated enzyme activities, e.g. ascorbate peroxidase activity, while no significant changes in its activity were observed in Zn-exposed plants

The biochemical bases of metal phytotoxicity is well described and mostly due to three negative effects [61]: (1) metal-induced oxidative stress and damages (cfr. infra), (2) direct effects of metal ions with sulfydryl groups in membrane proteins leading to their dysfunction and (3) inactivation of important enzymes by replacing activation cations with other metal ions [228]. The multiplication of the primary metal toxicity effects leads to functional disorders in the cardinal physiological processes and anatomic-morphological changes and damages.

Metals contact first the root system that shows reduced elongation upon exposure. This often resulted in appearance of “stubby” roots having higher specific dry mass content. Instead of a well-structured root system, brown short laterals are developed. In addition, cell division is lowered due to different damages in the nucleus structures and mitosis [65, 225].

After root metal uptake, deficiencies and imbalances of mineral nutrients can be induced. They can reduce nutrient uptake and translocation through competition, affect root cells membranes, ATP-ases and other carriers resulting in decreased unsuberized root tips and damage of the permeability of root cells [37, 183]. For example, Cd decreased root concentrations of Zn, Cu and Mn in barley plants and *Salix viminalis* cuttings [234, 239]. The decreased essential nutrient content may be also caused by ion leakage from damaged roots and immobilization of elements in roots, resulting in their strong deficiency in the shoots [203]. The most pronounced such effect is K^+ leakage as consequence to Cd-provoked disturbed membrane permeability [146, 229].

Excess metals induce disorders in plant water relations, such as reduced water uptake, translocation and transpiration [11]. The reduced water uptake in metal-exposed plants can be partly explained by root growth inhibition, but binding of metals, for example Zn, to water-channel proteins in the membrane also occurs [115]. Furthermore, the water movement into xylem vessels is also affected by metals [133]. The reason for the reduced water movement is both a decreased vessel radius and number of vessels due to Cd, Zn and Cr induced inhibition of division, elongation and differentiation of cambium cells [11]. In addition, accumulation of lignin-like insoluble phenols and depositions of Ca oxalate can cause structural disorders in the vessels and hence decrease the water movement. The disturbed plant water relations resulted in decreased relative water content (RWC), water potential (Ψ) of leaves of metal-exposed plants, which may have far going consequences for many physiological processes [233]. Diminished leaf water content decreased transpiration intensity, which in turn enlarged stomatal limitation of photosynthesis [133, 237].

Most of the observed physiological disturbances in metal-exposed plants may finally be focused on photosynthetic performance. In addition to limited access of CO_2 through stomata, metals may affect photosynthesis at other levels, e.g. pigments, thylakoid ultrastructure and electron transport, activities of Calvin cycle enzymes, etc. [107, 230].

The reduced chlorophyll content in metal-exposed plants may be due to inhibition of its biosynthesis [213], metal-induced Fe and Mg deficiency [233], Mg-substitution in the chlorophyll molecule [114], chlorophyll degradation resulting from oxidative damage or enzymatic degradation [129, 249]. Baryla et al. [14] have reported that leaf chlorosis in Cd-exposed oilseed rape was due to neither of the mentioned reasons, but it was attributable to a marked decrease of chloroplast density caused by a reduction in the number of chloroplasts per cell.

Metal-induced disorders in chloroplast and thylakoid ultrastructure – swelling of thylakoids, disruption of envelope, etc, are well documented [8, 231] as well as their negative effects on PSII and PSI activities, analysed *in vitro* [16, 235] and *in vivo* [39, 108]. These negative effects may be partly explained by the enhanced lipid peroxidation at chloroplast level. Evidence for this was obtained by increased ethylene production together with diminished total fatty acids content in isolated thylakoids from Cd- and Cu-exposed barley plants [236, 238]. Furthermore, the electron transport might be limited by changes in the concentrations of the electron carriers [119] due to a decrease in essential cations as well as metal-induced alterations in chlorophyll molecule integration into pigment-protein complexes [87].

A lower photosynthetic performance in metal-exposed plants was observed by several authors [120, 239] and supports the opinion of Krupa et al. [108] that metal-induced alterations in primary C metabolism may lead to a down-regulation of PSII activity due to a reduced demand for ATP and NADPH. That also agrees with a lower capacity for ^{14}C photoassimilation and partitioning of labeled photoproducts [230] as well as increased pools of ATP and ADP in leaves of Cd-exposed plants [204]. Furthermore, metals may indirectly decrease photosynthetic rate by changing the sink-source relationship, with a consequent diminished requirement for photosynthetic products [36]. The metal-induced growth inhibition may cause phloem overloading leading to decreases in enzyme activities and energy consumption by Calvin's cycle reactions, and finally reflecting in downregulation in PSII.

6.4.3 Metal Stress: An Oxidative Challenge

Elevated metal concentrations in the environment cause great losses in plant biomass production worldwide. A better understanding of the underlying molecular mechanisms of metal phytotoxicity is most useful to develop or adjust strategies for growing non-food crops on metal-contaminated agricultural soils. The cellular oxidative stress signature leading to oxidative signalling or damage is an important determinant in metal phytotoxicity [196].

Multiple studies have shown that different metal stresses lead to elevated amounts of reactive oxygen species (ROS) and changes in the antioxidative defence systems in plants (Table 6.1). Depending on the chemical behaviour of metal ions, the metal-induced oxidative stress differs [51, 56, 210]. Metal ions, able to perform monovalent oxidoreduction reactions, easily convert molecular oxygen, O_2, to ROS, e.g. superoxide ($O_2^{\circ -}$) and hydrogen peroxide (H_2O_2) by electron transfer. Furthermore redox-active metals like Cu, Fe… promote hydroxyl radical (°OH) formation through the Fenton reaction [81; Fig. 6.1], leading to oxidative damage of macromolecules and cellular malfunctioning. Unlike harmful effects, such as DNA-oxidation, lipid peroxidation… that can be a direct consequence of enhanced ROS production, these molecules also exert an important role as signalling molecules. The balance between damage versus signalling is an oxidative challenge imposed by metal ions to the cells and is characterized by the duration, intensity and frequency of metal-induced ROS production [55]. In the next paragraphs emphasis will be on the cellular ROS balance, i.e. ROS production and antioxidative defence, and consecutively the oxidative damage and signalling under metal stress.

In addition to direct metal-induced ROS production through Fenton and Haber-Weiss reactions [190], also other indirect pathways come into play when investigating oxidative stress responses from bivalent cations such as Cd, Zn, Pb not able to perform redox-reactions. Under natural conditions, ROS are produced in organelles with a highly oxidizing metabolic rate or having electron transport chains (e.g. peroxisomes, chloroplasts, mitochondria) [81]. In multiple studies it has been described that metal stress enhances the ROS production in these organelles, by disturbing photosynthesis and respiration (cfr. supra). A quick burst in ROS was detected in *Arabidopsis* cells exposed to Cd as a consequence of morphological and functional changes in mitochondria and chloroplasts [20]. Superoxide levels were elevated under Cr stress by inactivation of the electron transport chain in pea root mitochondria [64]. Elevated H_2O_2 and $O_2^{\circ -}$ contents were observed in the peroxisomes after exposure to Cd [182 and references therein].

Whereas the enzymatic oxidative burst is well studied under pathogenic attack [223], NADPH-oxidases are clearly involved in ROS production after metal application. Remans et al. [178] demonstrated a metal-specific upregulation of NADPH oxidase gene expression in the roots for Cd, whereas Cu caused a metal-specific downregulation of NADPH oxidase genes. Nevertheless ROS production by NADPH-oxidases under Cu stress cannot be ruled out as Navari-Izzo et al. [155] observed an early, but transient induction of NADPH-oxidase activities in Cu-exposed wheat roots.

Table 6.1 Responses of the antioxidant defence system in plants exposed to elevated metal concentrations

Metal	Concentration	Exposure time	Plant	Antioxidant defence mechanisms	References
Cd	3–10–30 µM	Minutes to 24 h	*Medicago sativa*	Altered AsA, GSH	[158]
	5–10–20 µM	24 h	*Arabidopsis thaliana*	Altered transcription, Px↑, GR↓	[209]
	5–10 µM	24 h	*Arabidopsis thaliana*	Altered transcription, CAT↑, APx↑, altered AsA, GSH	[56]
	5 µM	96 h	*Phaseolus vulgaris*	Altered APx, CAT, GR	[31]
	1–10 µM	7 days	*Arabidopsis thaliana*	AsA↓, GSH↓, *GR*↓, APx↑, CAT↑, SOD↑, GR↑, GPOD↑	[192]
	6–30 µM	7 days	*Zea mays*	Altered GSH, APX↑	[177]
	3–10–30 µM	7 days	*Medicago sativa*	AsA↑, biothiols↑, APx↑, GR↑	[212]
	75 µM	7 days	*Arabidopsis thaliana*	α-tocopherol↑	[40]
	10–25–50 µM	15 days	*Brassica juncea*, *B. napus*	Non-protein SH↑, SOD↓, CAT↓, GR↓, APx↓	[156]
	300–500 µM	21 days	*Arabidopsis thaliana*	SOD↑, GPx↑, APx↑, GR↑	[33]
Pb	1–10–100–200–500 µM 1–10 mM	3, 24 h	*Arabidopsis thaliana*	Altered transcription, SOD↑, Px↑	[122]
	100–1,000 µM	12, 24 h	*Taxithelium nepalense*	AsA↑, GSH↑, Px↓ GR↓	[35]
	10–100–1,000 µM	24 h	*Taxithelium nepalense*	AsA↑, GSH↑, SOD↑, CAT↓, Px↓, GR↓	[34]
	200–500–800 ppm	12 days	*Macrotyloma uniflorum*, *Cicer arietinum*	SOD↑, CAT↑, Px↑, GR↑, GST↑	[175]
	10–50–100–200 µM	14 days	*Phaseolus vulgaris*	SPx↑, GPx↑, APx↑, GSH-Px↑, DHAR↑, GR↑	[76]
	500–1,000 µM	5, 10, 15, 20 days	*Oryza sativa*	Altered CAT, SOD↑, GPx↑, APx↑	[242]
Cu	100 µM	1 min to 6 h	*Brassica napus*	GSH↓, GR↓ in roots, GSH↑, GR↑ in leaves	[184]
	2–5 µM	24 h	*Arabidopsis thaliana*	Altered AsA, GSH, CAT↓, APx↓, GR↓ in roots CAT↑, APx↑, GR↑ in leaves	[56]
	25 µM	96 h	*Solanum lycopersicon*	GPx↑, SOD↑, CAT↑, APx↑, GR↑	[30]
	15–150–1,500 µM	5 days	*Hordeum vulgare*	Altered non-protein SH, CAT↑, GSH-Px↑, SOD↓	[58]
	50 µM	7 days	*Phaseolus vulgaris*	AsA↑, GSH↑, MDHAR↑, DHAR↑, GR↑, APx↑	[52]
	75 µM	7 days	*Arabidopsis thaliana*	α-tocopherol↑, AsA↑	[40]

(continued)

Table 6.1 (continued)

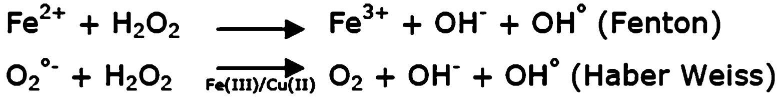
Metal	Concentration	Exposure time	Plant	Antioxidant defence mechanisms	References
	10–50–75–100–150–200–300 µM	21 days	*Brassica juncea*	SOD↑, APx↑, GPx↑, CAT↑	[207]
Zn	0.1–1–10–100 mM	2, 4, 6, 8 days	*Triticum aestivum*	AsA↑, GSH↓, CAT↓, GPx↓,SOD↓	[163]
	100 µM	96 h	*Phaseolus vulgaris*	Altered Px, MDHAR activities	[31]
	50 µM	7 days	*Phaseolus vulgaris*	APx↓, GR↓ in roots, AsA↑, AsA-GSH pathway↑ in leaves	[53]
	1–5 mM	11 days	*Verbascum thapsus*	APx↑, SOD↑, Px↑, MDHAR↑, GR↓, DHAR↓	[150]
	0.15–0.3 mM	15 days	*Lemna minor*	AsA↑, SOD↑, Px↑, CAT↓	[173]
Al	25 µM	2–48 h	*Arabidopsis thaliana*	Transcription of antioxidant enzymes↑	[179]
	30–50–100 µM	24 h	*Triticosecale*	SOD↑, Px↑	[121]
	10–50 µM	24, 48 h	*Pisum sativum*	Altered transcription, activities, AsA, GSH	[162]
	2–4–6–8 mM	48, 72 h	*Hordeum vulgare*	Altered SOD, Px, APx activities	[205]
	0.001–0.01–0.1–1.0 mM	9 days	*Vigna radiata*	AsA↓, GSH↓, CAT↓, SOD↑, Px↑, GR↑	[164]
	0.15–0.3 mM	15 days	*Lemna minor*	SOD↑, Px↑	[173]
As	10–100–1,000 µM	24 h	*Taxithelium nepalense*	AsA↑, GSH↑, SOD↑, CAT↓, Px↓, GR↓	[34]
	100 µM	3, 10 days	*Arabidopsis thaliana*	*Cu/ZnSOD*↑, Cu/ZnSOD↑, *FeSOD*↓, FeSOD↓	[2]
	2–5 mg/L	5 days	*Phaseolus vulgaris*	Px↑	[214]
	10–50 µM	7 days	*Phaseolus aureus*	SOD↑, GPx↑, GR↑, CAT↓	[206]
	50–100 µM As(III) 100–500 µM As(V)	10 days	*Oryza sativa*	SOD↑, APx↑, Px↑, GR↑	[202]
Cr	100–1,000 µM	12,24 h	*Taxithelium nepalense*	AsA↑, GSH↑, Px↓, GR↓	[35]
	50–100–200 µM	1, 3, 5, 7 days	*Brassica juncea*, *Vigna radiata*	SOD↑, APx↑, CAT↑, GR↑	[63]
	0.1–1–10–100 mM	2, 4, 6, 8 days	*Triticum aestivum*	AsA↑, GSH↓, CAT↓, GPx↓ SOD↓	[163]
	0.2–2–20 µM	1, 2, 3, 4, 5, 15 days	*Brassica juncea*	SOD↑, APx↑, CAT↑, GR↑, GST↑	[165]

Hg	3–10–30 μM	Minutes to 24 h	*Medicago sativa*	Altered AsA, GSH, APx↑	[158]
	6–30 μM	7 days	*Zea mays*	Altered GSH, APx↑	[177]
	3–10–30 μM	7 days	*Medicago sativa*	AsA↑, biothiols↑, GR↓ in roots, GR↑ in leaves	[212]
	10–50 μM	10, 20 days	*Lycopersicon esculentum*	SOD↑, CAT↑, Px↑	[32]
	20–30–40 μM	21 days	*Arabidopsis thaliana*	Transcription of antioxidant enzymes↑	[85]
Mn	183–1,830–18,300 μM	5 days	*Hordeum vulgare*	Altered AsA, CAT↑, GSH-Px↑, SOD↓, APx↓	[58]
	50–100 μM	6 days	*Vigna unguiculata*	Altered AsA, Px	[68]
	600 μM	11 days	*Cucumis sativus*	AsA↓, GSH↓, SOD↑, Px↑, APx↑, DHAR↑, GR↑	[201]
	50–100–250 μM	11 days	*Pisum sativum*	AsA↓, GSH↓, SOD↑, APx↑, DHAR↑, GR↑, CAT↓	[75]
Ni	100 μM	1, 3, 7, 14 days	*Zea mays*	Px↑, APx↑, SOD↑, CAT↓	[113]
	10–200 μM	3, 6, 9 days	*Triticum aestivum*	Px↑, GST↑, SOD↓, CAT↓	[74]
	50–100–200–400–800 μM	7 days	*Luffa cylindrica*	SOD↑, GPx↑, CAT↑	[246]
	200–400 μM	5–20 days	*Oryza sativa*	AsA↑, GSH↓, SOD↑, GPx↑, APx↑, AsA-GSH pathway↑	[128]

For each metal, the effects of acute and prolonged exposure to low or high concentrations are summarized for different plant species based on available literature

Underlined enzymes indicate affected transcript levels

APx ascorbate peroxidase, *AsA* ascorbate, *CAT* catalase, *DHAR* dehydroascorbate reductase, *GPOD* guajacol peroxidase, *GPx* glutathione peroxidase, *GR* glutathione reductase, *GSH* glutathione, *GST* glutathione-S-transferase, *MDHAR* monodehydroascorbate reductase, *Px* peroxidase, *SOD* superoxide dismutase, *SPx* syringaldazine peroxidase



$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^\circ \text{ (Fenton)}$$

$$O_2^{\circ -} + H_2O_2 \xrightarrow[Fe(III)/Cu(II)]{} O_2 + OH^- + OH^\circ \text{ (Haber Weiss)}$$

Fig. 6.1 Fenton and Haber Weiss reaction

Besides electron transfer, energy transfer to O_2 results in the conversion to singlet oxygen ($^1O_2$) with a highly oxidizing capacity [70]. Under metal stress, this process can happen in the chloroplast by inefficient transfer to the complexes of the electron transport chain, but $^1O_2$ molecules are also formed as a by-product of lipoxygenase activities [98]. Lipoxygenase gene expression [56, 178, 209, 210] and enzyme activity [99, 219, 258] are elevated under Cd, Hg and Cu stress, possibly leading to a higher production of $^1O_2$. In *Arabidopsis* cell cultures exposed to Cd, an immediate burst of $^1O_2$ was noticed that was not high light dependent (Van Belleghem, personal communication, 2007). Lipoxygenases catalyze the addition of molecular oxygen to polyunsaturated fatty acids that lead to lipid peroxidation but it can also be subsequently modified to bioactive compounds such as oxylipins [69]. Jasmonates are lipid-derived signalling compounds with a role in normal plant growth and development, as well as in the response of plants to (a)biotic stress factors [56, 118, 208, 248].

As sessile organisms, plants cannot escape from toxic surroundings, so in order to counterbalance the stress-induced ROS production plant cells contain a lot of antioxidants, *i.e.* enzymes and metabolites. It is essential to prevent the production of °OH-radicals, having a very short half-life and attacking everything around it [81]. Superoxide radicals are the primary ROS formed after electron transfer and superoxide dismutase (SOD) converts these molecules to H_2O_2 and O_2. In plants 3 different groups of isoforms exist, each containing a redox-active metal in the active site to perform the reaction: CuZnSOD, FeSOD, MnSOD located in different subcellular locations (for a review see 148). Although changes in the SOD activities under metal stress have been described (Table 6.1), currently more information becomes available on the transcript level as well as on the transcriptional and posttranscriptional regulation. In conditions of Cu-deficiency [106, 254] as well as during Cu-excess [1, 153] the presence of GTAC motifs in the promotors of genes are essential in Cu-sensing and homeostasis [62 and references therein]. The presence of Cu induces the *CSD* (CuZnSOD) gene expression and simultaneously inhibits *FSD* (FeSOD) gene expression through the presence of Cu negative *cis*-acting elements in the promotors of miRNA398 (negative posttranscriptional regulator of *CSD* gene transcripts) or the *FSD* gene itself. Recently, the opposite (a downregulation) was observed for the *CSD* gene transcripts under Cd-stress together with un upregulation of *miR398* [56]. Future experiments are needed to reveal the processes by which metal stress affects gene regulation at different biological organisation levels, *i.e.* epigenetics, transcriptional and posttranscriptional regulation.

Hydrogen peroxide is the subsequent ROS in the electron transfer that needs to be scavenged in order to prevent °OH formation. Catalases and peroxidases are very important scavengers of H_2O_2 and are stimulated under metal stress (Table 6.1). Furthermore peroxiredoxins and associated redoxins come into play to detoxify H_2O_2 by the use of their thiol groups. Although investigations are ongoing for these components in H_2O_2 detoxification [224], the information under metal stress is rather scarce. Conversion of H_2O_2 to H_2O and O_2 links enzymatic systems directly to the antioxidant metabolites, more specifically ascorbate (AsA) and glutathione (GSH). They are electron donors for peroxidases and GSH is also involved in the regeneration of oxidized AsA as well as glutaredoxins. Both AsA and GSH are highly abundant, soluble metabolites present in different cellular compartments [71] and form important constituents of the redox balance in plant cells that can be affected by metal exposure (Table 6.1). During metal stress, special attention should be given to GSH, since its functional group is susceptible for different metals such as Hg, Cd ... showing high affinities to thiols. In this regard it plays a central role in metal chelation (as a precursor for phytochelatins) as well as through its antioxidant capacities.

The steady state level of ROS in the different cellular compartments is determined by the interplay between multiple ROS-producing pathways and ROS-scavenging mechanisms. As mentioned before, ROS are capable of modulating signalling networks that control physiological processes and stress responses [71, 148]. ROS, such as H_2O_2, are ideal signalling molecules as they are small and able to diffuse over short distances. Because H_2O_2 production is an immediate response to increased metal stress [20, 56, 150, 247], it is probably a key molecule that can trigger signal transduction events after plant metal exposure, mediating the acquisition of tolerance [19, 130, 131]. Whereas oxidative signaling is very important under metal stress, the complex interaction with other signaling pathways [54] needs further attention.

In conclusion, the term ‘metal-induced oxidative stress’ can be more specified in either oxidative damage and oxidative signalling that together forms an oxidative challenge for the cells to cope with metal stress.

6.5 Conclusions

Nutrient uptake by plants is essential for their development and for the passage of minerals into the food chain, but faces several limitations. The plant possesses several mechanisms to explore the soil for minerals such as root development, releasing siderophores, organic acids, etc... but the symbiosis with microorganisms clearly improves the ability of plants to overcome these limitations and needs further attention in the study of plant-soil interactions. Also in the research on plant metal stress and its cellular responses, microorganisms are shown to be important players in the plant protection to excess metal exposure.

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Chapter 7
Heavy Metals and Metalloids as Micronutrients for Plants and Animals

Brian J. Alloway

Abstract Much of the emphasis of the chapters in this book is on heavy metal(loid)s as soil contaminants, their bioavailability and possible toxicity to plants, ecosystems, animals and humans. However, many of the heavy metal(loid)s are actually micronutrients, that is they are essential (in small quantities) for the normal growth of plants and/or animals. Copper (Cu), manganese (Mn), molybdenum (Mo), nickel (Ni) and zinc (Zn) are the heavy metals that are essential for higher plants. For animals and humans, chromium (Cr), Cu, cobalt (Co), Mn, Mo, selenium (Se), vanadium (V) and Zn are the micronutrient heavy metal(loid)s. Iron (Fe), not usually considered a heavy metal is essential for both plants and animals. Several other elements, including arsenic (As), cadmium (Cd), lead (Pb) and tin (Sn) may possibly have an essential role at very low concentrations. This chapter briefly covers the essential functions of these heavy metal(loid)s in plants and/or animals and the significance of relatively low and high available concentrations in soils. Deficiencies and toxicities of micronutrients adversely affect plant and animal health, cause reductions in growth rate (and yield), overt symptoms of physiological stress and, in extreme cases, the death of the plant or animal. In many parts of the world, the adverse effects of deficiencies of essential heavy metal(loid)s are more important economically than toxicities arising from soil contamination.

Keywords Micronutrients • Essentiality • Hidden deficiency • Toxicity • Symptoms • Enzymes • Plant nutrition • Human nutrition • Homeostasis

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7.1 Introduction

‘Micronutrients’ are the trace elements required in small, but critical, quantities for the normal healthy growth of plants and animals. There are eight micronutrients required by higher plants and these are: boron (B), chlorine (Cl), Cu, iron (Fe), Mn, Mo, Ni and Zn. In addition, Co is essential for the bacterial fixation of nitrogen (N) in nodules on the roots of legumes [5, 8, 9]. With the exception of B and Cl, these elements are all classed as heavy metals. In higher animals and humans, the proven micronutrients are: chromium Cr, Cu, Fe, iodine (I), Mn, Mo, Se, V and Zn. Other elements which are being investigated for possible essential functions in animals and humans include: B, silicon (Si), As, fluorine (F), lithium (Li) and Sn. There is even some evidence that Cd, Pb and Sn may be essential at very low concentrations [12, 28, 31]. However, the micronutrients which have been conclusively proven to be essential in animal and/or human nutrition and whose concentrations in diets are critical are Co (ruminants only), Cr, Cu, Fe, I, Mn, Mo, Se and Zn.

An element can be considered ‘essential’ for plants if they cannot complete their life cycles without it, it cannot be replaced by other elements and it is directly involved in plant metabolism [8]**.** Essential trace elements are also known as ‘micronutrients’. For animals and humans, Reilly [28] quotes the definition of essential elements used by many nutritionists as: “The trace element must: (1) be present in healthy tissue, (2) its concentration must be relatively constant between different organisms, (3) deficiency induces specific biochemical changes, (4) the changes are accompanied by equivalent abnormalities in different species, and (5) supplementation with the element corrects the abnormalities.”

All micronutrient heavy metal(loid)s have homeostatic mechanisms in plants and/or animals which regulate the bioavailable concentrations of the elements. It is when these mechanisms break down and are unable to maintain the optimal range of supply of a particular micronutrient that either deficiencies or toxicities can occur.

7.2 Heavy Metal Micronutrients in Plant Nutrition

It is very important that the micronutrient requirements of crops are met as well as their macronutrient needs (e.g., N, P and K) if they are to yield satisfactorily and bear products, such as grains, fruits, vegetable leaves or storage roots, of acceptable quality. In comparison with macronutrients, which are often present in thousands of mg kg^{-1}, micronutrients are only required in relatively small amounts (5–100 mg kg^{-1} DM). The dose response curves for all micronutrients show that yields can be affected by both deficiencies and toxicities. Typical dose-response graphs for micronutrients and non-essential elements are shown in Fig. 7.1. Although these are primarily based on generalised plant data, dose response graphs for animals show similar trends.

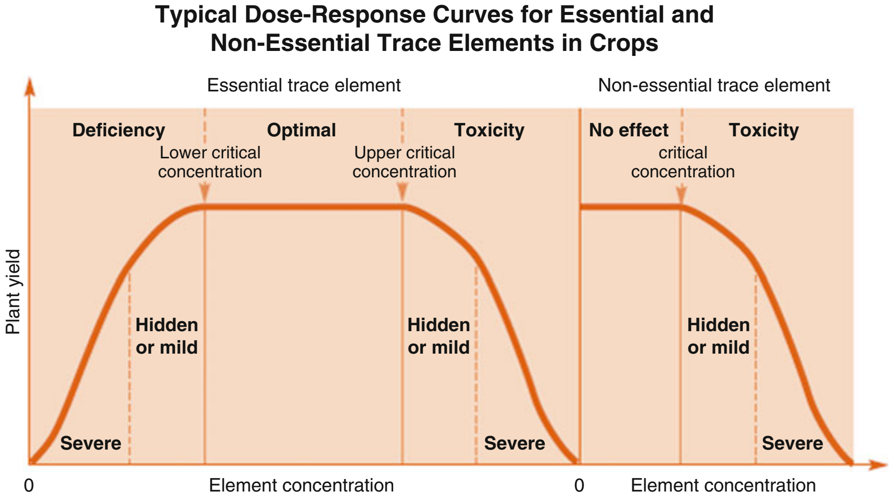

Fig. 7.1 Typical dose-response curves for essential and non-essential trace elements (Reproduced from Alloway [3] (Copyright (2008) with permission from International Zinc Association and International Fertiliser Industry Association))

Micronutrient deficiency problems in crops have only been widely recognised and treated in the field over the last 70 years. These deficiencies became apparent with the intensification of arable farming in many parts of the world and also with the cultivation of virgin and/or reclaimed land. Intensification involves the increased use of N, P and K fertilisers, growing new and higher yielding crop cultivars, increased use of pesticides and, where necessary, liming to optimise soil pH and/or increased use of irrigation. Prior to this intensification, much lower crop yields were usually accepted as the norm in many parts of the world, but the crop cultivars grown were generally well adapted to local soil and climatic conditions [2]. A similar situation has arisen with intensively managed livestock, but in the case of humans, trace element malnutrition is often related to poverty and restricted diets with either a shortage of foods containing adequate concentrations of micronutrients, or foods, such as grains containing relatively high levels of antinutrients such as phytates, which reduce the availability of some micronutrients [31, 33].

The functions of the plant micronutrients are briefly summarised in Table 7.1. All of these essential heavy metals have roles as constituents or activators of enzymes in physiological pathways. Although Fe is not normally considered to be a 'heavy metal' it is included in Tables 7.1 and 7.2 because of its very important functions and the fact that it interacts with several heavy metals such as Mn, Cu and Zn and macronutrients such as Ca.

Critical deficiency concentrations of these micronutrient heavy metals in most crop plant species are generally in the range (in mg kg^{-1} DM): Cu 1.0–5.0, Fe 50–150, Mn 10–20, Mo 0.015–0.05, Ni 0.01–10 and Zn 15–20 [6, 7]. Critical concentrations in soils vary with the soil test procedure used, the crop and the type of soil. For Cu extracted with ethylenediamine tetraacetic acid (EDTA) deficiencies are highly likely <0.5 mg EDTA Cu kg^{-1} and still possible 0.5–08.

Table 7.1 Brief summary of the essential functions of metal micronutrients and beneficial elements in plants

Element	Functions
Cobalt	Not a plant micronutrient, but is essential for the symbiotic fixation of N_2 in the root nodules of legumes and some non-legumes by *Rhizobium* and other N_2- fixing microorganisms in which three enzymes are known to be Co-dependent. It may also have beneficial roles in some higher plant families.
Copper	Plays important structural and functional roles in oxidative enzymes (including: super oxide dismutase (SOD), cytochrome oxidase, ascorbate oxidase, polyphenols oxidase and electron-transfer proteins (e.g., plastocyanin in chloroplasts)). The physiological processes involving these Cu-dependent enzymes and proteins affect photosynthesis, carbohydrate metabolism, respiration, protein metabolism, lignification of cell walls (and water transport) and pollen formation. It is also required for N-fixation in root nodules of legumes.
Iron	Constituent of cytochromes (electron-transfer proteins) and metalloenzymes and is essential for many biochemical and physiological processes in plants. These include: photosynthesis, utilization of N and S, production of the plant hormone ethylene and biosynthesis of chlorophyll. Iron is generally incorporated into heme and non-heme proteins, such as cytochromes. Heme proteins are involved with the formation of lignin and suberin and in catalase enzymes which breakdown hydrogen peroxide in cells. In legumes, Fe-containing heme proteins called leghemoglobins, regulate the supply of O_2 to N_2-fixing bacteria in root nodules.
Manganese	Activates a large number of enzymes which catalyse oxidation-reduction, decarboxylation and hydrolytic reactions and affects the production of lignin, flavonoids, fatty acids, the growth hormone indole acetic acid (IAA) and N metabolism. In C4 plants, such as maize and sugar cane and plants which fix their C at night, Mn is required for CO_2 assimilation. Only two enzymes contain Mn: the Mn protein in photosystem II, which catalyses the photolysis of water in photosynthesis and a superoxide dismutase (MnSOD) which protects tissues from damage caused by the oxygen free radical (O_2^-).
Molybdenum	Required for the functioning of several enzymes involved in redox reactions including nitrate reductase which is essential for the reduction of NO_3 to allow it to be assimilated into plants and aldehyde oxidase which is involved in the synthesis of growth hormones. Molybdenum is also a component of the bacterial enzyme nitrogenase involved the fixation of N_2 in legume root nodules.
Nickel	Constituent of the enzyme urease and therefore essential for the few plant species that produce this enzyme and other plants supplied with urea as the sole source of N. It is required for healthy embryo and seedling vigour in cereals and is also important in plant disease resistance. Nickel is also a component of the enzyme hydrogenase involved in N fixation by bacteria.
Zinc	Constituent of several enzymes with roles in carbohydrate and protein synthesis, gene regulation, structure and integrity of biomembranes, protection of cells from damage due to free radicals, regulation of auxin synthesis and pollen formation. Meristematic tissues have a high Zn requirement and the Zn-containing enzyme carbonic anhydrase is required for photosynthesis. Plants with C4 –type CO_2 fixation in photosynthesis have a higher requirement for carbonic anhydrase, than C3 plants and are therefore more sensitive to Zn deficiency, but Zn deficiency reduces net photosynthesis in all plants. As a result of its role in maintenance of biomembranes, roots of Zn-deficient plants tend to 'leak' amino acids and phenolics. Classic symptoms of Zn deficiency, such as stunting and 'little leaf' are due to the oxidative degradation of auxin (growth hormone).

Adapted from: Marschner [19], Bell and Dell [6], Srivastava and Gupta [30], Fageria et al. [9], Brown [7], Humphries et al. [14] and Asher [4]

Table 7.2 Some common visible symptoms of micronutrient deficiencies in crops

Element	Symptoms	Sensitive crops
Copper	Wilting, melanism, white twisted tips, reduction in panicle formation, disturbance of lignification and of the development and fertility of pollen	Cereals, sunflower, spinach, onions, carrots and alfalfa
Iron	Interveinal chlorosis of young leaves	Fruit trees (citrus), grapes, peanut, soya bean, sorghum and calcifuge species
Manganese	Chlorotic spots and necrosis of young leaves and reduced turgour. Necrotic spots on cotyledons of peas	Cereals, legumes and fruit trees (apples, cherries and citrus)
Molybdenum	Chlorosis of leaf margins, “Whiptail” of leaves and distorted curding of cauliflower; “fired” margin and deformation of leaves due to NO_3 excess and destruction of embryonic tissues	Brassicae and legumes
Nickel	Leaf tip necrosis (legumes), chlorosis and patchy necrosis (*Graminae*)	Pecan, wheat, potato, bean, soya bean
Zinc	Interveinal chlorosis (mainly in monocotyledons), stunted growth, “little leaf”, rosetting of trees and violet-red points on leaves	Cereals (especially maize and rice), grasses, flax/linseed and fruit trees (citrus)

Adapted from Kabata-Pendias [15] and Fageria et al. [9]

Mg EDTA Cu kg^{-1} [1]. For Zn extracted with diethylenediamine pentaacetic acid (DTPA) typical threshold concentrations are 0.1–1.0 mg DTPA Zn kg^{-1} [21] (see Sect. 17.5.1), but around the world the critical range can extend up to 2.0 mg DTPA Zn kg^{-1} [3].

When the supply of a micronutrient to plants is either deficient or excessive, in addition to crop yields and quality being affected, visible symptoms of physiological stress are often observed, especially in cases of severe deficiency or toxicity [5]. Although plant species differ in the nature of the symptoms of micronutrient deficiencies and toxicities which they display, there are several generalizations which can be made. In most cases, severe deficiencies will cause stunted growth, discoloration and, in some cases, necrotic spots on leaves. The discolouration will usually commence as chlorosis when, instead of the normal green colour of chlorophyll, either all or part of the leaves turn yellow, or even white, but they can also turn brown. Deficiency symptoms can also include smaller or twisted leaves, and loss of turgour. Leaf symptoms are usually seen only on old leaves in the case of Mo, on new leaves with Fe, Mn and Cu, on both young and old leaves with Zn, and in terminal buds with B deficiency. Green veins (on chlorotic leaf laminas) are seen on new leaves with Fe and Mn deficiency and yellow veins with Cu deficiency [27]. A summary of the main types of deficiency symptoms associated with each of the plant micronutrients is given in Table 7.2. Less severe deficiencies may not manifest themselves until later stages in the development of the plant. Visible symptoms can provide a convenient and low-cost means of identifying micronutrient deficiency problems, but can sometimes be confused with deficiencies of other macro or micronutrients, toxicities of metal(loid)s or symptoms of disease, drought, heat stress, or damage by agrichemicals [5].

Symptoms of severe toxicity in plants vary with the metal(loid) involved (including non-essential and micronutrient elements), but certain symptoms tend to be commonly found. These include: chlorosis (Co, Cr, Cu, Hg, Mn, Mo, Ni, Se, Tl and Zn); stunted or deformed roots (As, Cd, Cr, Cu, Co, Hg, Mn, Mo, Ni, Pb, Ni and Zn); dark green leaves (Cu, Fe and Pb); grey green leaves (Ni); brown necrotic spots on leaves (As); brown leaf margins (Cd); white or necrotic leaf tips (Zn) and general stunting (Cd, Hg and Zn) [15]. Upper critical concentrations (in mg kg^{-1} DM) causing a 10% depression in yield (due to toxicity) are in the range: As 1–20, Cd 10–20, Cr 1–10, Cu 10–30, Hg 1–8, Ni 10–30 and Zn 100–500 [18].

In cases of marginal deficiency or toxicity, the manifestation of symptoms is often less distinct and more difficult to recognize in the field. The yields of many crops, especially cereals, can be significantly reduced (sometimes by 20% or more) and the quality of crop products impaired, without the manifestation of distinct visible symptoms due to marginal deficiencies of micronutrients such as Cu and Zn. These are usually referred to as hidden deficiencies, 'hidden hunger', latent, and/or sub-clinical deficiencies. In many parts of the world, this type of deficiency is more widespread and has a greater economic impact than acute micronutrient deficiencies. The apparent absence of deficiency or toxicity symptoms in a crop does not necessarily imply that the supply of micronutrients is optimal. More than one element may be deficient or causing phytotoxicity at a particular site (multi-micronutrient deficiencies or toxicities). In correcting a diagnosed deficiency of one element, there is a risk that the available concentration of another micronutrient may be reduced in some way, thereby inducing a deficiency of this element instead. This has been found with Cu and Mn, Cu and Zn, and Mn and Fe.

From Table 7.3 it can be seen that crop species vary considerably in their susceptibility to deficiencies of different micronutrients. Maize, rice, citrus and fruit trees are particularly susceptible to Zn deficiency, which is the most ubiquitous micronutrient deficiency disorder in crops. Small grain cereals, such as wheat, barley and oats as well as citrus and alfalfa are highly susceptible to Cu deficiency. However, although wheat is considered reasonably tolerant of Zn deficiency, in many countries, especially those with calcareous soils, Zn deficiency in wheat is a major problem (due to low availability) (see Chap. 17, Sect. 17.5) [21]. Intra-specific variations (between varieties or cultivars) can sometimes be even greater than differences in susceptibility between species, but all crops will be affected by a severe deficiency of any of the micronutrients. The main difference between genotypes is in the critical concentrations at which the supply of a particular micronutrient becomes inadequate. These will be significantly lower for the more tolerant genotypes (cultivars).

Cultivars which are able to grow normally in soils with marginally low available concentrations of a micronutrient are classed as being 'efficient' for that particular micronutrient and those which are unable to tolerate such low levels of this micronutrient are 'inefficient'. Genotypic variations in efficiency have been reported for: B, Cu, Fe, Mn and Zn in crop plants [11]. Differences in micronutrient efficiency are probably due to genotypic variations in the volume and length of roots, root-induced changes in rhizosphere, increased absorption through vesicular

Table 7.3 The relative susceptibility of crops to deficiencies of micronutrients

	Micronutrient					
Crop	B	Cu	Fe	Mn	Mo	Zn
Alfalfa	High	High	Med[a]	Med	Med	Low
Apple tree	High	Med	Low	High	Low	High
Barley	Low	High/Med	Med	Med	Low	Med
Bean	Low	Low	High/Med	High	Med	High
Cabbage	Med	Med	Med	Med	High/Med	–
Citrus	Low	High	High	High	Med	High
Cotton	High	Med	High/Med	Med/Low	Low	High/Med
Flax	Med	–	High	Low	–	High
Grapevine	High/Med	Med	High	High	Low	Low
Maize	Med/Low	Med	Med	Med/Low	Low	High
Oats	Low	High	Med	High	Med/Low	Low
Pea	Low	Med/Low	Med	High	Med	Low
Peanut[b]	High/Med	–	High	–	High	Low
Potato	Low	Low	–	High/Med	Low	Med
Rapeseed[c]	High	Low	–	Med	–	Med
Rice	Med/Low	Low	High/Med	Med	Low	High/Med
Rye	Low	Low	Low	Low	Low	Low
Sorghum	Low	Med	High/Med	High/Med	Low	High
Soya bean	Low	Low	High/Med	High	High/Med	Med
Spinach	Med	High	High	High	High	Med
Sugarbeet	High	Med	High/Low	High/Med	Med	Med
Sunflower	High	High	–	–	–	Med
Tomato	High/Med	Med	High	Med	Med	Med
Wheat	Low	High	Med/Low	High	Med/Low	Low

Derived from: Martens and Chesterman [20], Prasad and Power [25], Rashid and Ryan [26] and Loué [17]

[a] Med = medium susceptibility, – = no information

[b] Peanut (*Arachis hypogea* L.) also called groundnut

[c] Rapeseed (*Brassica napus* L) also called oil seed rape or canola

mycorrhizae, release of root exudates to facilitate uptake, efficiency of utilization of the micronutrients once absorbed into plants, recycling of elements within the tissues of the growing plant, or tolerance of factors, which inhibit uptake, such as HCO_3^- and Zn in rice [10, 13, 19].

In a large-scale programme of field experiments at 190 sites in 28 developing countries plus Finland, Silanpää [29] found that Zn deficiency occurred in 49% of the experimental sites, B deficiency in 31%, Mo deficiency in 15%, Cu deficiency in 14%, and Mn deficiency in 10%. However, for all elements except Zn, much higher percentages of these deficiencies were of the latent or hidden type (e.g., Cu 4% acute and 10% latent; Mo 3% acute and 12% latent), but in the case of Zn, there were almost equal percentages (25% acute and 24% latent) for the two types of deficiency.

7.3 Heavy Metal(loid) Micronutrients in Animal and Human Nutrition

Just as in plants, the heavy metal(loid)s essential for higher animals and humans are constituents and/or activators of enzymes. Their essential functions are given in Table 7.4.

In grazing livestock, Mn deficiency is rare, but when it does occur it often results in lameness. Zinc concentrations in herbage need to be above 20 mg kg^{-1} in order to avoid Zn deficiency whose effects include, loss of appetite, poor growth and reduced fertility. With more severe deficiency (intakes <5 mg Zn kg^{-1}) symptoms include loss of hair and wool, reduced immunity to disease and thickening and cracking of the skin. Copper deficiency can be associated with low Cu contents in herbage, but also to elevated Mo contents (see Sect. 18.4). Mild Cu deficiency symptoms, like those of Zn, tend to be non-specific and include poor growth and/or roughness and loss of pigmentation in coat. More severe Cu deficiency is accompanied by symptoms including diarrhoea, anaemia, and lameness. In sheep, Cu deficient lambs can develop a neurological condition called 'swayback' (or enzootic ataxia) [32].

The US Recommended Dietary Allowances (RDAs) [23] for Cu, Mn, Fe, Zn and Se for humans are shown in Table 7.5.

Apart from the proven essential trace elements, some other heavy metal(loid) s are being investigated to see whether they are also essential for animal and human nutrition. Several of these, such as As, Cd and Pb have only been considered as potentially toxic elements until recently, but there is some evidence that very small amounts of these elements may be essential. In most cases, the experimentation has involved using diets depleted of the elements of interest and some responses in growth rate and other parameters have been observed. This work is likely to be most relevant in medicine where patients may have to be maintained on total parenteral nutrition (TPN) [28]. However, it is highly unlikely that cases of deficiency of these elements will be found in humans consuming mixed diets or in livestock under normal agricultural conditions. The possible functions of the metal(loid)s currently under investigation are shown in Table 7.6.

7.4 Soil Types Commonly Associated with Micronutrient Deficiencies

The effects of soil type and soil conditions on the bioavailable concentrations of heavy metalloids are covered in detail in Chaps. 3, 6 and 9–18. However, Table 7.7 summarises the most typical soil conditions leading to either deficiencies in crops, or low concentrations of micronutrients required by animals in herbage and crop products. Boron and Fe are also included because of the agronomic importance of them being deficient.

Table 7.4 Functions of essential heavy metal(loid)s in higher animals and humans

Element	Functions
Chromium	Important in carbohydrate metabolism as a constituent of the 'glucose tolerance factor' (GTF) a dinicotinic acid-glutathione complex, which potentiates the action of insulin. Chromium participates in lipoprotein metabolism and there is some evidence that an improved Cr status has a beneficial effect on blood lipid levels in elderly persons. Improved Cr status may also reduce factors associated with cardiovascular disease as well as with diabetes.
Cobalt	Its only known function is as a constituent of Vitamin B12 which can only be synthesised by bacteria in the rumen or in the soil and plays a major part in animal cells where active division is taking place e.g., blood-forming tissues of bone marrow. Vitamin B12 cannot be absorbed on its own and has to combine first with a glycoprotein produced in the stomach lining, called the 'gastric intrinsic factor'. Vitamin B12 deficiency in humans causes pernicious anaemia and severe effects on the nervous system. In livestock it causes progressive loss of appetite and wasting leading to death. It is called 'bush sickness' in New Zealand and "Coast disease" in south Australia, but is found in many other countries.
Copper	Essential for the immune system, the nervous system, skeletal health, Fe metabolism and the formation of red blood cells. It is involved in redox systems and the scavenging of free radicals (Cu–SOD). It is a constituent of more than 12 metalloenzymes and a few genes which regulate Cu-dependent transcription factors. In sheep Cu deficiency can cause swayback disease (enzootic ataxia) in lambs and loss of crimp in wool. In cattle, deficiency causes depigmentation of the facial hair and sudden death. Subclinical Cu deficiency can cause reductions in liveweight gain and fertility and occurs much more widely than acute forms, especially in more intensively farmed livestock.
Iron	Although not considered a heavy metal, Fe is vitally important in animal physiology because it is a component of haemoglobin which carries oxygen in the red blood corpuscles. Iron requirements differ with species, gender, age and level of activity; shortage of Fe causes anaemia and can also result in increased absorption of potentially harmful elements such as Cd and Pb.
Manganese	Manganese is involved in bone formation and in the metabolism of amino acids, cholesterol and carbohydrates. It is a constituent of six key enzymes and affects the functioning of other enzymes such as glycosyltransferases and xylosyltransferases which are involved in bone formation and proteoglycan synthesis. Manganese activates a number of enzymes, but some can also be activated by other metals, especially Mg. The most common Mn deficiency symptoms in livestock are impaired reproduction, skeletal deformities and shortened tendons in the newborn, can also cause impaired insulin production, lipoprotein metabolism, oxidant defence and growth factor metabolism.
Molybdenum	In animals, Mo is required for the functioning of several enzymes involved in transformations of C, N and S. It is a co-factor in the enzymes sulphite oxidase, xanthine oxidase and aldehyde oxidase. Sulphite oxidase is very important in humans because it is involved in the metabolism of S-containing amino acids and bisulphite preservative in foods. In grazing livestock, a close connection between Mo, Cu and S is involved in the condition called "teart" (or molybdenosis) which is a Mo-induced Cu deficiency.
Selenium	Selenium has antioxidant and anti-inflammation functions and is involved in thyroid hormone metabolism. It also has roles in the prevention of certain infections, some forms of cancer and diabetes in humans. It appears to have valuable detoxification properties for As and Hg. Selenium deficiency is thought to affect 0.5–1.0 billion people worldwide. "Keshan disease" (a fatal cardiomyopathy) and "Kashin Beck's disease" (osteopathy) in humans can be prevented by dietary supplementation with Se. In livestock, muscular dystrophy

(continued)

Table 7.4 (continued)

Element	Functions
	(“White muscle disease”) in sheep and cattle and a myocardial disease in pigs can also be prevented with Se supplementation (often in combination with Vitamin E). Livestock require higher intakes of Se than humans. Excess Se causes various toxic (selenosis) conditions, including “alkali disease” lack of vitality, loss of weight, loss of hair, hoof deformation, dermatitis and lameness.
Zinc	Zinc is essential for DNA and protein synthesis, cell division and growth. It is required for male and female reproduction and neurological function and is also essential for immune function. In humans, the main consequences of Zn deficiency are: impaired immunocompetence, increased prevalence of childhood infections such as diarrhoea and pneumonia, impaired growth and development among infants, children and adolescents and impaired maternal health and pregnancy outcome. Animals cannot store Zn, so a continuous adequate supply is required. However, in general, few cases of Zn deficiency are reported in farm animals. Symptoms of deficiency disorders such as decreased growth, testicular atrophy, alopecia and dermal lesions are normally observed mainly in young animals. Hidden (or subclinical) deficiency is probably more important than acute deficiencies.

Based on: WHO [33], Kabata-Pendias and Mukerjee [16], Reilly [28] and Bell and Dell [6]

Table 7.5 Recommended dietary allowances (RDAs) in humans of the US National Academy of Sciences for copper, manganese, zinc, iron and selenium

Gender and age	Cu (mg d^{-1})	Mn (mg d^{-1})	Zn (mg d^{-1})	Fe (mg d^{-1})	Se (μg d^{-1})
0–6 months	0.2	0.003	2	0.27	15
7–12 months	0.22	0.6	3	11	20
Children					
1–3 years	0.34	1.2	5	7	20
4–8 years	0.44	1.5	8	10	150
Males					
9–13 years	0.7	1.9	11	8	40
14–18 years	0.89	2.2	11	11	55
19–30 years	0.9	2.3	11	8	55
31–50 years	0.9	2.3	11	8	55
50–70 years	0.9	2.3	11	8	55
>70 years	0.9	2.3	11	8	55
Females					
9–13 years	0.7	1.6	8	8	40
14–18 years	0.89	1.6	9	15	55
19–30 years	0.9	1.8	8	18	55
31–50 years	0.9	1.8	8	18	55
50–70 years	0.9	1.8	8	8	55
>70 years	0.9	1.8	8	8	55
Pregnancy					
≤18 years	1.0	2.0	12	45	60
19–30 years	1.0	2.0	11	45	60
31–50 years	1.0	2.0	11	45	60
Lactation					
≤18 years	1.3	2.6	13	45	70
19–30 years	1.3	2.6	12	45	70
31–50 years	1.3	2.6	12	45	70

From US Food and Nutrition Board of the National Academy of Sciences [23] and Reilly [28]

Table 7.6 Possible functions of other heavy metal(loid)s in animals and humans

Element	Possible functions
Arsenic	Various adverse responses to As deprivation diets (<12 μg As kg^{-1} rats and chicks and <35 μg As kg^{-1} goats) have been reported, including: depressed growth, abnormal reproduction (impaired fertility and perinatal mortality); depressed serum triglyceride concentrations and myocardial damage during lactation in goats. Arsenic appears to be involved in the methylation of metabolically or genetically important molecules whose functions are associated with methyl incorporation. Abnormally low As intake in patients undergoing haemodialysis correlated with injuries to their central nervous system, vascular diseases and cancer. Some beneficial effects of supranutritional doses of As in treatment of acute promyelocyte leukaemia through apoptotic (programmed cell death) mechanisms. If humans are found to need As, the requirement would probably only be 12–25 μg d^{-1}.
Cadmium	Cadmium-deprived goats and rats have shown depressed growth which was improved by increasing their intake of Cd. However, Cd has a long body half-life so even slightly elevated intakes could result in harmful accumulations (WHO max safe intake 70 μg d^{-1} for 70 kg person), typical daily intake is 10–20 μg.
Lead	Low dietary intake of Pb has been found to cause adverse effects in pigs and rats (depressed growth, anaemia, elevated serum cholesterol, phospholipds and bile acids; disturbed Fe metabolism, decreased liver glucose). Lead supplementation improved growth and alleviated Fe deficiency in rats. Any requirement for Pb is only likely to be very small (5–50 μg d^{-1}). Toxicity from excessive Pb intakes is much more important and is not dependent upon the route of exposure and can be predicted by blood Pb concentrations. When blood Pb reaches 10–15 μg dL^{-1}, toxic effects can occur in bone development, mental development and blood pressure. Anaemia, nephrotoxicity and more overt neurological impairments occur when blood concentrations are above 30 μg Pb dL^{-1}.
Nickel	Not proven to be essential, but experiments with Ni-deprived animals show it to be a bioactive element with some beneficial functions. Deprivation affects reproductive function in goats and rats, changes carbohydrate and lipid metabolism – possibly through depressed activities of enzymes degrading glucose and enzymes involved in the citric acid cycle. Nickel has beneficial effects in bone and may also have a function affecting Vitamin B12 (Ni can alleviate Vit B12 deficiency). If proved essential, Ni intake should probably be <100 μg d^{-1}.
Tin	Dietary deficiency of Sn has been reported to cause hair loss, depressed growth, response to sound, feed efficiency, heart zinc, tibial Cu and Mn, muscle Fe and Mn, spleen Fe, kidney Fe and lung Mn (Typical intake 1–40 mg Sn).
Vanadium	A bioactive element, whose only proven essential role is in several types of marine algae where it controls bromoperoxidases and iodoperoxidases. In humans and animals, it appears to have insulin-like actions at the cellular level stimulating cellular proliferation and differentiation. Bone abnormalities have been reported in V-deprived goats and so it appears to play a role in the formation and function of bone and connective tissue. Requirement is probably only 1–2 μg d^{-1}.

Based on: WHO [33], Kabata-Pendias and Mukherjee [16], Reilly [28], Neilsen [24] and Asher [4]

Low total concentrations of micronutrients (and most non-essential trace elements) are often found on sandy textured soils (e.g., Podzols) and/or on heavily weathered tropical soils (e.g., Ferralsols) and can give rise single and/or multi-element deficiencies. High soil pH values (>7.0) such as are found on calcareous, heavily limed or saline soils are likely to cause deficiencies of B, Cu, Fe, Mn, Ni and Zn. Multi-element deficiencies are also highly likely on these soils. In contrast, Mo

Table 7.7 Soil factors associated with micronutrient deficiencies

Soil Factor	Micronutrients likely to be deficient or low uptake
Sandy texture (low total concentrations)	B, Co, Cu, Fe, Mn, Mo, Ni, Se, Zn
Heavily weathered tropical soil (low total concentrations)	B, Co, Cu, Fe, Mn, Mo, Ni, Se, Zn
High organic matter content	B, Co, Cu, Fe (calcareous), Mn, Se
Low organic matter content	B, Cu, Zn
Free $CaCO_3$	B, Co, Cu, Fe, Mn, Ni, Zn
High Fe, Mn, Al oxides	Co, Fe, Mo, Se, Zn
Clay-rich soils (liable to waterlogging)	Cu, Mn, Zn
High pH	Co, Cu, Fe, Mn, Ni, Zn
Low pH	Cu, Mn, Mo, Se, Zn
High salt content	Cu, Fe, Mn and Zn
High HCO_3^-	Fe, Zn
Gleying/flooded soil	B, Co, Cu, Se, Zn (especially paddy soils)
Free drainage	Mo
High P status	Cu, Fe, Zn
High N Status	Cu, Zn
High concentrations of other nutrients	Co (Fe & Mn), Cu (Zn), Mn (Fe), Se (S/SO_4^-)

Based largely on Kabata-Pendias [15], Fageria et al. [9] and Alloway [2]

is likely to be highly available in high pH soils, but can be deficient in acid soils. Organic matter-rich soils, such as peats (Histosols), muck soils and heavily manured mineral soils are likely to have low available concentrations of B, Cu, Mn, Se and Zn [2]. However, as shown in Table 7.7, low organic matter contents can also predispose to deficiencies of B, Cu and Zn.

Clay-rich soils which usually have relatively high adsorptive capacities and tend to be imperfectly to poorly drained (gleyed) can be deficient in Cu, Mn and Zn. Paddy soils used for wetland rice production are prone to Zn deficiency, but can have toxic Fe concentrations due to the reduction of insoluble Fe oxides. In general, micronutrient deficiencies in crops and herbage, tend to be reflected in low intakes in animal and human diets. However, in the case of grazing livestock the soil-plant-animal pathway may be bypassed by direct (usually accidental) ingestion of soil and so the amount of metal(loid)s ingested by the animals may not be affected by soil-plant barriers. However, the presence of adsorbent minerals and antagonistic elements in the animal GI tract can modify the availability of the micronutrient to the animal.

7.5 Plant Factors Associated with Micronutrient Deficiencies

The plant factors associated with the onset of deficiencies in crop plants are covered in detail in Chap. 6, but one or more of the following factors are often found to be involved:

- Plant genotype (i.e., micronutrient efficient/inefficient cultivars),
- Nitrogen supply (effects on growth rate, dilution, elements locked up in proteins in foliage),

- Phosphate supply (effects on growth rate – dilution e.g., Cu, and metabolism e.g., Zn)
- Moisture stress (uptake reduced in drought conditions),
- Temperature stress (high and low temperatures),
- High/low light intensity,
- Rooting conditions (restrictions in rooting zone will reduce the volume of soil explored by roots),
- Mycorrhizal infection (increases the effective volume of roots),
- Secretion of root exudates (e.g., phytosiderophores),
- Pathological disease,
- Agrochemicals (e.g., glyphosate-induced deficiencies of Mn & Zn),
- Antagonistic effects of other micronutrients (e.g., Cu–Zn, Fe–Cu, Fe–Mn, Cu–Mn etc.),
- Previous crop species – there is some evidence that the mineralization products of some plant species can render certain micronutrients less available in the soil. An example of this is Cu deficiency in wheat following oil seed rape (canola).

Based on: [2, 7, 9, 12, 13, 19, 22]

7.6 Concluding Comments

This short chapter has been included in this latest edition of ‘Heavy Metals in Soils’ to draw attention to the importance of many heavy metals such as Cu and Zn which are micronutrients in both plants and animals and the metalloid Se, a vitally important micronutrient in animals and humans (see Chap. 16, Sect. 16.4). More details are given in Chaps. 9–17 and 21 dealing with the respective heavy metal(loid)s, but it is useful to see them dealt with as a group, to allow comparisons to be made between them. Ongoing and future research may increase the number of heavy metal(loid)s classed as micronutrients.

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Chapter 8
Critical Loads of Heavy Metals for Soils

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Abstract To enable a precautionary risk assessment for future inputs of metals, steady-state methods have been developed to assess critical loads of metals avoiding long-term risks to food quality and eco-toxicological effects on organisms in soils and surface waters. A critical load for metals equals the load resulting at steady state in a concentration in a compartment (e.g. soil solution, plant, fish) that equals the critical limit for that compartment. This chapter presents an overview of methods to assess critical limits and critical loads of metals, with a focus on cadmium (Cd), lead (Pb), copper (Cu) and zinc (Zn) in soils in relation to impacts on: (i) agriculture (food quality and crop health) and (ii) ecology (plants, invertebrates and soil organisms involved in nutrient cycling processes). Results are presented using generic input data. Furthermore, examples of national and European applications are shown. Results are discussed in view of the uncertainty and applicability of the critical load concept for heavy metals in future agreements on the reduction of metal emissions. It is concluded that for policy applications, dynamic models are also needed to estimate the times involved in attaining a certain chemical state in response to input (deposition, fertilisers or manure) scenarios.

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Keywords Critical loads • Critical limits • Dynamic models • Food quality • Soil organisms ecotoxicological impacts • Human health impacts

8.1 Introduction

8.1.1 Ecotoxicological and Human Health Impacts of Elevated Metal Inputs

Concern about the input of metals to terrestrial ecosystems is related to: (i) the ecotoxicological impact on soil organisms and plants [12, 46] and on aquatic organisms due to runoff to surface water and (ii) the uptake via food chains into animal tissues and products, which may result in health effects on animals and humans [16]. Effects on soil organisms, including micro-organisms/macrofungi and soil fauna, such as nematodes and earthworms, are reduced species diversity, abundance and biomass and changes in microbe mediated processes [8, 31, 72]. More information on these effects are also given in Chap. 5 [39]. Effects on vascular plants are reduced development and growth of roots and shoots (toxicity symptoms), elevated concentrations of starch and total sugar, decreased nutrient contents in foliar tissues (physiological symptoms) and decreased enzymatic is activity (biochemical symptoms) [18, 51]. A review of these phytotoxic effects is given by Balsberg-Påhlsson [7]. Effects on aquatic organisms, including algae, crustacea and fish, include effects on gill function [58], nervous systems [6], and growth and reproduction rates [42]. Environmental quality standards or critical limits (often also denoted as Predicted No Effect Concentrations or PNECs) for metals in soils and surface waters related to those effects serve as a guide in the environmental risk assessment process for those substances.

Next to effects on soil organisms, metals may be transferred via food chains to cause effects on animals and humans (secondary poisoning). This may affect (i) humans by reducing food quality of crops and animal products and (ii) animal health through accumulation in organs of cattle, birds and mammals (secondary poisoning). Heavy metal accumulation in food chains is specifically considered important with respect to Cd and mercury (Hg), and to a lesser extent for Pb, for all of which no biological functions in terrestrial organisms are known [16]. In several countries, there is also concern about the excess input of Cd, Cu and Zn in agriculture [43]. An excess of these metals may cause reduced crop production and in case of Cd it may lead to agricultural products violating food quality criteria [3, 30].

8.1.2 Risk Assessment Approaches for Metal Contamination and the Critical Load Approach

Common practice in risk assessment of metal contamination is to compare present concentrations with critical concentrations at which adverse effects are to be expected. With this approach it is impossible to assess future risks due to metal inputs which may cause accumulation and possibly leads to future exceedance of critical limits. A method to assess future risks is the critical load approach. The United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (LRTAP) defines a critical load as "the highest total input rate of a potential pollutant below which significant harmful effects on defined receptors (e.g. human health, ecosystem structure and function) will not occur in a long-term perspective (at steady state), according to current knowledge" [71]. In defining a critical load, the aim is to achieve long-term sustainability of the ecosystem. In this context, sustainability can be defined as the situation where accumulation of heavy metals does not exceed critical limits in defined ecosystem compartments (e.g. soil solid phase, soil solution, groundwater, plant, sediment, fish etc.). According to its definition, a critical load of a metal equals the load resulting at steady state in a concentration in a compartment that equals the critical limit.

A critical load can be used to optimise the protection of the environment for a given international investment in pollution control by minimising the difference between present loads and critical loads on a regional scale. The concept has been applied successfully in international negotiations on the reduction of atmospheric emissions of nitrogen (N) and sulphur (S). Its use in international negotiations on the reduction of metal emissions is still under debate.

The method to calculate critical loads of metals is based on the balance of all relevant metal fluxes in and out of a considered ecosystem in a (distant) future steady-state situation. First approaches were described in 'Manuals for Calculation of Critical Loads of Heavy Metals in Terrestrial Ecosystems' [19] and aquatic ecosystems [21]. These methods were discussed at various international workshops within the framework of the Coordination Centre for Effects (CCE) of the ICP Modelling & Mapping under the LRTAP Convention [32, 33]. A state-of-the-art methodology manual, developed under the LRTAP Convention, has been adopted for the "priority metals" Cd, Pb and Hg [23, 71]. The focus was on these metals as they are part of the 1998 Heavy Metals Protocol to the LRTAP Convention that has been ratified by 29 countries, and came into effect at the end of 2003. The attention focuses not only on ecotoxicological risks to terrestrial ecosystems, where metal deposition is the only external source, but it also includes human toxicological risks by including agricultural systems. In these systems, the load refers to the input by fertilisers, animal manure (sometimes also sewage sludge) and atmospheric deposition. Until now, the approach has mainly been applied within Europe [e.g. 56] and Canada [28].

8.1.3 Aim of This Chapter

This chapter discusses approaches to derive critical metal loads and presents examples, limiting ourselves to terrestrial ecosystems (soils). We first present an overview of methods to assess critical limits for metal concentrations in soil or soil solution related to ecotoxicological impacts, to human health impacts (food quality criteria for crops and animal products) and animal health impacts (Sect. 8.2). We then describe the methodology to compute critical loads and target loads (Sect. 8.3) followed by results on a local scale, using generic input data, national scale and European scale (Sect. 8.4) Finally, limitations of the approach are discussed in view of the applicability of the critical load concept for heavy metals in future negotiations on the reduction in metal emissions (Sect. 8.5).

8.2 Assessment of Critical Limits for Metals in Soil and Soil Solution

8.2.1 Relevant Receptors and Related Critical Limits

8.2.1.1 Relevant Receptors

With respect to risks on terrestrial ecosystems, a distinction can be made between risks/effects on the health of: (i) soil organisms/processes and plants (primary ecotoxicological risks) and (ii) animals, including both domestic and wild animals and humans that use ground water for drinking water or that consume crops, meat or fish (secondary poisoning). A description of major pathways of metals in terrestrial ecosystems, including the link with aquatic ecosystems, is given in Fig. 8.1.

Relevant receptors in terrestrial ecosystems, distinguishing arable land, grassland and non-agricultural land (forest, heath lands, uplands and peat lands) are presented in Table 8.1. Possible effects on soil organisms and plants (phytotoxicity) and terrestrial fauna are of concern in all types of ecosystems. Food quality criteria are, however, of relevance for arable land and grassland (limits for animal food), whereas possible secondary poisoning effects on animals are relevant in grassland (cattle) and non-agricultural land (wild animals).

8.2.1.2 Related Critical Limits

A critical limit concentration defines the threshold of potential risk to a defined receptor. For most of the receptors or compartments indicated in Table 8.1, critical limits have been defined related to ecotoxicological or human-toxicological risks, such as:

- Soil: critical limits related to effects on soil organisms (micro-organisms and soil invertebrates) and plants (mg kg^{-1}).
- Plants/terrestrial fauna: critical limits in plant tissue, animal products (meat) or target organs, such as kidney, related to effects on plants and/or animals and on humans by consumption (food quality criteria) (mg kg^{-1}).

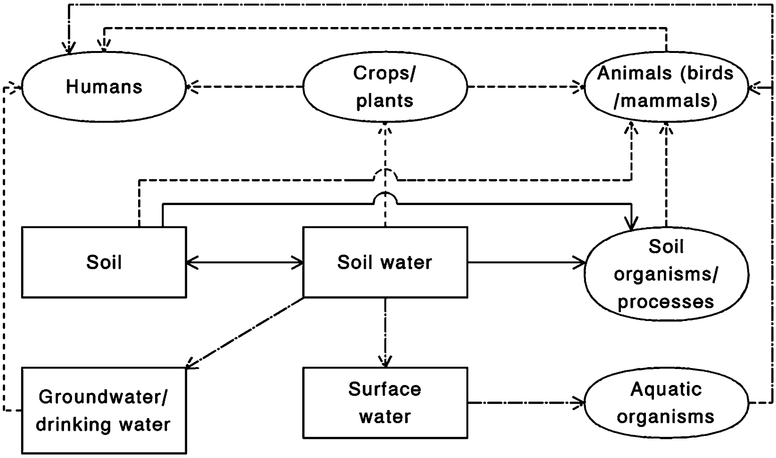

Fig. 8.1 Overview of the fluxes and impact pathways of metals from the soil to other compartments in terrestrial and aquatic ecosystems. *Boxes* are key "pools" and *ovals* are key "receptors" [24]

Table 8.1 Receptors of concern in three main types of terrestrial ecosystems

	Type of ecosystem		
Receptors of concern	Arable land	Grassland	Non-agricultural land
Ecosystem			
Soil micro-organisms	+	+	+
Soil invertebrates	+	+	+
Agricultural plants	+	+	–
Wild plants	–	–	+
Human health/animal health			
Plants			
Food crops (human health)	+	–	–
Fodder crops (animal health)	–	+	–
Ground water[a] (human health)	+	+	+
Animals			
Cattle (human and animal health)	–	+	+
Birds/mammals (animal health)	+	+	+

[a] This refers specifically to ground water used as drinking water

- Ground water: critical limits in drinking water related to effects on humans by consumption (μg L^{-1}).
- Humans: acceptable daily intake or ADI (μg kg^{-1} day^{-1}). This dose is the quantity of a compound to which man can be orally exposed, on the basis of body weight, without experiencing adverse effects on health.

Critical limits related to ecotoxicological effects on soil organisms and plants are limited to metal contents in the soil, based on No Observed Effect Concentrations (NOECs) from laboratory studies with plants and soil organisms, such as soil

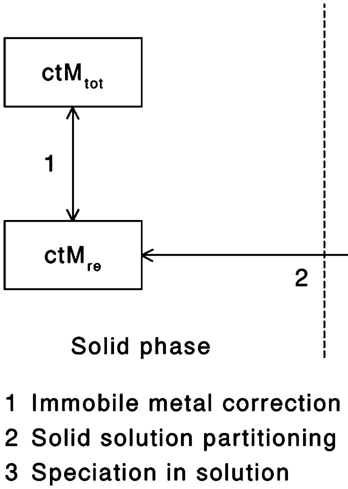

Fig. 8.2 Overview of relations between metal concentrations in soil solid phase and soil solution

microbiota and soil invertebrates [70]. The risks from heavy metal pollution, however, depend on their availability which is influenced by soil properties such as pH, clay and organic matter content [9, 35, 55]. The use of a single soil metal concentration as a critical limit for ecotoxicological effects upon soil organisms has therefore been criticized [2], since it does not account for observed variations in the toxicity of cationic metals among soils of differing chemistry [59]. The impacts of soil properties on the bioavailability and toxicity of metals thus have to be accounted for in critical limits assessment.

Effects on microorganisms, plants and, to a large extent, also to invertebrates occur through the soil solution [52]. In accordance with the principles of the free ion activity model (FIAM) [15, 44] and the Biotic Ligand Model (BLM) [27, 60], metal uptake leading to toxicity can be considered to occur by interaction of the free metal ion (FMI) in soil solution (e.g. Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}) with the organism. The extent of this interaction, and thus the degree of toxic effect due to a given FMI concentration, will also depend upon the concentrations of solution cations (e.g. H^+, Na^+, Ca^{2+}) that in the BLM framework compete with the toxic metal for binding to the organism. Thus, an approach to set critical limits for FMI is in particularly appropriate to evaluate the risks of effects. Furthermore, in view of critical load assessments for terrestrial ecosystems, there is a need for critical metal concentrations in soil solution since the critical metal leaching rate is the most important term in deriving critical loads. Since free metal ion concentrations in soil solution are hardly ever measured, such concentrations need to be derived using models for solid-solution partitioning and speciation of metals in soil solution (Fig. 8.2). The use of empirical models for solid-solution partitioning which relate metal concentrations in solution to metal concentrations in the solid phase and soil properties (so called transfer functions) and the approach to use them in deriving critical limits for Cd, Pb, Cu and Zn in soil and soil solution is presented below

Table 8.2 Values for α_{CRIT} and γ_{CRIT} used to calculate critical limits for FMI concentrations in soil solution

	FMI concentration	
Metal	α_{CRIT}	γ_{CRIT}
Cd	−0.32	−6.34
Cu	−0.91	−3.80
Pb	−1.23	−2.05
Zn	−0.31	−4.63

(Sect. 8.2.2). Furthermore, critical limits related to human-toxicological risks are mainly accounted for by quality criteria for metals in food crops, animal products (cows/sheep), fish and drinking water (ground water) consumed by them. These critical limits need to be converted to critical soil metal concentrations as described in detail in Sect. 8.2.3.

8.2.2 Critical Limits for Soil Metal Concentrations Related to Ecotoxicological Impacts

8.2.2.1 Critical Free Metal Ion Concentrations in Soil Solution

Critical free metal ion (FMI) concentrations in soil solution can in principle be derived from critical reactive metal concentrations (see also below) using a transfer function (see Fig. 8.2). Lofts et al. [41] applied such a transfer function and directly derived critical dissolved FMI concentrations based on available NOEC data for soil organisms and plants, together with soil properties affecting its availability (pH, organic matter content). The critical FMI concentrations were derived as a function of soil solution pH, according to a procedure described in Lofts et al. [41] and De Vries et al. [24]:

$$log[M]_{free,crit} = a_{crit} \cdot pH + y_{crit} \tag{8.1}$$

where $[M]_{free,crit}$ is the critical FMI concentration (mol L^{-1}). The pH dependence of the critical FMI concentration is considered to result from a ‘protective’ effect of H^+ against toxicity, resulting from the competitive interactions of solution cations with the organism, as noted in Sect. 8.2.1. Values used for the empirical coefficients α_{CRIT} and γ_{CRIT} are given in Table 8.2. These critical FMI functions are based on: (i) data sets with both NOEC or EC10 (Effect Concentrations affecting 10% of the organisms) toxicity data for soil from major organisms including information on soil properties affecting bioavailability, (ii) transfer functions, describing the relation between FMI concentration and reactive metal content (assumed to equal the added metal content in the toxicity test) and (iii) statistical approaches for deriving limit functions and applying a 95% protection level (HC_5). The data set included (i) decomposers, comprising micro-organisms or microbe-mediated soil processes (e.g. enzymatic activity), (ii) consumers, such as invertebrates (earthworms and arthropods) and (iii) primary producers, specifically plants, drawn from several draft reports on EU Risk Assessment procedures for these metals. More information on the approach and the data sets used is given in Lofts et al. [41] and De Vries et al. [24].

8.2.2.2 Critical Total Metal Concentrations in Soil Solution

When the critical limit is defined in terms of a critical FMI concentration, the total metal concentration in soil solution has to be determined as the sum of the concentration of (i) the FMI, $[M]_{free}$, (ii) dissolved inorganic complexes, $[M]_{DIC}$, such as MOH^+, $MHCO_3{}^+$, MCl^+, and (iii) metals bound to dissolved organic matter, $[M]_{DOM}$, according to:

$$[M]_{tot} = [M]_{free} + [M]_{DIC} + [M]_{DOM} \cdot [DOM] \tag{8.2}$$

where $[M]_{tot}$ is the total metal concentration (mol m^{-3}), $[M]_{DOM}$ is the metal concentration bound to dissolved organic matter (mol kg^{-1} DOM) and $[DOM]$ is the concentration of dissolved organic matter (kg m^{-3}). By assuming geochemical equilibrium, the partitioning and speciation of metals over the various fractions can be calculated. Given the free metal activity the concentrations of the other metal species can be estimated with a equilibrium speciation model. A model often used is the Windermere Humic Aqueous Model (WHAM) model VI, further denoted as WHAM-VI [61, 62]. The calculation takes into account the dependence of metal binding to DOM on pH and competitive effects due to major cationic species of Mg, Al, Ca and Fe [64, 66]. A customised program (W6-MTC), based on WHAM-VI was used; in one of the model application examples (Section 8.4.1) for a detailed description of the calculation procedure see De Vries et al. [23]. Binding of metals to DOM is calculated assuming that 65% of DOM acts as fulvic acid and 35% of DOM is not involved in metal binding. This fraction is based on application of WHAM-VI to field and laboratory data for waters and soils involving Al [65, 66], Cu [14, 29, 73], and Cd [63]. DOM is calculated as 2·DOC, assuming a carbon content of 50%.

8.2.2.3 Critical Reactive and Total Metal Concentrations in the Soil Solid Phase

Critical reactive soil metal concentrations related to ecotoxicological effects on soil organisms and plants have also been derived by Lofts et al. [41] on the basis of NOECs for the concentration of added metal in laboratory experiments. These added metal concentrations are assumed to equal reactive soil metal concentrations that are potentially available for exchange with the soil solution. It excludes metals that are incorporated in mineral lattices which are not directly

Table 8.3 Values for the coefficients b_0–b_2 to compute the critical limit for the reactive soil metal content (in mg kg^{-1}) for Cd, Pb, Cu and Zn as a function of soil properties [24]

Metal	b_0	b_1	b_2
Cd	−2.27	0.33	1.00
Pb	0.58	0.11	0.66
Cu	0.26	0.02	0.68
Zn	−0.74	0.14	1.07

Units converted from mol g^{-1} to mg kg^{-1}

available for dissolution. For field soils, the reactive fraction is generally established by an extraction using 0.43 M HNO_3 solution or by using an EDTA extraction. The impacts of soil properties affecting the bioavailability and toxicity of metals, have been accounted for by relating the critical value to soil solution pH and soil organic matter content, using a procedure described in Lofts et al. [41] and De Vries et al. [24]:

$$\log ctM_{re,crit} = b_0 + b_1 \cdot pH + b_2 \cdot \log OM \tag{8.3}$$

where $ctM_{re,crit}$ is the critical reactive metal concentration in the soil (mg kg^{-1}); pH is the soil solution pH and *OM is* soil organic matter content (%). Values derived for b_0, b_1 and b_2 are given in Table 8.3. Results are based on the same data sets as those for which the critical FMI concentrations were derived. Critical total metal concentrations, which are relevant for the assessment of target loads, can be derived by a relationship with concentrations of reactive metal according to Römkens et al. [53]:

$$\log ctM_{tot,crit} = c_0 + c_1 \cdot \log ctM_{re,crit} + c_2 \cdot \log OM + c_3 \cdot \log clay \tag{8.4}$$

where $ctM_{tot,crit}$ is the critical total (added) metal concentration in the soil (mg kg^{-1}) and *clay* is the clay content (%); and values for c_0–c_3 are given in Table 8.4. Regression relations were derived from a Dutch dataset containing 630 soil samples which were both extracted with 0.43 M HNO_3 and *aqua regia* [53].

8.2.3 Critical Limits for Soil Metal Concentrations Related to Health Impacts

Critical total metal concentrations in soil related to agricultural impacts can be derived from critical metal concentrations in plants or animal organs in terms of food quality or crop/animal health, combined with relationships for soil-plant transfer, soil-animal transfer and plant-animal transfer [26]. Food quality criteria for metals in crops or target organs (liver and kidney) of grazing animals are available for Cd and Pb only, whereas data for the toxic impacts on the crop or animal itself can be derived for all metals based on an acceptable daily intake (ADI).

Table 8.4 Values for the coefficients c_0–c_3 in the relationship between reactive, (0.43N HNO_3), and pseudo-total (aqua regia) soil concentrations of Cd, Pb, Cu and Zn (8.4), using a Dutch dataset [53]

Metal	c_0	c_1	c_2	c_3	R_{adj}^2	se-y_{est}[a]
Cd	0.028	0.877	0.009	0.081	0.96	0.10
Pb	0.323	0.810	0.035	0.136	0.92	0.13
Cu	0.318	0.761	0.044	0.191	0.94	0.10
Zn	0.614	0.753	−0.107	0.275	0.96	0.12

The relationships hold for both M_{tot} and M_{re} in mg kg^{-1}

[a] Standard error of the y-estimate on a logarithmic basis

Table 8.5 Values for the coefficients a_0–a_3 and n in the soil– plant relations for Cd in grass, maize, wheat, potatoes and sugar beet

Crop	a_0	a_1	a_2	a_3	n	R^2	se-y_{est}[a]
Grass	1.45	−0.38	–	–	1.22	0.63	0.23
Maize	0.90	−0.21	–	−0.32	1.08	0.50	0.28
Sugar beet	1.33	−0.22	–	−0.13	0.62	0.83	0.15
Wheat	0.22	−0.12	−0.33	−0.04	0.62	0.64	0.20
Lettuce	2.55	−0.33	−0.39	−0.19	0.85	0.71	0.08

[a] Standard error of the y-estimate on a logarithmic basis

8.2.3.1 Critical Soil Metal Concentrations Related to Food Quality Criteria for Crops

Critical soil metal concentrations can be derived from critical metal contents in plants, related to food quality or crop health, from a non-linear relationship between both metal concentrations, accounting for the impact of soil properties that control the (bio)availability of metals in soils [1, 13], according to De Vries et al. [25]:

$$\log ctM_{plant,crit} = a_0 + a_1 \cdot pH_{KCl} + a_2 \cdot \log OM + a_3 \cdot \log clay + n \cdot \log ctM_{tot,crit} \tag{8.5}$$

where $ctM_{plant,crit}$ is the critical limit for metal concentration in plant (mg kg^{-1}) and n is a coefficient describing the non-linear relationship between the metal concentration in plant and in soil. Values for the various regression coefficients in Eq. 8.5 have been derived for Cd, Cu, Pb and Zn in grass, maize, sugar beet, wheat, potatoes, lettuce, endive and spinach [54]. The relationships obtained for Cd and Zn were much better than those for Cu and Pb. For the majority of crops, soil-plant relationships for Cu and Pb are not statistically significant and can therefore not be used. Furthermore, the critical limit of Zn related to phytotoxic effects by far exceeds the measured plant values in the database, which limits the application of the regression model (strong extrapolation). Critical soil concentrations related to food quality criteria are thus mainly relevant for Cd. Values for a_0–a_3 and n for Cd, derived for Dutch soils, are given in Table 8.5. More information on soil-plant relationships is also given in Chap. 6 [17].

8.2.3.2 Critical Soil Metal Concentrations Related to Food Quality Criteria for Animal Products and Impacts on Animal Health

The derivation of critical soil metal concentrations from acceptable daily intakes (ADI) by animals is relevant for grazing animals (specifically cows). Acceptable daily intakes (ADI) of metals can be related to critical metal contents in fodder (grass) and soil according to:

$$ctM_{plant,crit} \cdot I_{plant} + ctM_{tot,crit} \cdot I_{soil} = ADI \tag{8.6}$$

where ADI is acceptable daily intake of metals (mg d^{-1}); I_{plant} is intake of plants (fodder) (kg d^{-1}) and I_{soil} is intake of soil (kg d^{-1}). The critical soil metal concentration can be derived by combining Eqs. 8.5 and 8.6, in which $ctM_{tot,crit}$ is solved iteratively using a given ADI and given coefficients in the soil-plant relationship (see Table 8.5 for grass). As with food quality criteria for plants, the derivation of a critical soil metal concentration from ADI values is mainly relevant for Cd. Information on the derivation of ADI values for Cd, using food quality criteria for Cd in the kidney of cows, and data on the intake of plants and soil are given in De Vries et al [25].

8.3 Concepts and Calculation Methods to Compute Critical Loads and Target Loads

8.3.1 Concepts

A critical metal load equals the input rate that will in the long run – at steady state – lead to the critical metal concentration (critical limit) for a defined receptor. A critical load does not consider finite buffers for the metal and thus neglects the delays between the (non-exceedance) of the critical load and the (non-violation) of the critical limit. To gain insight into this temporal behaviour, dynamic models are needed. The various possibilities that can occur are graphically illustrated in Fig. 8.3, showing the change in metal concentration as a function of time for various combinations of initial concentrations, the critical concentration and steady-state concentrations for a constant input. In the left figure, the initial metal concentration is below the critical limit. A metal input below the critical load results in a steady-state concentration below the critical limit. An input above the critical load results in a steady state above the critical limit and it takes a finite time to exceed this critical limit, called the damage delay time (DDT). In the right figure, the concentration is initially above the critical limit (in other words, the system is already potentially at risk). An input equal to the critical load results (technically, after infinite time) in a steady state, with the concentration equalling the critical limit. Again, inputs above/below the critical load eventually result in steady states

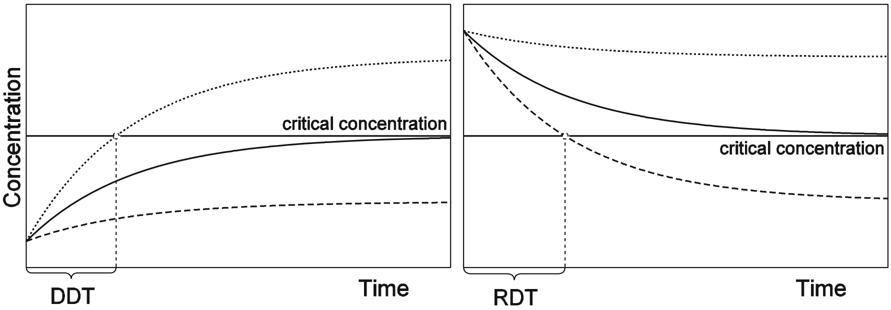

Fig. 8.3 Schematic diagram showing the change in metal concentration at constant input as a function of time with the initial concentration below (*left*) and above (*right*) the critical concentration (*DDT* damage delay time, *RDT* recovery delay time). The *dotted*/*solid*/*dashed* lines are for metal inputs above/at/below the critical load

above/below the critical limit. And the time it takes to reach the critical limit from above is called the recovery delay time (RDT). An in-depth discussion and illustrative examples of these concepts can be found in Posch and De Vries [49].

8.3.2 Steady-State Model to Compute Critical Loads

Critical loads are calculated from a simple mass balance of all relevant metal fluxes into and out of the relevant soil compartment at steady state. As in the Mapping Manual [71] and its background document [23], the metal fluxes considered are limited to the metal input, M_{in}, the net metal uptake by the harvested parts of plants, M_u, (both in g ha^{-1} a^{-1}) and the metal leaching/runoff, which balance at steady state:

$$M_{in} = M_u + Q \cdot [M]_{tot} \tag{8.7}$$

where Q is the drainage water flux and $[M]_{tot}$ is the total soil water concentration of the metal (mg m^{-3}). Various assumptions are made in this steady-state model: (i) the soil is homogeneously mixed, (ii) the soil is in an oxidised state and metal partitioning can be described with equilibrium sorption and complexation with DOC, (iii) the transport of water and metals only occurs vertically (no metal gain or loss by seepage flow, surface runoff or bypass flow), (iv) metal weathering and erosion are not considered, (v) the internal cycling of metals is neglected, and (vi) the metal input is chemically reactive and 100% available for exchange with the solution phase. The limitations due to these assumptions are discussed in De Vries et al. [23] and in De Vries and Groenenberg [20]. The critical load of metal M for a given effect, $CL(M)$, is the input flux at which the steady-state metal concentration is at its critical value:

$$CL(M) = M_u + Q \cdot [M]_{tot,crit} \tag{8.8}$$

where $[M]_{tot,crit}$ is the critical total soil water concentration (mg m^{-3}). A critical limit is either given directly (e.g., for drinking water quality) or converted from e.g. a food or soil quality criterion by methodologies specific to each indicator, as described in Sects. 8.2.2 and 8.2.3. These methodologies may require additional input variables. For example, the calculation of critical total soil water concentrations for Cd and Pb, relating to ecotoxicological effects, uses a geochemical speciation model (e.g., WHAM-VI) and requires inputs of soil water pH, dissolved organic carbon, % soil organic matter, and partial pressure of CO_2 in the soil atmosphere. A full description of methodologies for calculating $[M]_{tot,crit}$ for the different indicators can be found in the Mapping Manual [71] and its background document [23].

8.3.3 Simple Dynamic Models to Compute Target Loads

Critical loads are by definition a tool for quantifying the potential risk 'in the long term', where 'long term' means the length of time to (approximately) reach steady state. Dynamic modelling of metal cycling in terrestrial systems [20, 45, 49] indicates that, starting from the current situation, it may take decades to millennia to reach a steady state. Consequently, in a soil in which the critical limit is currently exceeded, an input of metals equal to the critical load would cause the system to remain at potential risk for a (very) long time. This time could be reduced by requiring a load *below* the critical load, termed a 'target load'. A target load is defined as 'the deposition for which a pre-defined chemical or biological status is reached in the specified target year and maintained (or improved) thereafter' [50]. Target loads are currently quantified under the LRTAP Convention for acidifying pollutants; and an approach for metals has been described by Posch and De Vries [49]. Target loads might also find application in maintaining concentrations of essential trace elements, such as copper and zinc, where this is important for agriculture and livestock rearing.

The computation of target loads requires that the changes in the solid and liquid metal pools are included in the model, which thus becomes:

$$\rho\, z \frac{d}{dt} ctM_{tot} + \theta\, z \frac{d}{dt}[M]_{tot} = M_{in} - M_u - Q \cdot [M]_{tot} \tag{8.9}$$

Where ctM_{tot} is the total content of heavy metal in the soil solid phase (mg kg^{-1}), ρ is the bulk density of the soil (kg m^{-3}), θ is the water content (m^3 m^{-3}) and z the thickness of the soil layer (m). Setting the time-derivatives in Eq. 8.9 to zero yields the steady-state equation (Eq. 8.7). To solve Eq. 8.9, a relationship between the total content and the total concentration in solution is required. In general, this is assumed to be in the form of a Freundlich isotherm:

$$ctM_{tot} = K \cdot [M]_{tot}^{n} \tag{8.10}$$

with a metal-dependent exponent n and a site-specific constant K. In the case of a linear relation between the metal content in the solid phase and the concentration in solution ($n = 1$), Eq. 8.9 can be solved analytically in terms of elementary functions (exponentials) and the concentration as a function of time t is obtained as:

$$[M]_{tot}(t) = [M]_{tot,ss} + ([M]_{tot,0} - [M]_{tot,ss})e^{-t/t_c} \tag{8.11}$$

where $[M]_{tot,ss} = (M_{in}–M_u)/Q$ is the steady-state concentration for the constant input M_{in}, $[M]_{tot,0}$ is the initial concentration in soil solution, and t_c is given by:

$$t_c = \frac{\rho \cdot K \cdot z + \theta \cdot z}{Q} \tag{8.12}$$

The quantity t_c has the dimension of a time and is characteristic for the system under consideration; t_c is also called e-folding time, i.e. the time required to decrease a quantity to 37% of the original amount. It is the total metal pool in the soil at steady state divided by the steady-state net metal input, $Q \cdot [M]_{tot,ss}$. The characteristic time t_c is thus the time needed to completely fill the soil metal pool with (steady-state) net inputs. From Eq. 8.11 also the time to reach a pre-scribed concentration can be easily derived. For example, for $[M]_{tot,ss} > [M]_{tot,crit} > [M]_{tot,0}$ (see left panel in Fig. 8.3) the damage delay time, DDT, is obtained as:

$$DDT = t_c \cdot \log \frac{[M]_{tot,ss} - [M]_{tot,0}}{[M]_{tot,ss} - [M]_{tot,crit}} \tag{8.13}$$

The same formula holds for the recovery delay time, *RDT*; in this case $[M]_{tot,ss} < [M]_{tot,crit} < [M]_{tot,0}$ (see right panel in Fig. 8.3). In the linear case also an explicit expression for the target load, $TL(M)$, can be derived for any given target year t_{tar}:

$$TL(M) = M_u + \frac{Q}{1 - e^{-t_{tar}/t_c}}\left([M]_{tot,crit} - [M]_{tot,0} \cdot e^{-t_{tar}/t_c}\right) \tag{8.14}$$

This equation has been used to compute target loads of Cd, Cu, Pb and Zn for a generic deciduous forest on five major soils in the Netherlands differing in texture and organic matter content [20]. The amount of metal in the soil solution is in most cases small compared to the total amount of metals in the solid phase. Therefore the change in the liquid phase is often neglected in simple dynamic models (this can be done by setting $\theta = 0$ in Eq. 8.10). For example, Posch and De Vries [49] investigated the solutions of Eq. 8.9 for $\theta = 0$ for the general non-linear case of metal partitioning (Eq. 8.10). Also in this case a characteristic time can be defined which, however, is also dependent on the constant net metal input:

$$t_c = \frac{\rho \cdot z \cdot K}{Q^n \cdot (M_{in} - M_u)^{1-n}} \tag{8.15}$$

A comparable approach is the CEH Simple Dynamic Model for Metals (SDMM) [4, 5].

8.4 Examples of Critical Load and Target Load Calculations for Terrestrial Ecosystems

8.4.1 *Critical Loads and Target Loads of Cadmium, Lead, Copper and Zinc for Generic Soil Types*

De Vries and Groenenberg [20] presented calculation examples for Cd, Cu, Pb and Zn for a deciduous forest on five major soils differing in texture and organic matter content, including a non-calcareous sandy soil and a loess, clay and peat soil. The influence of soil type on the critical loads and target loads for Cd, Pb, Cu and Zn in the mineral layer is shown in Table 8.6 using the approach described in this chapter (Eq. 8.8 for critical loads and Eq. 8.14 for target loads). The small differences that occur are the result of differences in hydrology, forest growth, pH and DOC concentrations. Critical loads for Cd and Zn do not differ too much for the different soils, but for Cu and Pb a larger variation is found. This is due to the fact that the total concentration of these metals (including metal bound to DOC) depends much more strongly on pH and DOC concentration than the Cd and Zn concentrations. The highest CLs are calculated for peat soils because of the high DOC concentration. The target loads are significantly larger than the critical loads, specifically for Cu and Pb. This implies that the present metal content is not yet in equilibrium with deposition levels for the different soils. The impact of soil type on the target loads is limited. For Cd the target loads are highest for clay soils whereas the reverse is true for Cu and Zn. For Pb the lowest target loads were calculated for loess soils.

The examples by De Vries and Groenenberg [20] assume a linear relationship between soil and dissolved metal. Posch and De Vries [49] computed characteristic times for sand, clay and peat soils using average Dutch data for grasslands and a uniform soil depth $z = 0.1$ m, while accounting for non-linear speciation (Table 8.7). As can be seen, Pb shows by far the slowest response for all soil classes, whereas Zn shows the widest variability among different soils. In general, the characteristic times for all metals and soils listed show that steady state is reached very slowly, and that they are far beyond the time horizons usually considered in (environmental) policies.

Table 8.6 Critical loads and target loads for Cd, Cu, Pb and Zn for different soil types

	Critical load (mg m^{-2} $year^{-1}$)				Target load (mg m^{-2} $year^{-1}$)			
Soil type	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Sand	1.5	12	9.6	47	1.7	65	38	64
Loess	1.0	5.0	5.0	39	1.6	75	17	73
Clay	2.7	14	5.6	53	3.1	38	71	49
Peat	1.9	28	20	62	1.9	72	59	62

Table 8.7 Characteristic times t_c of Cd, Pb, Cu and Zn for sand, clay and peat soils computed from the average data for grasslands in the Netherlands

	Characteristic time t_c (year)			
Soil type	Cd ($n = 0.50$)	Pb ($n = 0.67$)	Cu ($n = 0.51$)	Zn ($n = 0.61$)
Sand	297	2,002	225	148
Clay	1,179	5,435	643	1,296
Peat	648	4,234	491	342

8.4.2 Critical Loads and Exceedances of Cadmium, Lead, Copper and Zinc for Natural and Semi-natural Habitats in the United Kingdom

Critical loads and limits and their exceedances of Cu, Zn, Cd and Pb have been calculated and mapped for the entire United Kingdom to assess potential environmental effects in different habitats [4, 5, 38]. The results are summarised in Table 8.8. Critical loads are highest in the north and west, and at higher altitudes, where soils tend to be acid and runoff is high. The total area of critical load exceedance is greatest for Pb, followed by Zn and Cd, most instances occurring in the south and east of the country, where critical loads are lower. Forested ecosystems are most vulnerable, due to the greater scavenging effects of the vegetation. It is difficult to generalise about current soil metal levels in relation to critical limits. The total area of critical limit exceedance is greatest for Zn, the main areas affected being near to the old industrial centres of south Wales, northern England and the Central Lowlands of Scotland. Cadmium is the least problematic of the four metals. Considering all four metals together, only in a very few locations are both critical loads and critical limits exceeded. The low degree of critical limit exceedance for Pb, despite the fairly high critical load exceedance, may reflect the long times required to approach steady state (see the aspect of *time scales* in Sect. 8.5).

8.4.3 Critical Loads of Cadmium, Lead and Mercury at the European Scale

The methodological manual, developed under the LRTAP Convention, has been adopted for the metals Cd, Pb and Hg [23, 71]. Critical loads of these metals have been derived for European ecosystems using human and environmental endpoints in the framework of activities under the LRTAP Convention. Altogether, 18 countries submitted critical loads of heavy metals. Critical loads of Cd, Pb and Hg were computed by 17, 17 and 10 countries, respectively, addressing either ecotoxicological effects on aquatic and terrestrial ecosystems or human health effects. Table 8.9 presents the indicators used in the computation of critical loads, limited to ecotoxicological effects on terrestrial ecosystems and human health effects. Critical loads were not calculated for animal products nor a CL(Hg) for

Table 8.8 Exceedances of critical loads and critical limits for UK natural and semi-natural habitats, expressed as percentages of total area

		Exceedances (%)				
Type of exceedance	Metal	Forests	Grasslands	Heathlands	Bogs	Total
None	Cu	57	79	98	99	80
	Zn	36	51	74	74	56
	Cd	91	92	95	99	92
	Pb	60	96	99	99	86
Critical load	Cu	13	3	0	0	5
	Zn	17	5	0	0	6
	Cd	0	0	0	0	0
	Pb	40	3	0	0	13
Critical limit	Cu	12	13	2	1	8
	Zn	29	40	26	26	31
	Cd	9	8	5	1	8
	Pb	0	1	1	1	1
Critical load and critical limit	Cu	18	5	0	0	7
	Zn	18	4	0	0	7
	Cd	0	0	0	0	0
	Pb	0	0	0	0	0
Area (km^2)[a]	–	15,709	14,144	18,934	4,019	52,806

[a] Areas for Cd are 10,295, 7,971, 3,222, 1,015 and 22,503 km^2 respectively because data for Scotland are lacking

Table 8.9 Overview of indicators used in the computation of critical loads

Endpoints	Heavy metals of concern	Land cover types to be considered	Indicator/critical limit
Human health effects	Cd, Pb, Hg	All ecosystems	Total concentration in soil water below the rooting zone (to protect ground water)
	Cd, Pb, Hg	Arable	Content in food, fodder and crops
	Cd, Pb, Hg	Grassland	Content in grass and animal products (cows, sheep)
Ecosystem functions	Cd, Pb	Arable land, grassland, non-agricultural	Free ion concentration in view of effects on soil micro-organisms, plants and invertebrates
	Hg	Forest soils	Total concentration in humus layer in view of effects on soil micro organisms and invertebrates

food crops. Critical loads maps of the metals have been published, based on results by the various European countries, as presented in Slootweg et al. [56]. The European synthesis of the country submissions was done by first taking the minimum critical load of health effects and of ecosystem effects for each ecosystem. Then for each grid cell and for each metal, the fifth percentile of the distribution of these minimum critical loads was calculated for health effects and ecosystem effects separately. Figure 8.4 shows the fifth percentile of the minimum

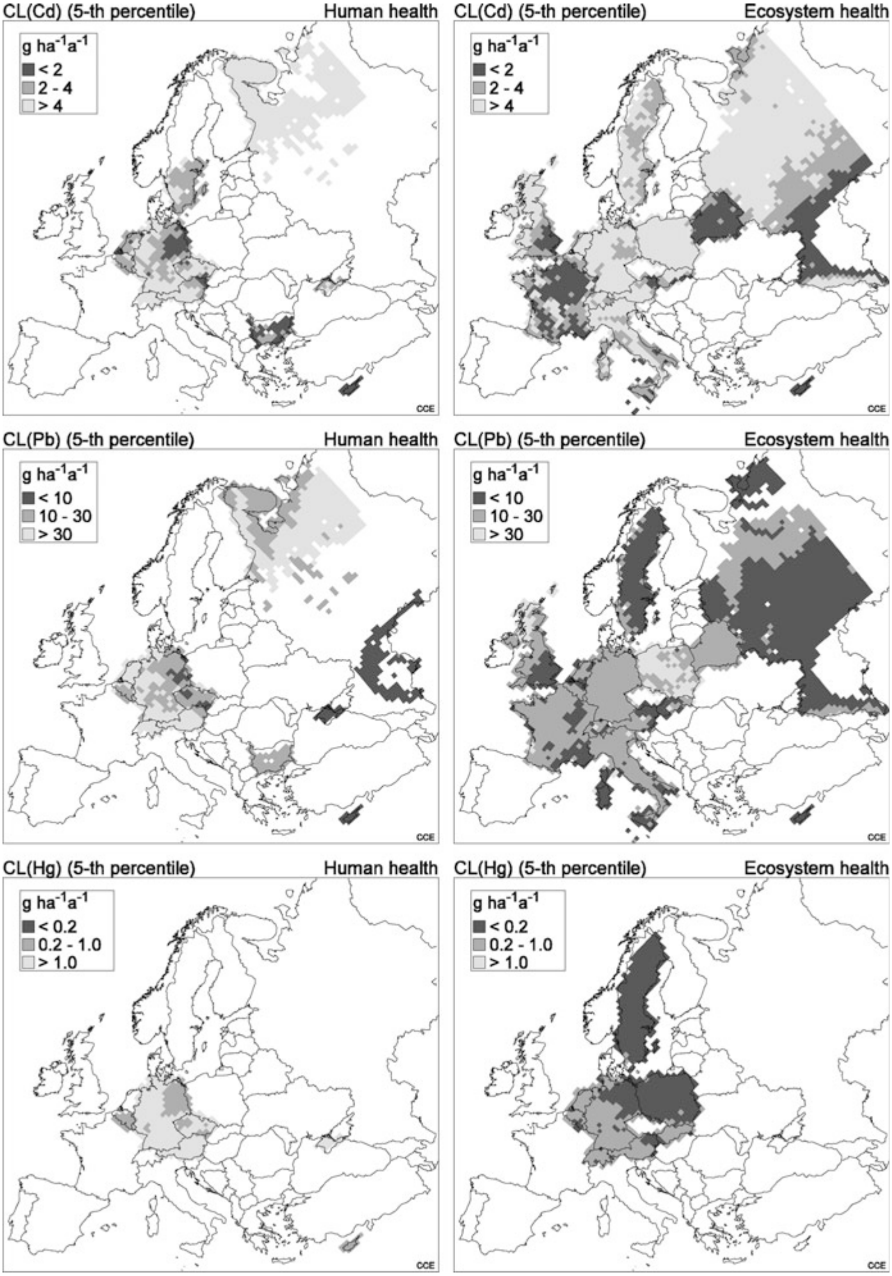

Fig. 8.4 Critical loads of cadmium (*top*), lead (*middle*) and mercury (*bottom*) aiming to protect 95% of the terrestrial ecosystems from risks for human health (*left*) and ecosystem health (*right*) (see Table 8.9). The *darker* the shade the more sensitive the area

critical loads for human health (left) and ecosystem health (right) of Cd (top), Pb (middle) and Hg (bottom), while limiting the results to terrestrial ecosystems.

Depositions were compared to critical loads to identify areas where ecosystems are at risk, i.e. where deposition exceeds critical loads. Depositions were computed with a long-range atmospheric dispersion model by the EMEP Meteorological Synthesizing Centre East under the LRTAP Convention. The methods used are described in Ilyin and Dutchak [40]. Results showed that the risks of effects of Pb are more widespread than those of Cd.

8.5 Issues for Consideration in Deriving Critical Loads

8.5.1 Choice of Receptors and Exposure Pathways and Derivation of Critical Limits

The choice of receptors of potential concern is crucial in quantifying critical limits. The prioritization of these receptors and identification of important exposure pathways should occur *a priori* based on factors such as land use and societal/political considerations. Such analysis should include identification of exposure pathways, apportionment of total exposure to different pathways including via the food chain, and interactive effects of contaminants on exposure. Exposure pathways and quantification of exposure are crucial in quantifying critical limits. Transfer along food chains needs to be considered in the context of the speciation of metals within organisms and the likelihood of their becoming available higher up the food chain. The approach to derive critical soils limits and related critical loads, in view of human and animal health aspects (including the occurrence of bioaccumulation) is presented in Sect. 8.2.3 and reviewed in detail in De Vries et al. [25].

8.5.2 Reliability of the Critical Loads and Target Loads

8.5.2.1 Parameters Influencing the Reliability

The reliability of critical loads and target loads mainly depends on the reliability of the various parameters determining these loads. Both loads are influenced by metal uptake (yield and metal content in stem wood) and the water flux leaving the root zone. In the case of CLs, the uncertainty is further influenced by the critical dissolved metal concentration, while target loads are also influenced by the present metal content in soil and the Freundlich adsorption constant, K_f, which in turn is influenced by the uncertainty in the transfer function coefficients and soil properties (specifically pH and soil organic content). Ashmore et al. [4] concluded from an uncertainty analysis that the uncertainty in the terms α_{CRIT} and γ_{CRIT} in the critical

Table 8.10 Mean absolute errors of dissolved total metal concentrations (mg m^{-3}) calculated with W6-MTC compared to measured concentrations using measured and default values for DOC

	Mean absolute error (log-concentration)	
Metal	DOC measured	DOC default
Cd	0.32	0.38
Cu	0.40	0.57
Pb	0.45	0.55
Zn	0.11	0.13

limit function dominates the uncertainty in critical loads. As mentioned by these authors, this reflects the limited database available for the derivation of the critical limit function. The uncertainty in the critical dissolved total metal concentration is further determined by the uncertainty in the chemical speciation model, such as W6-MTC, calculating total metal concentrations from free metal ion concentrations. With respect to target loads, the uncertainty in K_f is most relevant. Both aspects are discussed below.

8.5.2.2 Speciation Modelling in Soil Solution

The uncertainty of the calculation of total metal concentrations from free metal concentrations with a chemical speciation model, such as WHAM-VI, is due to uncertainties in the model approach, the model inputs (DOC, Al and Fe concentrations in solution) and the parameterisation of the model. Especially the variable fraction and binding properties of fulvic acids in dissolved organic matter contribute to substantial uncertainty in predicted metal speciation [36]. To get an idea of the adequacy of such an approach, De Vries and Groenenberg [20] used the WHAM-VI model to calculate total metal concentrations from FMI activities, similar to the approach in the CL calculations, for datasets in which both total and FMI concentrations in solution were measured [47, 48, 74]. The input data to WHAM-VI were the FMI activity, the organic matter content, the pH and DOC. Because DOC is usually not available for CL mapping, they also made calculations in which DOC was set to standard values from to the mapping manual [23]. The Mean Absolute Error (MAE) of the log-concentration (Table 8.10) varied between 0.11 for Zn and 0.45 for Pb when using the measured DOC concentrations. This means that the concentrations on a linear scale vary by a factor 1.3–2.8. The error is largest for the strongly complexing metals Cu and Pb, for which calculations are also most sensitive to variation in estimated DOC concentrations (compare DOC measured and DOC default in Table 8.10).

8.5.2.3 Uncertainties in Partition Relationships Between Soil and Soil Solution

Unlike critical loads, target loads are strongly influenced by the transfer functions for solid solution partitioning of metals. Sorption and ion exchange are reasonably

Table 8.11 Calculated and measured dissolved total metal concentrations in the mineral topsoil of 56 soil samples in five land-use types in the UK

	Dissolved total metal concentration (mg m^{-3})	
Metal	Calculated	Measured
Cd	0.6 (0.1–4.3)	0.6 (0.07–5.7)
Cu	5.5 (0.9–71)	8.2 (2.5–28)
Pb	53 (6.7–599)	12 (1.2–125)
Zn	216 (33–723)	44 (12–195)

Values are medians with the range between the 5th and 95th percentile between brackets

well understood under laboratory conditions, but measurements of the partition coefficient in the laboratory may differ from those needed for robust application to field modelling. To get an indication of the adequacy of the combined use of all relationships used in modelling metal speciation in and between soil and soil solution (see Fig. 8.2: reactions 1–3), De Vries and Groenenberg [20] compared results for calculated total dissolved metal concentrations, based on present total soil metal concentrations, with results of the measured metal concentrations in soil solution obtained in the field situation from 56 soil samples of five land-use types (acid grassland, heathland, upland and lowland coniferous forest and deciduous woodland) collected from 'background' sites in the UK [4]. Table 8.11 shows that the ranges (5–95% percentile) of calculated total metal concentrations correspond well with measured ranges for all Cd and Cu. Median values were, however, overestimated by a factor 4–5 for Pb and Zn. The MAE of the log-concentration is mostly between 0.3 and 0.5 (a factor 2–4 on a linear scale), which is within the error ranges calculated for the transfer function relating metal activities in solution to the reactive soil metal content [35].

8.5.3 Relevance of Dynamic Model Assessments in View of Time Scales

By definition, a critical metal load equals the load resulting at steady state in a metal concentration in a compartment (e.g. soil solution, plant, fish) that equals the critical limit for that compartment. As shown above, the time period before a critical limit is reached can be very long and dynamic modelling provides insight into the build-up in soils of anthropogenic inputs of metals over past centuries and future changes. Such dynamic assessments give crucial additional information to critical loads.

Tipping et al. [67, 68] used the CHUM-AM model to simulate combined acidification and metal behaviour for catchments in Cumbria (north-west England). The model includes WHAM-VI and can therefore account for the competitive binding of protons and major and minor metallic cations by soil organic matter. Representations are also included of hydrology, speciation in soil solution, adsorption by Al and Fe oxide phases in the deeper soil, chemical weathering, dissolved and particulate transport, and speciation in surface waters. Catchment soils were estimated to have retained 90% or more of previously-deposited anthropogenic Cu and Pb, but the proportions of metals that sorb relatively weakly to the soil (Ni, Zn, Cd) were smaller. Retention is lowest in acid soils. Model outputs suggested that the weakly-sorbing metals will respond on timescales of decades to centuries to changes in metal inputs or acidification status, while timescales for Cu and Pb will be centuries to millennia. Similar conclusions were drawn from applications of CHUM-AM to the Lochnagar catchment in Scotland [69] and a number of other catchments in England [4]. Soil metal levels in the future will depend particularly upon current soil metal levels (reflecting historical deposition), future metal deposition, acidification status, and changes in soil organic matter content [5].

Broader-scale application is possible through the Simple Dynamic Model for Metals (SDMM) [4, 5], which operates at constant metal deposition rate and soil pH. The SDMM calculates the time required for soil metal concentrations to rise or fall from their current level to within 10% of the concentration associated with the critical limit (defined in terms of free metal ion concentration). The model was applied to managed broad-leaved woodland soils in the UK, with Cu and Zn concentrations below the limit values, and for which the critical load is exceeded; most of the soils in question were in southern, central and eastern England. For soils with already high metal concentrations, very little time is needed to come to within 10% of the limit. At the other extreme, i.e. soil metal concentrations presently quite low and only slight exceedance of the critical load, the model predicts that up to 5,000 years are required. The median time was similar for the two metals, about 400 years.

De Vries et al. [22] and Groenenberg et al. [34] used a one layer mass balance model to estimate the impacts of Zn and Cu inputs, respectively, in Dutch agricultural systems on metal concentrations in soil and soil solution in the root zone/ plough layer. The metal inputs considered included the application of animal manure and fertilizers, the use of organic material and atmospheric deposition. Metal outputs included uptake by plants (grass, maize and arable land were considered) and leaching to deeper soil layers. Metal uptake was calculated as the product of yield and plant metal contents, which in turn were calculated from soil-plant relationships (Zn) or using average plant metal contents (Cu) [26]. Metal leaching was calculated from the yearly average downward water flux and the total metal concentration in solution calculated from the metal content in soil using a transfer function which relates total solution concentrations to reactive metal content and soil properties (soil organic matter content, pH, oxalate extractable Al and Fe) [53]. Soil metal contents were compared with critical metal contents (i.e. Predicted No Effect Concentrations PNEC) derived according to the method developed in the European risk assessment [RAR, 56]. The model was applied to the whole of the Netherlands using 4647 "STONE" plots which cover all the agricultural land. The plots consist of one or more 500 × 500 m grid cells with a unique combination of land use, soil type and ground water table class. Available data include basic soil properties (pH, organic matter and clay content and oxalate extractable Al and Fe content) and hydrology [75]. Initial soil metal contents were calculated with a geostatistical approach [13]. Geo-referenced data on annual metal inputs were derived for all individual STONE plots according to a method described in De Vries et al. [22]. Recently the model was extended to a multi layer model to enable the calculation of leaching fluxes to ground- and surface water [11, 37]. Metal contents at various depths for the whole soil profile were estimated using a depth dependent relation, using the metal content in the topsoil and the pH, organic matter and clay content at the subsequent depths [10].

Results of the one-layer mass balance models show that Cu and Zn inputs exceed the uptake and present leaching for 97% and 81% of the plots respectively, which consequently leads to accumulation of these metals in soils [22, 34]. Present Cu concentrations are all below the PNEC, whereas for Zn, PNEC values are only exceeded in historically contaminated sites (<1% of the area). Future metal contents will ultimately exceed PNEC values in 18% of the area for Cu and for 53% in case of Zn. The time to reach these levels however, takes about 100–4,000 years with average times of 800 and 1,660 years for grassland and arable land in case of Cu and average times of 250 and 650 years in case of Zn [22, 34].

8.5.4 Relevance of the Approach in Policy Making

As with their use for N and S, critical loads and targets loads for metals are a potential policy tool to optimise the protection of the environment for a given international investment in pollution control. However, unlike N and S, the time to reach steady state can be hundreds to thousands of years and this makes the approach less useful, unless used in addition to a dynamic modelling approach. The reason for this is that variations in metal transformation and transport, moderated by climate change and soil acidification over time, may influence exposure and effects more than the magnitude of the metal input. Climate change influences the soil water balance, changes vegetation types and drive land use change, thus affecting the carbon cycle, and thereby the concentration of dissolved organic carbon. Soil acidification, in terms of a change in pH, will influence complexation, sorption, precipitation and ion exchange processes. Such changes are not included in the assessment of target loads. Dynamic modelling is therefore important to assess the future risk of metal inputs, in addition to the use of critical loads and target loads.

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Part II
Key Heavy Metals and Metalloids

Chapter 9
Arsenic

Walter W. Wenzel

Abstract Arsenic (As), an ubiquitous element known for its toxicity to biota naturally occurs in several oxidation states between –III and +V. Total As concentrations in the soil solid phase range between 0.1 and 55 mg kg^{-1} in uncontaminated soils but may be as high as several percent in soils contaminated by mining, smelter and other industrial activities. In aerobic mineral soils, As is primarily associated with iron (Fe) (oxy)hydroxides whereas As sulphide minerals may precipitate in anaerobic conditions. In the presence of Fe (oxy)hydroxides only minor amounts of As are associated with (oxy)hydroxides of aluminium (Al) or manganese (Mn), clay minerals or organic matter. There is no evidence for significant association of As with calcium (Ca) minerals below pH 9.5. Binding of As to organic matter appears to be important in organic soils such as forest floors of peat, but the nature of this association is largely unknown. The main control of both As(III) and As(V) solubility in soils is sorption to Fe (oxy)hydroxides, mainly as inner-sphere bidentate (mononuclear and binuclear) and monodentate surface complexes, with a greater share of monodentate complexes at low As loads and increasing pH (at pH values >8), and predominance of binuclear bidentate complexes at highest As loads. The main As species in soil pore water are arsenate in aerobic soil and undissociated arsenous acid in anaerobic conditions, with little contribution of organic forms. Soil pore water in organic soils may also contain substantial amounts of organic As, primarily in methylated forms. Biological transformations of As include oxidation – reduction and methylation – demethylation reactions triggered by soil bacteria and fungi. Plant roots take up As(V) via phosphate transporters and As(III) by aquaporins and release As(III) back into their rhizospheres after internal reduction of As(V) to As(III). Arsenic pollution is a global phenomenon with a major

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contribution of anthropogenic emissions to the global As cycle. Large-scale risks to ecosystems and human health arise not only from (ancient) mining and smelter activities, but more recently also from of the use of As-contaminated water as a source of drinking water and for irrigation of crops, in particular paddy rice.

Keywords Arsenic • Soil • Iron • (oxy)Hydroxides • Carbonate • Sorption • Pollution • Contamination • Pore water

9.1 Introduction

Arsenic, the twentieth most abundant element in the earth's crust, is a metalloid with the atomic number 33 and atomic mass of 74.9216 g mol^{-1}. Its outer electron configuration is $4s^2 4p^3$. Together with nitrogen (N), phosphorus (P), antimony (Sb) and bismuth (Bi), As belongs to the fifth main group of the periodic table. The name "arsenic" is derived from the old Persian word "zarnikh", which means yellow orpiment, As_2O_3 [152]. As with other metalloids, As has semiconductor properties and occurs in nature in various oxidation states including +V, +III, 0, and −III. Arsenic shares chemical similarity with P and therefore acts as an analogue in various biological processes such as uptake in plants and micro-organism, and in terms of its chemical behaviour in soils. However, the soil chemistry of As is more diverse than that of P as As exists in more than one oxidation state, forms bonds with sulphur (S) and carbon (C) more readily, and undergoes biological transformations resulting in volatilisation from soil [136, 157].

In very small concentrations, As appears to be essential in animals [184] and beneficial in plants [42]. However, As is most renowned for its toxic effects in the environment. While its high toxic potential has been known and employed since ancient times, it received new and global attention when the large-scale disaster of As-poisoned drinking and irrigation water became known in the mid 1990s, stimulating substantial research on As and its fate in the environment.

This chapter is intended to provide an up-to-date overview on the behaviour and biogeochemistry of As in soils.

9.2 Geochemical Occurrence of Arsenic

9.2.1 Global Pools and Cycling

Estimates of global pools and cycling (fluxes) of As are depicted in Fig. 9.1. Arsenic in the soil reservoir globally amounts to $1.7–2.5 \times 10^9$ t which is 4–5 orders of magnitude less than the amount of As stored in the earth's crust and 25–30% of the As present in sea water (oceans) (Fig. 9.1). However, the As soil pool exceeds those in the atmosphere, freshwaters and terrestrial plants by 4–6 orders of magnitude.

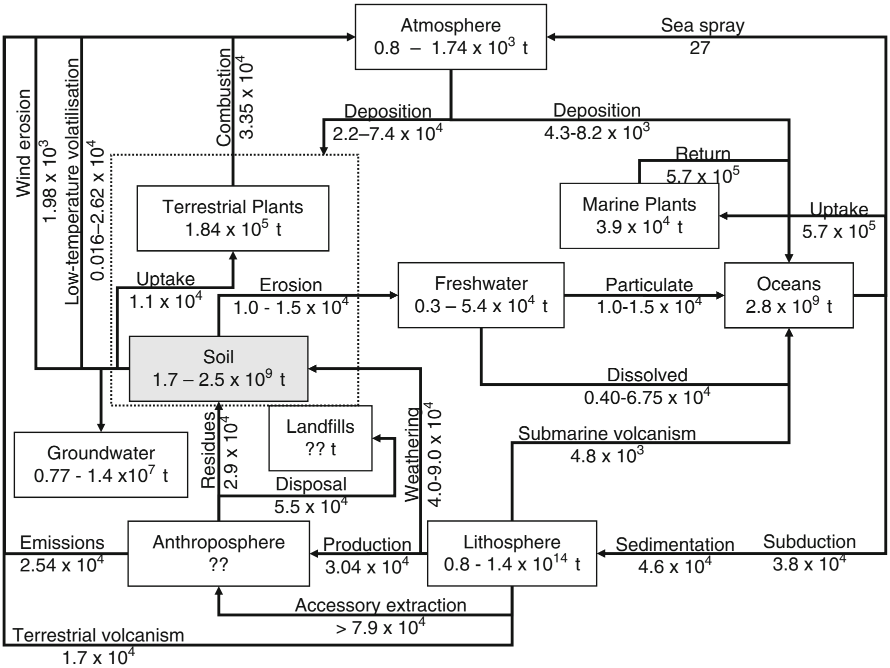

Fig. 9.1 Global pools and cycling of As. Data are obtained from Matschullat [120] unless stated otherwise. The total arsenic pool in soil was calculated using an estimated global soil mass (to 100 cm depth) of 3.3 × 10^{14} t [81] and average As concentrations of 5 and 7.5 mg kg^{-1} soil (Table 9.1). The pool of As in the lithosphere was calculated using an estimated pool mass of 5.7 × 10^{19} t [81] and average As concentrations of 1.5 and 2 mg kg^{-1} [120]. The pool of dissolved As in oceans was calculated using an estimated pool mass of 1.4 × 10^{18} t [81] and an average concentration of 2.0 μg L^{-1} [38]. The dissolved arsenic pool in freshwater was calculated using an estimate of the global pool masses of 3.2 × 1,013 t [81] and As concentrations of 0.1 (lower value) and 1.7 μg L^{-1} [120]. The annual flux of dissolved As via rivers to the oceans was estimated using the same As concentrations and an annual water flow of 3.97 × 10^{13} t [101], the flux of particulate As was calculated by assuming the same Arsenic concentrations in particulates as in soil (5 and 7.5 mg kg^{-1}) and a particulate (sediment) flux of 2 × 10^{9} t $year^{-1}$. The As pool and annual uptake in marine plants were calculated using estimates for the global marine phytomass of 3.9 × 10^{9} t, annual marine phytomass production of 5.7 × 10^{10} t $year^{-1}$ [199] and an average As concentration in marine plant biomass of 10 mg d.m. kg^{-1} (based on data compiled in [151]). Arsenic pool and annual uptake in terrestrial plants were calculated using estimates for global terrestrial phytomass of 1.84 × 10^{12}, annual terrestrial phytomass production of 1.13 × 10^{11} t $year^{-1}$ [199] and the "world reference arsenic concentration in plants" of 0.1 mg d.m. kg^{-1} Markert [118]. The As fluxes back to the soil and ocean water is assumed to be in the same order as the respective uptake fluxes in plants (not depicted). The lower estimate of global Arsenic input to soils via weathering was estimated using the global mechanical and chemical weathering rate of 2 × 10^{10} t $year^{-1}$ estimate given by Garrels and Mackenzie [55] and an average As concentration in the lithosphere of 2.0 mg kg^{-1} [120]. The higher estimate was taken from Nriagu [134]

Soil is not only an important compartment of As storage, but has a significant role in the global As cycle (Fig. 9.1). Using the input and output fluxes depicted in Fig. 9.1, the global net balance of As in soils is clearly positive, ranging between 9.38 × 10^{4} (lowest inputs, highest outputs) and 1.77 × 10^{5} t $year^{-1}$ (highest inputs, lowest outputs). This As accumulation can be related to anthropogenic inputs and its generally low mobility in soils (see Sect. 9.4), with an estimated retention time of 1,000–3,000 years [120]. Based on the analysis of As/Sc ratios in a Swiss peat bog profile relative to that in the earth's crust, Shotyk et al. [164] calculated enrichment factors of As varying between 7 and 10 around 2,100 years ago (Roman times), indicating substantial inputs of As to soils from mining and smelter activities. A dramatic increase of the enrichment factor was encountered from the early/mid 1900s with a distinct peak (ca. 140) around 1920, corresponding to an increase of Swiss coal imports and their use for combustion. The subsequent steady decrease of the As enrichment factor to present levels of about 20 can be related to the gradual substitution of coal by heating oil in Switzerland [164]. The present local enrichment factor of 20 for Switzerland compares to a global ratio of about 1.5 between the annual amount of As released into the atmosphere through anthropogenic activities and the amount released by terrestrial volcanism (Fig. 9.1) [24]. The annual rate of anthropogenic mobilisation of As from the earth's crust through mining activities (production + by-production) is estimated to be of the same order as natural mobilisation rates through weathering and volcanism (Fig. 9.1), further illustrating a substantial anthropogenic impact on the global arsenic cycle.

9.2.2 *Total Arsenic Concentrations in Soils*

Estimates of the global average concentration of As in soils are in the range of about 5–7.5 mg kg^{-1} (Table 9.1) [120], with a common range between 0.1 and 55 mg kg^{-1}. This is supported by data from major regions (continents) of the world (Table 9.1) [151]. Larger arsenic concentrations found at regional or local scale (Table 9.1) can generally be attributed to geogenic anomalies (bedrock) or anthropogenic activities (see section below).

9.3 Origin of Arsenic in Soils

9.3.1 *Soil Parent Materials*

Arsenic concentrations in source materials determining its concentration in soils are compiled in Table 9.2. The main natural source is weathering from parent materials (bedrock). Shales, clays and phosphorites (phosphates) commonly contain elevated concentrations of As whereas sandstones, limestones and igneous rocks show typically lower concentrations of As than the world average for soils (Table 9.2). Locally, mineralised bedrocks (ores) can contain extremely high As concentrations, resulting in geogenic anomalies in soil.

Table 9.1 Arsenic concentrations in soils of various world regions

Region/Location	Site/Soil information	N	Median	Mean	Geometric mean	Minimum	Maximum	Method	Reference
World	Uncontaminated soils			7.2		0.1	55		[1,37]
	Estimate		5						[99]
USA	Uncontaminated			7.4					[37]
USA	Topsoils (0–20 cm)	1,260		7.0		<0.1	93	Total	[162]
China	All soil types	4,100	9.6	11.2		0.01	626		[206]
Japan	All soil types	358		11		0.4	70		[79]
European Union	Topsoils (0–20 cm)	784	6					Aqua regia	[160]
European Union	C horizons	784	5					Aqua regia	[160]
European Union	Topsoils	1,590	6			2.5	410	Aqua regia	[100]
Northern America	A horizons	254	5					Total	[170]
Northern America	C horizons	263	6					Total	[170]
Canada	Ap horizons	1,270	6.6					Total	[56,57]
Argentina	All soil types	20		5		0.8	22		[207]
Austrian Alps	Geogenic and anthropogenic anomalies	186	77.1	236		1	3,000	Aqua regia	[198]
South-East Italy (Apulia)	Uncontaminated soils	51				0.12	22.0		[144]
South-East Spain (Almería)	Topsoils (0–20 cm), including contaminated	106	19.7	27.6		3.1	214	Total	[165]
South-East Spain (Almería)	Subsoils (20–40 cm), including contaminated	90	17.8	21.8		3.1	102	Total	[172]
Central Victoria (Australia)	Surface horizons (0–10 cm) under different land use	85	28.4	39.0		7.44	396		[143]
Czech Republic	Various major soil groups	162			30		3,030	Total	[139]
Netherlands	Topsoils (0–20 cm) from semi-natural land covering normal and elevated arsenic levels			0.15		0.01	0.67	Aqua regia	[139]
Finland	Organic layers from Satakunta region	41	2.02			1.05	11.2	HNO_3	[85]
Finland	Organic layers from Pirkanmaa region	39	2.26			0.59	12.0	HNO_3	[85]

(continued)

Table 9.1 (continued)

Region/Location	Site/Soil information	N	Median	Mean	Geometric mean	Minimum	Maximum	Method	Reference
Finland	Topsoils (0–25 cm) from Satakunta and Pirkanmaa region	120				0.1	16.2	Aqua regia	[85]
Finland	Subsoils (unweathered C material) from Satakunta and Pirkanmaa region	120				0.1	22	Aqua regia	[85]
Australia	Urban soils (Adelaide, Hobart, Melbourne, Sidney)					<0.2	45		[178]
USA (Missouri)	Topsoils (10 cm) from three undisturbed residential areas in Missouri	62	3.77	6.56				Total	[80]

Table 9.2 Arsenic concentrations of various source materials

		Unit	Estimate	Mean	Median	Minimum	Maximum	Comments	Reference
Parent materials	Igneous rocks	mg kg^{-1}		1.5–3.0		0.06	113	Various igneous rocks	[86]
	Granites, granodiorites	mg kg^{-1}	3						[99]
	Limestone	mg kg^{-1}	1.5						[99]
	Limestone	mg kg^{-1}		1.7		0.1	20		[86]
	Sandstone	mg kg^{-1}	0.5–1.0						[99]
	Sandstone	mg kg^{-1}		2		0.6	120		[86]
	Shales, schists	mg kg^{-1}	13						[99]
	Shale and clay	mg kg^{-1}		14.5		0.3	490		[86]
	Mafic (gabros, basalts)	mg kg^{-1}	0.7–1.0						[99]
	Ultramafic	mg kg^{-1}	0.7						[99]
	Phosphorite	mg kg^{-1}	21						[16]
	Phosphates	mg kg^{-1}		22.6		0.4	188		[86]
Atmospheric deposition	Air	ng m^{-3}				1.6	9.8	Range for four non-urban U.K. sites	[68]
		ng m^{-3}				0.008	1	Remote areas	[120]
		ng m^{-3}		<0.000021				Remote areas	[86]
		ng m^{-3}				<d.l.	0.16	Urban areas	[86]
		ng m^{-3}		15				Contaminated areas	[120]
	Bulk (total) deposition	ng L^{-1}				0.0009	80	Remote areas	[120]
						240	370	Rural areas	[120]
						900	12,300	Urban areas	[120]
	Aerosol	ng m^{-3}		4.7				Annual concentration average 1979–1980; rural forest plantation in Denmark	[73]
		ng m^{-3}		0.7				Annual concentration average 2002–2005; rural forest plantation in Denmark	[73]

(continued)

Table 9.2 (continued)

		Unit	Estimate	Mean	Median	Minimum	Maximum	Comments	Reference
Groundwater		μg L^{-1}				1.6	6.8	Range for selected areas in South Korea	[208]
		μg L^{-1}	0.5–0.9					World background estimate	[4]
		μg L^{-1}	0.1–230					World range estimate	[4]
		μg L^{-1}				1.25	5,114	Shallow groundwaters in Southern Thailand (Asian tin belt)	[200]
		μg L^{-1}				1	1,032	Deep groundwaters (caronate aquifers) in Southern Thailand (Asian tin belt)	[200]
		μg L^{-1}		320		<50	1,250	Groundwater from six districts in West Bengal (India);	[30]
Agricultural materials	Rock phosphate	mg kg^{-1}		7.7				Average for U.K.	[136]
	Lime	mg kg^{-1}			0.9/1.69/2.85	<0.4	5.02	Medians and range for three Austrian regions	[136]
	Irrigation water	μg L^{-1}		88				General irrigation water in South Korea	[208]
	Livestock wastewater	μg L^{-1}		23				Used for irrigation of paddy soils in South Korea	[208]
	Feed additives	mg kg^{-1}				10	15	Addition rate to feed of chicken, turkey and pigs	[136]
	Poultry litter	mg kg^{-1}		15.7	14.8	1.2	39.4	Poultry litter from U.S.A. (Alabama, Georgia, South Carolina); water solubility on average 71%	[82]
	Poultry litter	mg kg^{-1}				0.0	70.0		[167]
Waste/resused materials	Sewage sludge	mg kg^{-1}		6.9		0.45	52	Various sewage sludges from Japan	[25]
	Coal ash	mg kg^{-1}		88.6	65.4	2.3	513	Coal ashes of various origin	[32]

Wood ash	mg kg^{-1}		10			36 birch ash samples	[151]
Wood fly ash	mg kg^{-1}			1	60		[142]
Wood bottom ash	mg kg^{-1}			0.2	3		[142]
Wood preservatives (chromated copper arsenates, CCA)	mg kg^{-1}	220,000				CCA-C (most common CCA type in North America)	[210]

9.3.2 Atmospheric Deposition

Another important source of soil As is atmospheric deposition, especially in the vicinity of mining operations and metal smelters, and in urban areas. Concentrations of As in air from remote areas are very low with mean values typically <0.01 ng m^{-3} but may increase by several orders of magnitude in urban areas and mining districts. Arsenic is deposited on to soil surfaces via dry and wet deposition, together constituting the total atmospheric As input to soils of which 50–80% is typically present in soluble form [68]. Arsenic concentrations in total (bulk) deposition vary widely with values down to 0.0009 ng L^{-1} in some remote areas and up to 12,300 ng L^{-1} in urban environments (Table 9.2).

9.3.3 Groundwater

Soil in contact with (e.g., Gleysols) or under irrigation by groundwater (e.g., paddy soils) may receive additional input of As, especially where the aquifer is in contact with As-rich sediments [30] or (mine) waste materials [200]. The estimated world background for As concentrations in groundwater is in the range of 0.5–0.9 μg L^{-2} but As concentrations may exceed 1,000 μg L^{-1} due to geogenic or anthropogenic influences (Table 9.2). The probably most well-known case is the As calamity in West Bengal (India) and Bangladesh where not only hundred thousands of people suffer from diseases related to the use of contaminated tube well waters [30, 133], but irrigation of (paddy) fields has resulted in substantial As accumulation in soils [3, 17] and transfer into the food chain [126].

9.3.4 Agricultural Materials

In managed agricultural soils, As inputs may arise from the application of inorganic and organic fertilisers, lime, pesticides (insecticides, herbicides), defoliants (e.g., in potato crops), desiccants, soil sterilants, livestock wastes (where As compounds are used as a fodder additive) and biosolids such as composts or sewage sludge (Table 9.2) [9, 136]. These materials are also in use for the management of non-crop areas such as turfs, lawns, and roadsides.

In 1600, early uses of inorganic As as an insecticide (in rice crops) were documented in the *Chinese Encyclopedia of Medicine* [9]. Long-term excessive use of inorganic arsenical pesticides, in particular arsenic acid (H_3AsO_4), Ca and Pb arsenates, from the early 1860s until the introduction of DTT and other organic substitutes in the 1940s [9, 135] has left behind As accumulation in many (apple) orchard soils [50, 91, 127, 140, 188, 204]. Organoarsenical compounds, in particular monosodium, monoammonium and disodium methanearsonates, and dimethylarsinic (cacodylic) acid (CA) have been in use since the mid 1970s as selective herbicides for post-emergence control in cotton and citrus crops as well as for weed control in non-crop areas such as turf, for lawn renovation and along highways [1, 9]. Their repeated high application may lead to As accumulation in soils [90].

Most fertilisers and lime materials contain only low concentrations of As (Table 9.2). However, depending on the source of phosphate rock and the production process, phosphate fertilisers may be a significant source of As in heavily fertilised soils [136; Table 9.2]. At high livestock density and where inorganic As compounds are used as growth promoters in animal feeding (feed additive), recycling of organic manures and livestock waste waters to soils may contribute to As contents in soil. Arsenic concentrations in poultry litter of up to 77 mg kg^{-1} [167] and water solubility around 70% along with high land application rates in the U.S.A. suggest a potential detrimental effect in soil and water quality in the long term [7, 82].

9.3.5 Wastes, Biosolids and Other Sources of Arsenic

Biosolids such as composts and sewage sludge are partly recycled to agricultural and forest soils and are increasingly used in landscaping. Depending on the origin (industrial, communal), the collection (e.g., separated or mixed sewer system) and processing technology, some biosolids may contain high levels of As (Table 9.2). However, such materials are commonly banned from recycling to soil in some countries and progress has been made towards the production of “clean” biosolids, e.g., through separation of industrial and communal (household)-derived waste flows and separate sampling of metallic wastes. Therefore, biosolids are not a major source of As in soils where effective regulations are in place. Disposal and agronomic re-utilisation of some communal and industrial wastes, including biosolids, are another potential source of As in soils.

Coal and wood ashes may contain high As levels (Table 9.2) which – if applied repeatedly – may locally increase As concentrations in soil. The extent of As pollution depends largely on the quality of feed coal or wood and the ash fraction (bottom ash, coarse and fine fly ash) considered [32]. In Australia and New Zealand, Na arsenite has been widely used as cattle dip for controlling ticks, resulting in local As accumulation in the surroundings, with soil As concentrations as high as 14,800 mg kg^{-1} [122]. Chromated Cu arsenate (CCA) and ammoniacal Cu Zn arsenate (ACZA) has been widely used as wood preservative in the United States, Canada and many developing countries such as Bangladesh, resulting in widespread but very local (up to 0.5 m distance) As accumulation (and leaching) in soils around wooden utility poles [17, 131, 210].

9.4 Chemical Behaviour of Arsenic in Soil

9.4.1 Chemical Forms and Speciation of Arsenic in Soils

9.4.1.1 Solid Phase

Arsenic in soils is most commonly associated with its primary minerals derived from the parent material, secondary minerals (primarily Fe oxy/hydroxides; sulphides) formed in the course of mineral weathering, and As adsorbed to mineral surfaces. Association of As with soil organic matter and Ca (minerals) has been repeatedly claimed, mainly based on unquestioned interpretation of the Chang and Jackson [22] procedure for P extraction, but seem to be of minor importance in most mineral soil horizons. Organic As present in forest floor, peat, and other soil materials high in organic matter are typically derived from plant residues and throughfall. Relevant association with Ca (minerals) is likely to occur only in extremely alkaline environments and has only been inferred from studies with pure phases such as calcite [15, 44, 130, 148].

Primary Minerals of Arsenic in Soils

Primary minerals of As that have been detected in soils using scanning electron microscopy (SEM) combined with electron diffraction spectra (EDS) include: arseniosiderite ($Ca_2Fe_3(AsO_4)_3O_2.3(H_2O)$) in soils from Carinthia (Austria) developed on calcareous schist [109], and arsenopyrite [17]. Secondary minerals and other weathering products of As minerals identified in a range of (Austrian) soils include: Fe–As oxides such as scorodite ($Fe^{3+}(AsO_4)\cdot 2H_2O$), hydrous Fe–S minerals of As – sarmientite/zykaite (in soils developed on ancient mine tailings in the Austrian Alps), both derived from arsenopyrite, accumulation of As in the weathering rinds of As-free pyrite, indicating sorption rather than release by weathering from this mineral, and most commonly accumulation of As in Fe oxy/hydroxides films/precipitates on mineral surfaces such as quartz [17, 109]. Using SEM/EDS analysis, Sultan [172] identified FeAsS minerals in Australian soils with weathering rinds depleted of As. Generally, As seems to be associated with distinct mineral particles or Fe oxy/hydroxide coatings on such particles in the sand and silt fraction but was found to be homogenously distributed in clay fractions [196]. In weathered soils, primary minerals of As are typically scarce [17]. Filippi et al. [45] identified the secondary As minerals pharmacosiderite ($KFe_4(AsO_4)_3(OH)_4.6–7(H_2O)$), arseniosiderite, and scorodite, and associations of As with Fe oxy/hydroxides and jarosite ($KFe_3(SO_4)_2(OH)_6$) in soils on gold (Au) deposits in the Czech Republic. Evaluation of ion products determined for a number of metal arsenates in two contaminated orchard soils with a history of Pb arsenate treatment indicated stability of Pb and Mn arsenates under the measured pH and redox conditions [69].

Association of Arsenic with Carbonates and Calcium

Detailed SEM/EDS analysis of numerous samples from the Austrian Alps provides no evidence for association of As with Ca minerals. Moreover, in soils where the calcite content decreased from the sand to the clay fraction, As concentrations displayed the opposite trend [196]. Further evidence for the negligible role of Ca minerals is available from chemical extraction studies, where Ca carbonates where efficiently removed by 1M NaOAc/HOAc buffer solutions without significant concurrent extraction of As [197]. Using electron spin echo spectroscopy, Di Benedetto et al. [34] demonstrated that arsenate ions may substitute for CO_3^{2-} in calcite from travertine, suggesting that As may be immobilised by this mechanism where Fe oxy/hydroxides are not operating. Expansion of the unit cell volume of calcite (at pH 7.5) and gypsum (at pH 4.0, 7.5, and 9.0) minerals synthesised in the presence of either As(III) or As(V) also reveal a similar substitution mechanism without providing information on the initial Ca : As ratios in the slurries from which the minerals were precipitated [44]. However, even in highly calcareous soils, As seems to be mainly associated with Fe oxy/hydroxides [109]. Precipitation of basic Ca arsenate from As-doped $Ca(OH)_2$ pastes was demonstrated at highly alkaline pH in the presence of dolomite [148]. Using XRD analysis, Moon et al. [130] identified a number of Ca–As minerals precipitated from $Ca(OH)_2$ suspensions (solid : solution ratio 1:10, by weight; pH 12–13) spiked with As(III) or As(V) at molar Ca : As ratios between 1 and 4 in the absence and presence of kaolinite. In a similar study, Bothe Jr. and Brown [15] found Ca-Arsenate minerals precipitated from $Ca(OH)_2 - o$-arsenic acid slurries at molar Ca:As ratios between 0.8 and 4 and alkaline pH. None of these studies is indicative for the occurrence of these minerals in soils which hardly would have Ca:As and solid:solution ratios as used in the experiments. Moreover, the majority of soils, unless having sodic properties, would not meet the extremely alkaline experimental conditions. Interestingly, Reardon et al. [149] could not even confirm tricalcium arsenate (which is stable in extremely alkaline conditions) as solubility control of As in highly alkaline fly ash and proposed precipitation of As–Fe oxides and/or adsorption of As to Fe oxide phases as an alternative mechanism. Calcite precipitation from 0.5 N $CaCl_2/Na_2CO_3$ solutions (pH 7.5) in the presence of As(III) showed that solid solutions formed only at As concentrations $>1.5 \times 10^{-3}$ M, and that co-precipitation of As with calcite in natural environments is limited by As availability rather than by the ability of the mineral to incorporate As in its bulk structure during crystal growth [153]. However, the largest ever reported As concentration in pore water collected from a heavily contaminated field soil (total As $>2{,}000$ mg kg^{-1}) is only 171 μg L^{-1} [46, 198]. In the presence of Fe oxy/hydroxides, As incorporation in calcite is thus unlikely to be significant even in highly contaminated soils. This conclusion is also supported by batch and dynamic laboratory experiments as well as field experiments addressing the role of carbonates in As trapping at hydrothermal spring outlets in the presence of iron oxy/hydroxides [102]. The results of this study suggest that As was trapped during the precipitation of Fe oxy/hydroxides with subsequent control of desorption by these minerals whereas calcite was of minor importance for As immobilization. In another study, Juillot et al. [95] showed that Ca arsenates may precipitate from highly acidic waste pile leachates once they get in contact with carbonate subsurface layers. However, the high solubility of these Ca arsenate compounds do not make them relevant candidates for As immobilization in contaminated surface-near environments [95]. This is also supported by findings of Sadiq [156] showing undersaturation of 19 calcareous soils from Saudi Arabia even with respect to the thermodynamically most stable arsenic minerals ($Ca_3(AsO_4)_2$ and $Mn(AsO_4)_2$) expected in such environments [158].

Association with Organic Matter

Because 0.025 M NH_4-EDTA (pH 4.6) had been shown to extract metal fractions associated with soil organic matter, this agent was tested for its suitability to extract organic forms of As from various soils collected across the Austrian Alps [197]. However, the low extraction yields (2–7% of total As) and the lack of correlation with soil organic matter suggested only marginal importance of organically-bound As in (mostly) aerobic mineral soils. Dobran and Zagury [36] studied As solubility and speciation in four almost identical synthetic soils with organic matter (i.e., a mixture of peat moss and poultry manure) contents varied between 0.5% and 15%, and corresponding DOC between 0.02 and 0.30 g kg^{-1}. The soluble As concentrations increased along with soil organic matter and DOC, indicating that As mobilisation by DOC was more effective than sorption to organic matter in the solid phase. Moreover, organic matter and DOC have been shown to decrease arsenate sorption to goethite [64], hematite [150] and soils [88, 89, 106, 190].

Using sequential extraction (H_2O, 0.05 M $(NH_4)_2SO_4$ and 0.05 M$NH_4H_2PO_4$), Huang and Matzner [74] showed that only 5% the total As in highly-organic forest floor horizons (Oe and Oa) beneath Norway spruce (*Picea abies* [L.] Karst.) was readily soluble or exchangeable, with little contribution (ca. 1%) of the last two fractions. This indicates very weak sorption of As in these organic horizons. As the binding form of the residual 90% of As in the forest floor remained unclear, Huang and Matzner [74] speculated that in analogy to P, arsenate mono- and di-esters might make up most of the residual As fraction in litter layers. Arsenic species most commonly found in plants are primarily inorganic arsenate and arsenite [123, 128, 147, 154, 195], whereas organic species such as monomethylarsonate (MMA(V)), dimethylarsinate (DMA(V), also cacodylic acid (CA)), trimethylarsine oxide (TMAO), tetramethyl arsonium ion (TETRA), arsenobetaine (AsB), arsenocholine (AsC), and glycerol ribose have been detected in smaller amounts [123, 147]. However, after reduction to As(III) and co-ordination with glutathione and/or phytochelatins (PCs), most of the As appears to be sequestered in cell vacuoles [123, 161]. Arsenic-PC complexes may dissociate readily at pH >7.2 [123]. Even though all organic As compounds commonly detected in plants may be readily soluble [195], the extraction efficiency of methanol/water extracts ranged between 3.0% and 41.4% for a number of plant species [154], indicating that a substantial proportion of As may be bound in less soluble form to cell walls and other cell structures. It remains unclear in which form As is bound in this residual fraction and how it might be incorporated in soil humic substances in the course of humification.

Based on studies of model systems such as humic or fulvic acids, peats and composts, several authors suggested that As sorption to (solid) soil organic matter may be an important feature of As biogeochemistry in soils [132, 177]. The main mechanisms of As sorption to both solid and dissolved organic matter may include the formation of inner-sphere complexes of As with – at pH 7 positively-charged – humic acid amine groups [155] and ternary complexes via metal cation bridging (e.g., to fulvic acids), primarily with Fe, Al, Mn, Ca and Mg [104]. Mukhopadhyay and Sanyal [132] suggested the participation of both phenolic and carboxylic groups in the inner-sphere complexation of As by fulvic and humic acids. Dialysis (cut-off 500 and 3,500 Da) of water extracts obtained from five golf –course soils with varied peat content revealed that spiked As was primarily bound to (dissolved) peat-derived organic compounds of molecular size between 500 and 3,500 Da, which contained virtually no Fe, Al or Ca [23]. These findings indicate the existence of As-DOM rather than of ternary complexes in the investigated golf-course soils. Arsenic complexes formed with fulvic and humic acid fractions isolated from two West Bengali soils as evaluated by the ion exchange method were found to be quite stable [132]. The stability constants (Log$K$) were approximately inversely related to molecular weight and to properties that correlate with hydrophobicity of the organic acids. Exchange isotherms suggested a 2-phase exchange of As from its organic complexes by phosphate and nitrate, possibly indicating the existence of both outer-sphere and inner-sphere complexes of As with humic and fulvic acids [132]. However, the extent of exchange with both ions (i.e., nitrate and phosphate) was small [132], which is in accord with the low extractability of As from forest litter [74].

Surface-Bound Arsenic and Sorption

There is multiple evidence that As (arsenate and arsenite) sorption in soil is mainly controlled by the content and nature of Fe oxy/hydroxides such as amorphous or poorly crystalline ferrihydrite and crystalline goethite (α-FeOOH). Indirect (and early) evidence has been derived from correlation of As sorption with extractable Fe fractions in soils. Arsenate was more efficiently adsorbed in Indian soils containing larger amounts of sesquioxides; addition of Fe oxy/hydroxides to these soils enhanced arsenate adsorption, with a more pronounced effect of freshly-precipitated (amorphous) than of aged (higher degree of crystallinity) material [129]. After equilibration of 24 Wisconsin soils with different amounts of added arsenate, As retention against extraction with ammonium acetate or Bray-1 reagents increased with the content of citrate-bicarbonate-dithionite extractable Fe (referred to as free Fe oxides) in soil [83]. Arsenic solubility in three soils from the U.S.A after equilibration with three different amounts of arsenate was inversely related to the ammonium oxalate extractable Fe and NaOH-extractable Al content of the soils [205]. The role of Fe oxy/hydroxides was further substantiated in experiments conducted by the same researchers showing that removal of amorphous Fe oxides by treatment with ammonium oxalate considerably reduced the soils' sorption capacity for arsenate. In a kinetic study, both arsenate and arsenite were adsorbed more readily and completely by soils rich in ammonium oxalate extractable Fe [108]. Similarly, the rate of arsenite adsorption was related to the Fe oxide content of 5 soils from West Virginia [39, 40] and 15 Japanese soils [159]. De Brouwere et al. [31] found that 63% of the variation of measured solid-liquid distribution coefficients (K_d values) in 30 uncontaminated grassland soils was explained by the content of ammonium oxalate extractable Fe, indicating that arsenate sorption and solubility in these soils was related to the availability of binding sites on amorphous Fe oxy/hydroxides. Citrate-dithionite extractable Fe explained 83% and 68%, respectively, of the variation of the maximum arsenate sorption capacity of low and high energy surfaces (calculated using a two-surface Langmuir equation) in 16 Chinese soils [89]. Finally, the work of Fordham and Norrish [49] combining autoradiography using arsenate-73, electron microscopy and microprobe analysis to study arsenate adsorption by various soils components in acidic Australian soils provides direct evidence that Fe oxy/hydroxides are clearly more effective than any other soil component in taking up arsenate on a unit mass base. Predominant association of sorbed As with Fe (oxy)hydroxides was also shown by XANES analysis and sequential extraction in a paddy, seasonally flooded soil in Japan [174]. In ferromanganese coatings (i.e., alternate layers of ferrihydrite and vernadite, Mn oxide) on quartz grains, As was selectively associated with the Fe-bearing phase [116].

Mechanisms of arsenate binding on Fe oxy/hydroxide surfaces have been studied on synthetic model compounds including freshly precipitated and aged ferrihydrite [51, 84, 194], goethite [43, 66, 111, 117, 173, 194], akaganeite [194] and lepidicrocite [194] by employing indirect (IR, FTIR, kinetic experiments e.g. using pressure jump relaxation technique, H^+/OH^- release stoichiometry; electrophoretic mobility measurements for determination of the point of zero charge) and direct methods (EXAFS, XANES). In summary, speciation of both As(III) and As(V) on surfaces of Fe oxy/hydroxides includes mainly inner-sphere bidentate (mononuclear and binuclear) and monodentate surface complexes, with a greater share of monodentate complexes at low As loads and increasing pH (at pH values >8), and predominance of binuclear bidentate complexes at highest As loads [43, 111, 117, 194]. At low pH the Fe–O–As(III) bonds appear to remain partly protonated (e.g., $Fe{-}O(H)As(OH)_2$ or $FeO_2(H)_2AsOH$) and are electrically neutral [84]. Deprotonation of As(V) surface species has been implied from the observed large increases in negative surface charge [117]. There is no evidence for precipitation of ferric arsenates or formation of As-bearing surface precipitates or solid solutions [107, 194]. The first step of As(V) adsorption involves an initial ligand exchange reaction of the aqueous arsenate species with OH ligands at the oxy/hydroxide surface, forming an inner-sphere monodentate surface complex, followed by a second ligand exhange reaction, resulting in the formation of an inner-sphere bidentate surface complex [66]. The initial rapid adsorption reactions on the exterior of Fe oxy/hydroxide aggregates are followed by diffusion of As to interior surface sites [51, 186]. As the chemical sorption step for arsenate is rapid [65], sorption-related non-equilibrium observed in breakthrough experiments of arsenate in soil columns are likely to be related to limited pore, film, and/or intraparticle diffusion [29]. This needs to be considered when using rate parameters obtained in batch environments in modelling the transport of As in soils over a range of pore water velocities [29]. Especially at low pH and in dry conditions, As(III) adsorbed to Fe oxy/hydroxides is less stable than in solution as indicated by higher As(V)/As(III) ratios at goethite surfaces. The conversion of As(III) to As(V) on oxy/hydroxide surfaces as well as in solution may be further enhanced and mediated by the presence of Mn oxides such as birnessite (δ-MnO_2) [173].

It has been claimed that Al oxy/hydroxides and clay minerals might also play an important role in As sorption in soils [1, 157]. Indeed, Livesey and Huang [107] and Wauchope [193] found better correlations of arsenate adsorption maxima in four Saskatchewan soils with ammonium oxalate extractable Al than for Fe. However, these findings are in contrast to most other studies, including those based on a larger number of soils [31, 89] and may be related to greater abundance of Al oxy/hydroxides relative to those of Fe [49]. Direct evidence for the minor role of gibbsite compared to Fe oxy/hydroxides for arsenate sorption by nine acidic Australian soils is available from autoradiography using arsenate-73 combined with electron microscopy and microprobe analysis [49]. These authors showed that on a unit mass basis, gibbsite was much less effective than Fe or titanium (Ti) oxides in adsorbing arsenate and could only contribute significantly to arsenate sorption if present in sufficiently large amounts. Recently, it was shown by means of XAS and XRF that in podzolic B horizons arsenate may be effectively sorbed to proto-imogolite allophanes [72].

Likewise, it has been suggested that clay minerals may be involved in As sorption in soils. The parabolic adsorption envelope of As(V) on a montmorillonitic, calcareous Vertic Torrifluvent soil after removal of the carbonates was similar to those on the main constituents in the clay fraction, montmorillonite and kaolinite [62]. However, the sorption maxima on the clay minerals were near pH 5 but close to 7 on the soil, indicating that other minerals contributed to As(V) adsorption on the Torrifluvent. Fordham and Norrish [49] showed that clay minerals, including kaolinite, illite, vermiculite, and muscovite, as well as potassium-feldspar and quartz were taking up little arsenate when they were free of surface deposits of finely-distributed Fe oxy/hydoxides.

Significant adsorption on As on carbonate minerals phases has been demonstrated in pure systems [62, 153]. In contrast to oxy/hydroxides of Fe and Al, carbonate minerals such as calcite exhibit positively charged (protonated) surfaces in the pH range between 7 and 9 and have therefore been claimed to control sorption of As in calcareous soils [157]. Goldberg and Glaubig [62] found that in a montmorillonitic, calcareous soil, the adsorption maximum at pH near 10.5 was much reduced after removal of the carbonates, indicating that carbonates may play a major role in arsenate adsorption at pH above 9, corresponding to the adsorption maximum on pure calcite. However, these researchers also concluded that adsorption of arsenate on carbonates in field situations may be of minor significance, as Suarez [171] reported a mean pH of 7.41 ± 0.13 for a calcareous soil in the field under different moisture conditions. In general, calcareous soils exhibit pH values ranging mainly between 7 and 8. Moreover, Oscarson et al. [138] report substantially decreased adsorption (at pH 7) of As(III) on birnessite (δ-MnO_2) coated with $CaCO_3$ as compared to pure birnessite. They explain this finding with low (if any) sorption capacity for As which was also demonstrated by the extremely low sorption of As(III) on pure $CaCO_3$ in their study. All together, these findings suggest that carbonate minerals are of minor importance for arsenic sorption in soils with pH <9.

Sorption of As to organic compounds has been demonstrated in pure systems [177, 191]. Formation of inner-sphere complexes of As with amine groups which are positively-charged at pH >7 [155, 177], carboxylic and phenolic groups [132], and of ternary complexes with polyvalent bridging cations, in particular Ca, Al, and Fe [104, 150, 177] has been proposed as mechanisms of As sorption on organic matter. However, in mineral soils it appears that organic matter often does not significantly contribute to [31, 209] or may even decrease As sorption to the soil solid phase [88, 89]. This has been explained by occupation of (high-energy) sorption surfaces on Fe oxy/hydroxides by organic matter due to formation of organo-mineral complexes, organic matter coatings on minerals [150], and competition of dissolved organic carbon [64] for sorption sites.

Comparative investigations of As sorption on pure mineral phases and related organo-mineral complexes (or minerals coated with organic matter) suggest a rather complex interaction. Both arsenate and arsenite sorption on colloidal hematite (α-Fe_2O_3) were reduced on samples pre-treated with natural organic matter in the presence of Na as background electrolyte or desorbed upon addition of these materials [150]. Similar results were obtained with synthetic goethite (α-FeOOH) and Na as background electrolyte; humic and fulvic acids decreased arsenate and arsenite sorption on goethite over a wide range of pH values when added either before, during, or after reaction of the arsenic species with the iron mineral [64]. Independent of pH, humic acid-coated kaolinite also adsorbed less arsenate than the crude mineral in the presence of Na electrolyte [27, 155], but arsenate sorption was greater on the crude kaolinite at pH >5 when Na was replaced by Ca electrolyte of identical ionic strength (0.01 M) [27]. Decreasing the Ca concentration to 0.0005 M resulted in lower arsenate adsorption on both the crude and humic acid-coated kalolinite [27]. In an earlier study, arsenate sorption on humic acids varied with pH, adsorbate concentration and the ash content of the samples [177]. Reduction of the ash content by acid washing, sample purification, or addition of fluoride or EDTA resulted in lower As sorption, suggesting a role of Ca and other polyvalent cations in As binding to humic substances [177]. From the cited work it appears that Ca can enhance arsenate sorption on minerals and organic-mineral complexes, and – in a certain range of pH and Ca concentration – (partly) reverse the apparent negative effect of organic substances on As sorption on soil minerals. This effect of Ca may be related to increased positive surface charge [168] and/or Ca-bridging [104, 150, 177].

Factors Affecting Arsenic Sorption

Effect of pH: Arsenic adsorption to a variety of model compounds has been shown to be more or less dependent on the pH of the system, with typically less variation for As(III) compared to As(V) adsorption. The shape of pH-dependent sorption envelopes and corresponding maxima not only depend on the type and nature of adsorbent but also on experimental conditions such as strength and index ion of the background electrolyte and relative As load compared to the maximum sorption capacity.

Arsenic adsorption in soils appears to be generally less affected by changes in pH than found for some model compounds. Upon varying the pH of topsoil and subsoil horizons from two New Zealand soils between 3 and 7 using 0.01 M $Ca(NO_3)_2$ background, Carey et al. [20] found virtually no effect on As(V) adsorption apart from small increases at pH >5. The latter effect was attributed to the use of Ca as background electrolyte (see discussion further below). Similarly, pH did not contribute significantly to explain the variation of As(V) distribution coefficients (K_d) in 30 uncontaminated grassland soils from Belgium obtained in a 0.005 M $Ca(NO_3)_2$ background electrolyte [31], and was found unimportant in explaining variation of As(V) adsorption in 16 Chinese soils (0.02 M $NaNO_3$ background electrolyte) [88, 89] and 36 soil representing the major soil orders of the U.S. Soil Taxonomy (0.001 M $Ca(NO_3)_2$ background electrolyte) [209]. In a 0.1 M $NaNO_3$ background electrolyte, Goldberg and Glaubig [62] found a more distinct variation of As(V) adsorption on a montmorillonitic, calcareous Vertic Torrifluvent, with adsorption increasing from pH 2 to around 10.5, and a decrease above this pH. Adsorption of As(V) was considerably less in the pH range >9 after removal of the carbonates, indicating a role of these minerals for As(V) sorption in highly alkaline soils (compare also discussion further above) [62]. In the absence of carbonates, the adsorption maximum was close to pH 7. In a study of As(V) adsorption to 49 surface and subsurface soil horizons belonging to six different soil orders of the US Soil Taxonomy, As(V) adsorption (background electrolyte 0.1 M $NaNO_3$) generally increased with increasing solution pH, showing a maximum around pH 6–7, and decreased as pH further increased [63]. However, variation of As(V) adsorption with pH was small or virtually nil in most of the soils for which details are presented in the article. In contrast to the findings of Goldberg et al. [63], As(V) adsorption (0.01 M KCl background) on seven soils from Italy and China decreased when pH was increased from 4 to 8 [190]. Changes were generally small below pH 5 but more notable for some soils above this pH. Likewise, As(V) adsorption on four Australian soils (0.03 M $NaNO_3$ background electrolyte) generally decreased as pH increased from 2 to 8.5, with less variation in highly oxidic soils [168]. The findings were explained by two interacting factors, the increasing negative surface potential on the plane of sorption, and the increasing amount of negatively-charged As(V) species in soil solution [168]. The same authors reported a considerable increase of As(III) adsorption in two of the soils as pH increased. These results were obtained in a 0.03 M $NaNO_3$ background electrolyte. Varying the electrolyte concentration did not change the principal shape of the adsorption envelope of As(III), but resulted in a parabolic As(V) adsorption edge with a maximum at pH around 6 if the background concentration was lowered to one tenth (0.003 M) and in a much more pronounced decrease with increasing pH if raised to the tenfold (0.3 M) [168]. The possible reasons for the observed effects of ionic strength are discussed further below.

Arsenic adsorption on model compounds has been studied extensively under various experimental conditions. At high As loads, As(V) adsorption on goethite has been shown to decrease with increasing pH [35, 66, 71, 117, 173, 190]. This pattern becomes less pronounced at lower As(V) loads [35, 53] with virtually no variation of As(V) adsorption across the entire range of pH as the As(V) load becomes very low [35, 64]. A similar pattern of As(V) adsorption has been observed for ferrihydrite/amorphous Fe oxides [35, 54, 61]. Adsorption of As(III) on both goethite and amorphous iron oxide typically shows a more or less pronounced maximum between pH 5–9 at high As loads but virtually no variation with pH at lowest As(III) loads [35, 61, 64, 173]. Adsorption of As(V) on amorphous Al oxides shows little variation in the lower range of pH but decreases considerably above a certain pH [6, 54, 61] that may depend on the initial As load, background electrolyte and properties of the specific Al oxide investigated. At low As load, Goldberg [61] observed a parabolic adsorption edge for As(III) on amorphous Al oxide with a pronounced maximum between pH 8 and 9. Adsorption of As(V) on gibbsite tends to increase in the most acidic range of pH (up to 4.5–5), followed by a steep decrease above pH 6 [71, 117]. The pH-dependent adsorption edges of As(III) and As(V) on clay minerals such as illite, kaolinite and montmorillonite tend to follow more complex shapes, often with more than one maximum [61, 62]. Adsorption of As(V) on calcite steeply increases between pH 5 and 12, followed by a decrease above this pH [62]. Adsorption of As(V) on purified humic acid shows a pronounced maximum between pH 6–7 at high arsenic loads which levels off as the As load is decreased [177].

In summary, the effect of pH on As(V) adsorption in soils appears to be generally small. However, contrasting As(V) adsorption envelopes (steady decrease versus sorption maxima around pH 6–7) have been reported where pH effects were observed. As shown for one soil, these patterns may be further modified in the presence of carbonates with As sorption increasing up to pH 10.5 [62], however, this finding was not confirmed in other studies including calcareous soils. Divergent results may be partly explained by the use of different background electrolytes in terms of index cation (divalent Ca versus monovalent Na, K) and ionic strength (ranging from 0.001 to 0.3 M), as Smith et al. [168] observed a steady decrease of As(V) adsorption with increasing pH at very low and moderate ionic strengths (0.003–0.03 M) but a parabolic adsorption envelope in the presence of a 0.3 M background electrolyte. Studies on the adsorption of As(III) on soils are generally scarce, with only one article presenting adsorption envelopes as function of pH [168], suggesting that As(III) adsorption may markedly increase at pH >5. Differences in arsenic load relative to the sorption capacity (surface coverage) are another source of contrasting findings between different studies and among soils. This is indicated by adsorption envelopes of As(III) and As(V) on model compounds (goethite, amorphous Fe oxy/hydroxide) determined for differential arsenic loads, indicating that the pH effect is less pronounced or disappears at low surface coverage.

Effect of ionic strength: The effect of ionic strength on As(V) adsorption has been investigated by Grossl et al. [66] for goethite and by Smith et al. [168] for two Australian soils. Whereas no effect of ionic strength (0.01 versus 0.1 M $NaNO_3$) was observed for As(V) adsorption on the goethite across the entire pH range investigated, a pronounced decrease of As(V) adsorption with increasing ionic strength (0.003–0.3 M NaO_3) occurred in the soils at pH >3–3.5, the inflicting point of the adsorption envelopes. Below this point of zero salt effect, an opposite trend was observed. The effect of ionic strength on As(III) adsorption in the same soils was much smaller and inverse to the pattern observed for As(V), indicating that As(V) was forming outer sphere complexes on these soils whereas As(V) adsorption on the goethite and As(III) adsorption on the soils was dominated by the formation of inner sphere complexes [66, 168]. It appears that in soils, the mechanisms of As(V) adsorption on oxide surfaces is modified by the presence of other compounds and factors, resulting in the occupation of specific surface sites and thus a greater contribution of outer-sphere complexes than observed in model systems.

Effect of Calcium: Calcium present in the background electrolyte or soil solution may increase arsenate adsorption on model compounds [27, 177] and soils [20, 129, 169] which has been attributed to increased positive charge near negatively-charged surfaces [20, 169]. This effect was more pronounced for adsorption of As(V) compared to As(III) and varied with the availability of sorption sites in the soil, i.e., the effect was greater where sorption capacity was small or sorption sites were occupied. Moreover, the effect of Ca is expected to become more important where Coulomb forces are significantly involved in As binding (i.e., for arsenate and low availability of specific sorption sites) to the surface and in variable charged soils [169].

Effect of Anion Competition: The presence of other anions competing for the same sorption sites generally results in decreased As (arsenate) adsorption or enhanced desorption of previously adsorbed As. Owing to their chemical similarities, phosphate and arsenate effectively compete for sorption sites on model substances and soils [11, 60, 71, 107, 117, 169, 190, 205]. At equimolar concentrations, the relative competitiveness of the two oxyanions varies with the mineral or soil considered [190] and as a function of anion load and pH. Generally, arsenate appears to be more competitive than phosphate on oxy/hydroxides of Fe, Mn and Ti and Fe-rich phyllosilicates whereas phosphate is sorbed more strongly than arsenate on oxy/hydroxides of Al and other Al-rich minerals such as allophanes, kaolinite and soils containing large amounts thereof [169, 190]. Arsenate is becoming more competitive at low pH and with increasing residence time [190]. Other inorganic anions which are commonly present in soil solutions at higher concentrations such as chloride, nitrate or sulphate have generally little effect on As sorption in soils [107].

Another interaction of environmental importance occurs with anions of low molecular organic, fulvic and humic acids that are commonly present in soil solutions.

The efficiency of these dissolved organic substances at decreasing As sorption to soil mineral surfaces has been demonstrated in batch [64] and column studies [105] and has been inferred in the interpretation of field observations of enhanced As leaching from organic soil layers [198].

9.4.1.2 Soil Pore Water

Information on As concentrations in soil pore water is generally scarce. Arsenic concentrations in pore waters obtained from 49 Dutch topsoils (0–20 cm) by centrifugation after equilibration with 2 mM $Ca(NO_3)_2$ solutions (moisture adjusted to pF $= 2$) ranged between 0.75 and 2,160 μg L^{-1} (mean 50.2). Corresponding total As concentrations ranged between 0.75 and 62 mg kg^{-1} (mean 14.2). The soils varied widely in their properties and were collected from sites with no or little agricultural impact covering the Netherlands. The high maximum is explained by spiking of this particular soil in the laboratory [139]. Solid-liquid distribution coefficients in 30 uncontaminated grassland topsoils from Belgium determined with isotope exchange ranged between 14 and 44,301 L kg^{-1} [31].

Arsenic concentrations in soil solutions obtained with tension lysimetry at various sites in Austria [198] and Germany [76] are compiled in Table 9.3. For the forest sites, comparison of soil solution data with As concentrations in throughfall below the tree canopy (Table 9.3) indicates that As is being mobilised from forest floors and readily fixed in the mineral soil [76, 198]. The exceptionally large concentrations in the subsoil at site St. Margareten are related to weathering of the primary mineral arsenosiderite and the high pH (7.5) of the calcareous soils [198]. Huang and Matzner [75] report As concentrations ranging between 0.2 and 2.5 μg L^{-1} in field-collected pore water (dialysis chamber method) from an acidic fen profile located in the German Fichtelgebirge mountains. The concentrations increased from April to June, indicating mobilisation by microbial methylation in the growing season [75]. Arsenic concentrations in soil pore water of a paddy soil in Japan measured using tension lysimetry ranged up to 2.35 μg L^{-1} in the top layers (0–1 m) subject to water table fluctuation, and up to 0.8 in the underlying clay sediment [174]. Seasonal variation of As solubility and speciation indicates that As was quickly released by reductive dissolution from Fe oxy/hydroxides (ferrihydrite) and reduction of As(V) to As(III). The contribution of reductive As dissolution was suggested by concomitantly increased Fe concentrations, whereas As(V) reduction was supported by increased As/Fe ratios in soil pore waters and the solid phase (XANES analysis) during the flooded periods [174].

Arsenic speciation in the "truly dissolved phase" (<0.45 μm) of soil pore waters is generally dominated by its inorganic forms, i.e. arsenate and arsenite as confirmed both in microcosm and field studies [36, 59, 76, 77, 98, 146, 175, 179], with organic forms being present only in traces in most mineral soils [77, 146]. Whereas inorganic As forms dominate even in highly organic soils and soil horizons, such as peat soils/fens [75] and forest floors [74, 76], organic As may constitute an appreciable proportion of total soluble As in such soils [74, 76]. Organic As species

Table 9.3 Arsenic concentrations in bulk precipitation, throughfall and soil solutions collected using tension lysimetry from sites in Austria, Germany and Japan

Location	Land use	Total soil arsenic mg As kg^{-1}	Source of pollution	Bulk precipitation µg As L^{-1}	Throughfall	Forest floor percolate	Irrigation water	Soil solution		Reference
								Topsoil	Subsoil	
Lend	Alpine pasture	109–11	Mining/ smelter	0.6 (0.2–6.8)				2.4 (1.0–7.4)	1.3 (0.5–6.1)	[198]
St. Margareten	Alpine pasture	2,180–2,070	Lithogenic	5.45 (1.9–28.6)				101 (69.1–147)	98.4 (64.1–171)	[198]
St. Margareten	Norway spruce	1,400–387	Lithogenic		(0.5–4.1)	25.7 (12.1–34.4)		14.0 (11.5–16.7)	13.1 (8.6–24.5)	[198]
Seetal	Norway spruce	(43) 263–38	Mining/ smelter		0.4 (0.2–5.0)	4.3 (1.5–6.9)		0.9 (0.3–2.7)	0.5 (0.1–2.3)	[198]
Brixlegg	Norway spruce	(326) 650–16	Smelter		2.2 (1.3–7.6)	68.8 (14.5–110)		2.8 (0.5–6.7)	0.4 (0.05–4.0)	[198]
Lehstenbach	Norway spruce		Air pollution	0.31 (0.14–1.21)	0.46 (0.18–2.86)	3.65 (2.37–7.65)		1.36 (0.27–2.02)	0.22 (0.03–0.63)	[76]
Tsukuba-Inashiki plateau	Paddy rice field	ca. 9/23–5	Irrigation water				0.4	ca. 0.0–2.35	ca. 0–0.8	[174]

that have been identified and detected in soil pore waters and extracts primarily include AsB, MMA, and DMA, [36, 59, 77], and smaller amounts of TMAO and TETRA [59, 74]. Huang and Matzner [74, 76, 77] also detected traces of up to four unknown organic As species some of which appeared to be derived from input to the soil with throughfall, while others were probably produced by/released from soil biota. From laboratory-scale studies, there is indirect evidence for As complexation by dissolved fulvic and humic acids [23, 132], and the formation of ternary complexes of As with DOM via bridging cations such as Fe, Al, Mn or Ca [104, 150], but their contribution to As speciation in field soil pore waters remains to be elucidated.

Speciation of inorganic As is thermodynamically controlled by pH and redox potential, and, at equilibrium, can be predicted from pe (Eh) – pH diagrams [14, 18, 69, 157]. In the common pH range of soils (pH 3–9), dissociation products ($H_2AsO_4^-$ at pH <7, $HAsO_4^-$ at pH >7) of As acid (H_3AsO_4) are predicted to predominate in pore waters of aerobic (oxic) soils (pe + pH > 10), undissociated As acid ($H_3AsO_3^0$) in anaerobic (unoxic; pe + pH < 8) conditions [157]. Thermodynamic predictions are well in line with speciation measurements of As(V) and As (III) at laboratory scale [108, 119, 146] and in soil pore waters collected from field soils [74–77, 174, 198].

Apart from "truly" dissolved constituents, soil pore waters may also contain colloids [1], very fine, suspended particles with dimensions between diameter 0.001 and 1.0 μm [70] that act as carriers of metal transport in aquatic environments [121] and soils [58]. These mobile particulate phases typically include clay minerals, oxy/hydroxides (distinct particles or as coatings on clay minerals), and humic substances [121]. As the transition from the "truly" dissolved phase to colloidal fractions is a continuum rather than defined by a clear cut-off [5], analytical partitioning (e.g., using centrifugation, dialysis or sequential filtration) of elements among the dissolved and colloidal fraction is operationally defined [58, 121]. In a dialysis study, Chen et al. [23] found virtually no association of As with Fe-, Al - and Ca-containing colloids (>3,500 Da) released from the soils upon peat addition to five golf-course soils. However, sequential filtration (employing 0.45, 0.2, and 0.1 μm membrane filters) of solutions from two contaminated soils (Austrian Alps) revealed substantial association (ca. 65 %) of As with Fe-bearing colloidal phases (0.1–0.45 μm) in a soil with pH 5.8, and lower but still significant contribution of colloids in soils with pH 3 (ca. 11%) and pH 6.7 (ca. 28%) [185]. Colloid-facilitated transport (fraction 0.2–20 μm) of As(III) in two soils from Louisiana and New Hampshire (pH 6.6 and 5.3) was generally small in column experiments if the ionic background of the input solution (0.01 M NaCl) was maintained constant, but increased upon replacement of the electrolyte solution by deionised water [211]. Concomitant peaks of colloid generation and Fe concentrations suggest mobilisation of Fe oxy/hydroxides and colloidal transport of As(III) sorbed to oxy/hydroxides surfaces, whereas organic matter coatings appeared to stabilise aggregates of colloidal particles [211].

9.4.2 Biogeochemical Transformations of Arsenic in Soils

Arsenic solubility, bioavailability, toxicity and volatilisation in soils are subject to changes due to chemical reactions and biochemical processes controlled by changing environmental conditions such as wetting (flooding) – drying cycles (e.g., in paddy soils), seasonal variation in temperature and soil moisture, input of organic materials, among others. The main processes involved are oxidation/reduction and methylation/demethylation of As [191]. Microbial metabolisms play a major role even though abiotic redox transformations of As may occur in soils, albeit at slower rates [2, 115]. Root activities not only create a specific environment for microorganisms but may directly contribute to As transformation and speciation in the surrounding rhizosphere soil [46].

9.4.2.1 Microbial Mechanisms Involved in Arsenic Transformation

Mechanisms employed by bacteria capable of either oxidising As(III) or reducing As(V) include energy generation/conservation and detoxification [115, 152]. In anaerobic growth conditions, arsenate is used by respiratory enzymes of strict or facultative anaerobes of the domain *Bacteria* as a terminal electron acceptor to generate energy, resulting in the production of arsenite (dissimilatory reduction, As respiration). Arsenite oxidases are used by both heterotrophic (e.g., *Agrobacterium tumefaciens*) and chemotrophic bacteria to use the reducing power from As(III) oxidation for growth. However, reduction of As(V) to As(III) by various soil microorganism (e.g., *Pseudomonas* spp., *Bacillus* spp.) occurs via detoxification activities encoded by a variably organised *ars* operon resulting in intracellular reduction of As(V) and subsequent excretion of As(III) via efflux pumps into the surrounding soil [87, 115, 152]. This As(III) efflux may explain apparent non-equilibrium conditions [115] indicated by the presence of significant levels of As (III) in aerobic (oxic) soil environments [114, 196]. Generally, bacteria with As(III) oxidising capabilities co-exist with As(V) reducers in soil environments and are considered important controls of inorganic arsenic speciation in soil pore waters.

9.4.2.2 Redox Transformations of Inorganic Arsenic

In a column study under aerobic (unsaturated) conditions, Macur et al. [115] observed rapid oxidation of arsenite to arsenate in a calcareous soil from California. From the same soil, these workers isolated bacterial strains with oxidising and reducing capabilities. Interestingly, two *Agrobacterium tumefaciens* isolates with 100% identical 16SrDNA sequences displayed opposite redox phenotypes. In a similar column study, Macur et al. [114] found arsenate as the predominant arsenic species in leachates from mine tailings under aerobic, sterile conditions but arsenite became predominant in the presence of microorganisms (non-sterile column), indicating that microbial reduction of As(V) in As-contaminated soils may occur in aerobic conditions within relatively short time.

The nature, surface area and arsenate surface coverage of hydrous oxy/hydroxides appear to determine the rate of As mobilisation during reduction. In a controlled Eh/pH chamber experiment (pH maintained at 7.5) where a microbial population extracted from an agricultural soil was inoculated to arsenate solutions, dissolved total As decreased by about 30% while As(III) concentration increased when the redox potential was lowered from 500 to 0 mV in the presence of goethite with high (molar As: Fe ratio 0.04) As surface coverage but increased seven fold at low (molar As: Fe ratio 5.3×10^{-4}) surface coverage [92]. Arsenic solubility increased 100-fold faster in the presence of ferrihydrite (molar As: Fe ratio 0.012) than in goethite suspensions at similar initial arsenate concentrations in solution [92]. Based on their findings, Jones et al. [92] suggested diverse mechanisms controlling As solubility during reduction: (1) reduction of As(V) to As(III) at initially high redox potentials may be related to microbial detoxification, subsequent reduction to As(III) may have been due to both detoxification and As(V) respiration; (2) decreased arsenic solubility upon lowered redox potentials at high As:Fe ratios may be explained by stronger adsorption of As(III) than As(V) to goethite at the experimental pH (7.5) (compare also [173]); (3) the opposite trend observed at low As:Fe ratios may be a result of weaker sorption of As(III) than As(V) on Fe oxy/hydroxides at low surface coverage (compare also [141]); aqueous As(III) formation in the presence of goethite was considerably slower than in solution only, and was probably controlled by desorption of As(V) with only little contribution of co-dissolution of arsenic from the goethite; (4) in the presence of ferrihydrite, increased iron solubility indicated co-dissolution of arsenic when the redox potential was decreased.

Huang and Matzner [75] investigated the dynamics of As speciation in field-collected pore waters from an acidic fen in Germany. Arsenic solubility and the ratios of As(III):As(V) increased substantially during the growing season, but were not correlated with concurrent changes of the redox potential, indicating the biological nature of reduction. Larger As(III):As(V) ratios in soil pore water compared to methanol-water (20% v/v) extracts suggest that reduction of As(V) mainly occurred in the aqueous phase [75]. Similarly, Takahashi et al. [174] provide evidence that reduction of As(V) to As(III) in the aqueous phase explained most of the As(III) formation observed during flooding periods in a paddy rice soil in Japan, along with some contribution of reductive co-dissolution of iron (oxy)hydroxides indicated by concurrent increase of iron solubility. Based on measured distribution coefficients of As(III) and As(V) and their speciation changes in the solid phase during flooded and non-flooded periods, Takahashi et al. [174] calculated that the reduction of As(V) to As(III) and the weaker sorption of the latter accounted for about one half of the observed increase of As solubility during flooded periods.

In an incubation experiment, flooding of two Texas soils for sixty days resulted in substantially increased solubility of native As, however, apart from the observed drop in the redox potential below +100 mV, all As was present as As(V) [137]. When As was added either as arsenite or arsenate, decreased As solubility was observed probably due to adsorption or precipitation of insoluble As compounds [137].

In contrast, Deuel and Swoboda [33] observed clearly increased As solubility upon decreased redox potentials, along with increased Fe solubility. They explained their findings by reductive co-dissolution with Fe oxy(hydroxides) rather than reduction of As(V) to As(III).

9.4.2.3 Biotransformation Processes Involving Organic Arsenicals

It has been suggested that methylation of As in soil follows the so called Challenger pathway [21] of alternate steps of reduction and oxidative methylation, ultimately producing volatile trimethylarsine (TMA(III)) (Fig. 9.2) [152]. However, other organic arsenicals have been measured in soil environments and alternative pathways of demethylation have been proposed in the literature (Fig. 9.2).

In laboratory conditions, the formation of volatile dimethylarsine and trimethylarsine (TMA(III)) was encountered in both aerobic and anaerobic soils; the rate of volatilisation was greater in aerobic conditions and affected by the arsenical compound (sodium arsenate, monosodium methanarsonate or cacodylic acid (CA)) applied to the soil [202]. Volatilisation losses of CA were found to depend also on the applied amount, soil type and soil moisture [203].

Gao and Burau [52] systematically studied the effect of As form and concentration, soil moisture and temperature, and cellulose amendment on microbial reduction, methylation and demethylation/mineralization of added inorganic and organic arsenical compounds in a non-calcareous silty clay soil from California. Arsine evolution increased in the order: sodium arsenate = sodium arsenite < methanearsonate (MAA(V)) < sodium cacodylate (CA). The rate of arsine formation from CA was generally small (0.001–0.4% within 70 days) with a maximum at soil moisture contents between 250 and 350 g kg^{-1} soil, and increased with temperature (25°C vs. 5°C) and addition of cellulose. Methylation of arsenate or MAA(V) to CA was negligible.

Arsenate formed as the main product of demethylation of CA and MAA(V), with higher mineralization rates observed for CA. Based on their data, Gao and Burau [52] suggested direct demethylation of CA to arsenate rather than MAA(V) as an intermediate. Demethylation of CA increased with CA amended, and with soil moisture content increased from 50 to 550 g H_2O kg^{-1} soil. Cellulose addition (0–5% w/w) resulted in suppressed CA mineralization. The percentage of CA and MAA(V) mineralized within 70 days ranged between 3% and 87% [52].

In synthetic chromated Cu arsenate (CCA)-contaminated soils inoculated with microorganisms from a surface field soil collected adjacent to a CCA-treated pole, Dobran and Zagury [36] could not detect any As(V) reduction or biomethylation within 40 days of aerobic conditions (80% of field capacity), irrespective of the amount of organic matter (peat moss, poultry manure) added.

In a microcosm study under anaerobic conditions, Deuel and Swoboda [33] found no detectable formation of volatile arsines from a number of Texas soils.

No detectable amounts of organic arsenicals were found in field-collected pore water from an acidic fen at the end of the dormant season (April) whereas during the

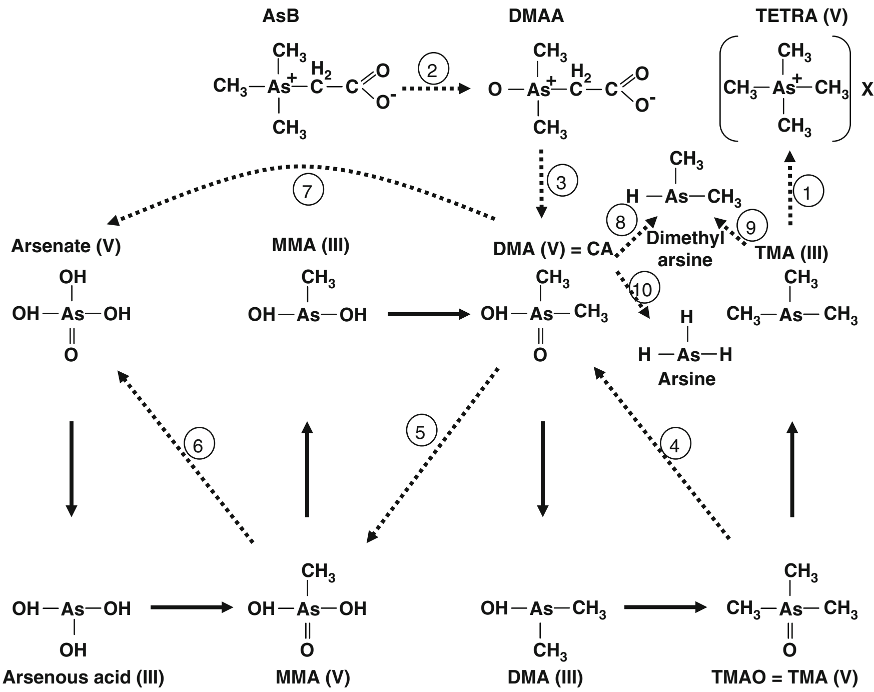

Fig. 9.2 Biotransformation pathways of As in soil. Reactions of the Challenger pathway [21] are depicted by solid arrows, other suggested biotransformation pathways are indicated by *dotted arrows* (*1* = methylation of DMA(III) to TETRA(V); *2* = rapid demethylation of AsB to dimethylarsenoyl acetate [78]; *3* = rapid demethylation of DMAA to DMA(V) [78]; *4* = demethylation of TMAO to DMA(V) (this work, based on data of [183]); *5* = demethylation of DMA(V) to MMA(V) [78]; *6* = slow demethylation of MMA(V) to arsenate [78]; *7* = direct demethylation of DMA(V) to arsenate [52].; *8* = reductive pathway of DMA(V) metabolisaton, i.e. bacterial reduction of DMA(V) to volatile dimethyl arsine [1, 13]; *9* = anaerobic pathway of TMA(III) metabolisation, i.e. demethylation with dimethyl arsine as stable end product [28]; *10* = arsine formation from DMA(V) [52]). Legend for compounds: *MMA(V)* monomethylarsonate, methane arsonic acid or (mono)methyl arsonic acid; *MMA(III)* monomethylarsonite; *DMA(V)* dimethylarsinate, dimethylarsinic acid or cacodylic acid (CA); *DMA(III)* dimethylarsinite; *TMAO = TMA (V)* trimethylarsine oxide; *TMA(III)* trimethylarsine; *TETRA(V)* tetramethylarsonium ion; *AsB* arsenobetaine; *DMAA* dimethylarsenoyl acetate (= demethylarsinyl acetate)

growing season (June) organic species made up to 70% of total soluble As, with substantial variation in the depth profile [75]. The predominant organic species were MMA(V), DMA(V) and AsB whereas TMAO, TETRA and three unknown species were present in lower concentrations. These findings provide evidence for *in-situ* microbial methylation of arsenic [75].

Huang et al. [78] observed rapid (half-lives: 3.6–12 days) demethylation of arsenobetaine (AsB) added to 0.1% pyrophosphate extracts obtained from a forest floor (incubated aerobically) and an acidic fen soil (incubated aerobically or un-aerobically) whereas DMA(V) demethylation was rather slow (half-lives: 187 days for forest floor, 46 days for the aerobic fen extract) or negligible (un-aerobically incubated fen extract). As they found dimethylarsenoyl acetate (DMAA) but no

TMAO as intermediate, they suggested that microbial metabolisation of AsB to DMA(V) occurred via this intermediate rather than TMAO (compare with Fig. 9.2).

Anaerobic demethylation of TMA(III) was shown to proceed only to dimethylarsine as this compound is stable in the absence of oxygen but readily oxidised in aerobic conditions [28].

9.4.2.4 Root–Rhizosphere Processes Involved in Arsenic Transformation

Similar to microorganisms, plants are able to detoxify As(V) via root uptake, subsequent intracellular reduction to As(III) and As(III) efflux into the surrounding rhizosphere [213], which may explain the co-existence of As(III) and As(V) in aerobic rhizospheres [182, 183, 189]. Reductive co-dissolution from Fe oxy/hydroxides has been suggested as another possible mechanism of As(III) production in the rhizosphere [48]. Both mechanisms may contribute to the build up of As(III) even in aerobic rhizospheres as found in a semi-hydroponic study for corn (*Zea máys* L.) [189]. Increased As solubility (As(V) and As(III)) may further be attributed to proton- and/or ligand-promoted co-dissolution of As and Fe oxy/hydroxides due to root exudation of protons and low-molecular organic compounds [46, 48, 189]. Exudation of organic anions may release adsorbed As into soil pore water via ligand exchange mechanisms [46]. Evidence for substantial As mobilisation by root activities, in particular enhanced DOC concentrations in the rhizosphere, is available for Chinese Brake fern (*Pteris vittata* L.), a hyperaccumulator of As [48, 166, 181]. The efficiency of some low molecular weight organic anions for mobilising both arsenate and arsenite from soils was also demonstrated in batch experiments [176, 212]. Strong correlations of organic anions with dissolved Fe, Al and Mn may suggest co-dissolution of As from oxy/hydroxides [212].

In addition to root activities, microorganisms may be involved in As transformations in plant rhizospheres. In a hydroponic study, inoculation of *Azospirillum brasilense* Sp245 to the sterile plant-growth medium was shown to increase the As (V):As(III) ratio by a factor of 1.5 [112], possibly indicating a role of rhizobacteria in oxidation of As(III) derived from root efflux. Indirect evidence for As mobilisation by rhizosphere microorganisms may be derived from experiments where As uptake in plants was enhanced upon inoculation of rhizobacteria or rhizofungi to sterile soil or plant-growth medium [26].

Biotransformation of inorganic As species to DMA(V) was shown in rhizobox and rhizobag experiments to occur in the rhizosphere of sunflower (*Helianthus annuus* L.) only upon inoculation with an arbuscular mycorrhizal fungus (*Glomus aggregatum*) [182, 183]. However, TMAO was only found in the presence of the native soil microbial community (non-sterile soil), irrespective of inoculation and root activities [182]. In contrast to the conclusion drawn by Ultra et al. [182, 183], their findings suggest demethylation rather than methylation of TMAO by the inoculated arbusular mycorhizal fungus in the mycorrhizosphere, resulting in the formation of DMA(V), as TMAO was detected in the non-sterile rhizosphere and bulk soil compartments independent of inoculation; TMAO may have been produced through methylation of inorganic As species by the native soil microbial community or derived from plant material.

Root mineralization may contribute to the release of As to the soil pore water [187], but the forms of As are not known. However, based on information on As speciation in plant tissues [123, 161], it is reasonable to assume that As released from decomposing roots is mainly inorganic (arsenite, after oxidation also arsenate) and associated with PCs. Apart from microbial degradation, As-PC complexes are expected to dissociate readily if released to near neutral and alkaline soil pore water as they become instable at pH >7.2 [161].

9.5 Soil–Plant Relationships of Arsenic

Plants can take up As from soils both in the form of arsenate or arsenous acid. It is generally accepted that arsenate, an analogue of phosphate, is taken up via phosphate transporters [8, 125]. More recently it was shown that arsenous acid may enter the plant via aquaporins owing to its similarity to silicic acid [113, 124]. There is no evidence for essentiality of As to plants [213] even though low levels may be beneficial for root development [42]. Once taken up, arsenate in root cells is rapidly reduced to arsenite which is released back into the external medium (As-III efflux), complexed by thiol peptides or transferred to shoots [213]. Arsenite efflux is thought to occur via anion channels as known for phosphorus or via bidirectional aquaporines [213].

Arsenic concentrations in plants are largely species/cultivar/ecotype-specific [47] and range between 0.009 and 1.5 mg kg^{-1} for most plants growing on non-contaminated soil [97]. However, on polluted sites even excluder plants may accumulate several thousand mg As kg^{-1} DM in shoots and more than 10,000 mg As kg^{-1} DM in root tissues [46]. Arsenic hyperaccumulation has been found in 12 species belonging to the *Pteridaceae* family of ferns [213], with arsenic concentrations in fronds up to >20,000 mg As kg^{-1} DM [67, 192].

Phytotoxic levels of As in soil vary primarily depending on the source of As and soil texture [163]. Based on a review of 60 datasets (crop–soil pairs) available in the literature, Sheppard [163] established geometric means of toxicity thresholds for sand and loam soils (40 mg kg^{-1} total As), and clay soils (200 mg kg^{-1}). The higher toxicity of As in light-textured soils is consistent with its higher solubility owing to lower specific surface area and Fe oxy/hydroxide content [109]. Tolerance limits for As hyperaccumulator ferns have been reported to range between 5,000 and 10,000 mg As kg^{-1} d. wt. [110, 180].

9.6 Polluted Soils

Arsenic-polluted environments are abundant in many major regions of the world [17]. Most of the highly-impacted areas are related to (abandoned) mining, smelter or metal processing activities (e.g. [10, 12, 19, 93, 94, 96, 103, 198, 201]). Total As concentrations in polluted soils were found to be as high as 360,000 mg kg^{-1}

measured at an industrial site in Belgium [19], but more commonly range between several hundreds and thousands mg kg^{-1}. Arsenic solubility in polluted, well aerated mineral soils containing common levels of Fe oxy/hydroxides is comparably low, rarely exceeding a few μg As L^{-1} [76, 198]. Again, the Belgium site studied by Cappuyins et al. [19] displays exceptionally high pore water concentrations up to 38,000 μg As L^{-1}.

Historical As depositions accumulated in forest floors continue to leach into the mineral soil for long periods after ease of the pollution source [41, 76, 198] where As is readily immobilised by Fe oxy/hydroxides [198]. Therefore even highly polluted soils have been observed to act as net sinks of As [41, 76, 198] except two sites in the Czech Republic [41] where the retreat of soil acidification through atmospheric deposition has been identified as a possible explanation of enhanced As leaching in recent years. In these soils, As may be mobilised due to the competition of hydroxyl anions.

Based on the analysis of 38 contaminated sites in the Austrian Alps and soil pore water measurements in selected locations, Wenzel et al. [198] established threshold levels for total As in aerobic mineral soils that may be considered safe in terms of groundwater protection. They found that for total soil As of <200 mg kg^{-1} soil pore waters are expected to contain <10 μg As L^{-1}, i.e. below the current drinking water standard of the WHO.

Surface soil contamination is often associated with enhanced uptake of As in plants even though most plants are As excluders [17]. Whereas As concentrations in plants normally range well below 0.5 mg kg^{-1} d.wt. [151], pasture herbage, crop plants and wild plants growing on As -contaminated soil have been reported to contain slightly elevated As levels up to several mg kg^{-1} [10, 17, 96, 103]. However, there are also reports of plants grown on extremely polluted mine land may contain several hundreds or thousands mg As kg^{-1} even in shoot tissues [12, 94, 145, 201].

9.7 Concluding Comments

A wealth of new information on the fate of As in soils has become available during the past two decades since the first edition of this book. With the availability of novel techniques to study As interactions with mineral surfaces on a molecular scale, our understanding of As sorption in soils has much improved. The general interest of our societies and researchers in the environmental behaviour of As and in particular in soils has been tremendously raised by large-scale calamities such as the As poisoning of drinking and irrigation water in the Bengal region and the accidental spill of As-rich material in Spain. Without doubt, this has further stimulated research activities to understand pathways of risks associated with As-polluted soils. Nevertheless, our understanding of some aspects of As in soil environments is still poor, in particular little is known about the chemistry and fate of As in organic soils and soil layers or in plant rhizospheres. The years to come will hopefully elucidate some of the remaining “white spots” on the landscape of As in soil.

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Chapter 10
Cadmium

Erik Smolders and Jelle Mertens

Abstract Cadmium (Cd) is naturally present in soils at concentrations 0.1–1 mg Cd kg^{-1}. Cadmium is readily available for uptake by food crops and food chain contamination with Cd from contaminated soil has led to effects on kidney functioning in humans, even reaching fatal levels in subsistence farmers who consumed rice from a contaminated area in Japan. Diffuse Cd sources, notably P-fertilisers and atmospheric depositions have increased soil Cd concentrations by about 0.1–0.3 mg Cd kg^{-1} above pre-industrial levels and actions have been taken worldwide to limit Cd emissions or Cd exposure to humans. Emissions of Zn–Cd smelters have been cut in numerous places but residual soil Cd contamination is still present. Cadmium retention in soil is controlled by sorption reactions and soil pH is the main determinant. Soil Cd availability for crop uptake varies by about a factor 10 among soils and generally increases 1.5-fold by decreasing soil pH with one unit. Crops differ in Cd uptake and hard wheat and potatoes have a considerable impact on the dietary Cd intake. Contrasting views exist on the food chain risk of Cd as both soil Cd and food Cd bioavailability may have been larger in the Japanese case study than in the general environment. In Europe, a generic Cd risk assessment in 2007 led to the conclusion that risk cannot be excluded for the general population environmentally exposed to Cd. However, limits on P fertilisers, as main determinants of Cd emissions, are not yet in place.

Keywords Cadmium • Kidney • P-fertiliser • Sorption • Bioavailability • Dietary • Itai-itai • Guano • Sewage sludge • $CdCl_n^{2-n}$ • DOM • Isotopically exchangeable • Biosolids • BCF • NOEC • PNEC • Creatinine • Phytoremediation

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10.1 Introduction: The Environmental Significance of Cadmium in Soil

Cadmium (Cd) is a non-essential metal that is naturally present in all soils. Cadmium occurs in soil as a divalent cation (Cd^{2+}) at concentrations typically ranging 0.1–1.0 mg kg^{-1}. Current Cd concentrations in soils are somewhat higher than pristine (geogenic) values because of the historical additions through atmospheric deposition and the use of P-fertilisers (see Sect. 10.3). The Cd concentration in soil represents only minute fractions (10^{-4}–10^{-6}) of the total soil exchangeable cations or of soil solution cations. Hence, the presence of Cd is unlikely to affect the chemistry of the soil. In contrast, Cd can affect the ecosystem function at trace levels because of its pronounced toxicity. Additionally, the toxicity of Cd in soil is persistent, not only because its residence time exceeds decades but also because its bioavailability does not decrease in the long term [54]. For these reasons, several actions have been taken worldwide to reduce environmental emissions of Cd. The industrial production and the use of Cd has declined sharply in USA and Europe as a result of the environmental concerns about Cd although the global numbers show only a weak negative trend due to increased use in China [63].

Risk of soil Cd to humans occurs at soil Cd concentrations well below those required to cause frank and visual effects on plants or soil biota. Human health effects are related to exposure via the food chain, i.e. the consumption of Cd contaminated crops. The dietary intake of Cd constitutes generally >90% of the human exposure to Cd in the general population and most of dietary Cd is derived from soil via uptake in main food items, i.e. cereals or potatoes. The chronic (lifetime) exposure matters far more than single high intake events because Cd has a long biological half-life of 15–20 years in humans and the effects manifest themselves mainly in older people (>50 years). This means that a rare consumption of a high Cd containing food item grown in a local Cd contaminated soil has less effect than the lifetime consumption of moderately contaminated food. For these reasons, risk of point soil Cd contaminations may be low if there is sufficient ‘dilution’ with food items grown elsewhere. Local soil Cd is at risk if people use the same soil to grow major food for an appreciable time of their life. This situation has occurred in subsistence farmers in Japan. The identification of the Cd toxicity to humans was already discovered before the end of the nineteenth century but it was not until the 1960s before risk of soil Cd became clear when an endemic bone disease in the Toyama prefecture (Japan) was related to Cd in soil [47]. The so-called ‘*itai-itai*’ disease is a bone disease with fractures and severe pain that was identified in the early 1950s in that prefecture. Patients were mainly women who had delivered several children and who consumed locally grown rice. The rice paddies (1–10 mg Cd kg^{-1} soil) had been irrigated with Cd contaminated water of the Jinzu River that drained a metal mining area. The chronic Cd intoxication induced tubular dysfunction of the kidney, leading to increased excretion of Ca and of low molecular weight proteins and finally to osteomalacia (softening of the bones). In the Jinzu basin, 188 cases of this disease were officially recognized [47]. Current understanding of the itai-itai disease shows that the cumulative (life-time) exposure is the best index for estimating the effects and that a total lifetime intake of 2–10 g of Cd led to severe intoxication and even death of the patients [32].

Table 10.1 shows the contrast between the human exposure at background (ambient concentrations) and that at the point of severe poisoning. The severe poisoning is identified at an estimated daily Cd intake via the food of about 300 μg day^{-1}. Such an intake was obtained by a combination of a large daily rice consumption with rice containing about 0.75 μg g^{-1}. Table 10.1 reveals a number of features that are typical for Cd. First, the *fatal* Cd toxicity in humans occurs at a dietary exposure that is only about 10–20-fold above natural background. *Moderate to tolerable* health impacts at population level are logically found well below those fatal impacts and can be expected closer to background concentrations. The most recent re-evaluation of the food chain risk of Cd by WHO (2010) has defined a tolerable monthly dietary intake value of 25 μg Cd kg^{-1} body weight, about 58 μg day^{-1} which is only about three to seven times the average intake value of the general population (Table 10.1). Along the same lines, broad agricultural surveys often find significant percentiles exceeding current crop Cd limits, even in soils well away from point sources [1]. A second observation is that Cd effects occur in the μg kg^{-1} range, i.e. accurate and precise monitoring of these concentrations is an analytical challenge. No Cd monitoring programme may be trusted without adequate quality control with certified reference materials. The relatively late identification of the cause of the itai-itai disease has been ascribed to the lack of good analytical facilities to identify Cd in the 1950s. As a final note, it must be realised that exposure and effects of Cd are not simply proportional to the total Cd concentration in soil. This is related to the large difference in Cd soil and food bioavailability and large differences in land use and dietary habits. The Cd bioavailability in soil and in the diet obviously complicates the risk assessment of Cd, but may be also taken as an advantage, i.e. Cd risks can be managed by reducing its bioavailability on its route from soil to humans as will be illustrated below.

10.2 Geochemical Occurrence of Cadmium

There are only a few specific Cd minerals in the environment such as greenockite (CdS) and otavite ($CdCO_3$). Cadmium does more commonly occur in Zn minerals and Cd was also first discovered in 1817 by purifying it from a ZnO sample. Cadmium has always been produced as a by-product of Zn and typical weight Cd:Zn weight ratios are 1:200. Cadmium concentrations are generally higher in sedimentary rocks than in igneous rocks (Table 10.2) and their concentrations generally rise with increasing P, S and C concentrations in rocks. Soil Cd concentrations (Table 10.2) are typically found in the 0.1–1.0 mg kg^{-1} range and the average or median values of different large scale surveys settle in the range 0.1–0.3 mg Cd kg^{-1} (Table 10.2). The Cd concentrations in non-contaminated soils generally increase with decreasing % sand since Cd is associated with the finer

Table 10.1 The human exposure to soil Cd at ambient conditions (away for point sources) and in the region where the Cd related itai-itai disease was first observed in the 1960s

Exposure conditions	Soil Cd (mg Cd kg^{-1})	Grain Cd (mg kg^{-1}, fresh weight basis)	Dietary intake for adult (µg Cd day^{-1})	Cumulative lifetime intake (g Cd)
Non-contaminated (ambient)	0.1–1	0.01–0.10 wheat 0.02–0.20 rice	8–20	0.1–0.4
Contaminated (Fuchu, Japan)	1–10	0.20–2.0 rice	160–600	2–10
Limits	0.8–39	0.10–0.40	70 (WHO 1992–2009[a])	
	Various legislations	Cereal grain, wheat and rice	25 (EFSA opinion, 2009[b])	
		FAO/WHO (CODEX, 2010)	58 (WHO 2010[c])	

The lifetime Cd intake that is associated with severe Cd disease onset for 50% of the itai-itai patients is 3.8 g Cd and is 5.4 g Cd at death [32] Environmental exposure to soil Cd mainly occurs via the intake of contaminated food; grains or potatoes are the major contributors to the human Cd diet. Numbers have been compiled by the author based on [22] and [19]

[a] Provisional tolerable weekly intake of 7 µg Cd kg^{-1} body weight and converted here for an adult of 70 kg

[b] Opinion of the European Food Safety Authority defined as 2.5 µg Cd week^{-1} kg^{-1} body weight and converted here for an adult of 70 kg

[c] Adopted in the 73th meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) June, 2010 and defined as a provisional tolerable monthly intake (PTMI) of 25 µg kg^{-1} body weight and converted here for an adult of 70 kg [34]

Table 10.2 Background concentrations of Cd in rock and in soils sampled away from industrial point sources

	Cd concentration (mg Cd kg^{-1} soil or rock dry weight)	References
Rocks		
Igneous	0.07–0.25	[57]
Metamorphic	0.11–1.00	
Sedimentary	0.01–2.60	
Soils		
Europe	0.06–**0.33**–0.87: min, mean and max of regional means/medians	[19]
	0.20–0.67–1.40: min, mean and max of regional P90s	
	0.05–**0.14**–0.48: P10, P50 and P90, n = 840	[52]
USA	<0.01–**0.20**–0.56: P10, P50 and P90, n = 3045	[29]
Australia	0.05–0.97: range of means in rural soils	[43]
China	**0.07** (geomean), 0.10 (average); n = 3,947	[11]
Jamaica	4.0–78: P50–P90	[37]

Data for Jamaica refer to geogenic (natural) Cd. Median or mean values are in bold

particles [2] and, therefore, soil texture may be used to better estimate the baseline Cd values of soil [64]. Soil Cd concentrations exceeding 1 mg Cd kg^{-1} may occur naturally, for example in soils developed on shales or in organic soils [29] (see Sect. 2.3.1.1). Unusually large soil Cd concentrations are widespread in Jamaica (Table 10.2) where the country median Cd concentration is 4 mg Cd kg^{-1} and concentrations up to 900 mg Cd kg^{-1} have been found [36]. The high Cd soils are found in highly weathered bauxitic soils and the source of Cd is attributed to dispersal of guano (sea bird droppings) deposits that formed in the Late Miocene or Pliocene [24]. Phosphorite concretions in Jamaican soils containing >1.1% Cd have recently been found [24] and are probably the highest reported concentrations ever in rock phosphates. Guano deposits are naturally high in Cd (high Cd:P ratio) and reflect the marine food web transfer of Cd from water into pelagic birds.

10.3 Cadmium Emissions to Soil and the Soil Cadmium Mass Balance in Agricultural Soils

Soil Cd is enriched by human activities via atmospheric deposition and through applications of P-fertilizers and sewage sludge. Cadmium mining, production, use and disposal are a net source of Cd that may end up in soil. Over 80% of the current Cd consumption is used for the production of rechargeable batteries [63]. Other uses such as PVC stabilizers, pigments and plating have declined sharply as a result of environmental regulations. The World Bureau of Metal Statistics (2009) estimates that the world annual consumption of Cd was about 18,000 tons in 2008, which is 10–20% lower than in 1991. Consumption of Cd has risen in China while it decreased in western countries. The reduced use of Cd and the

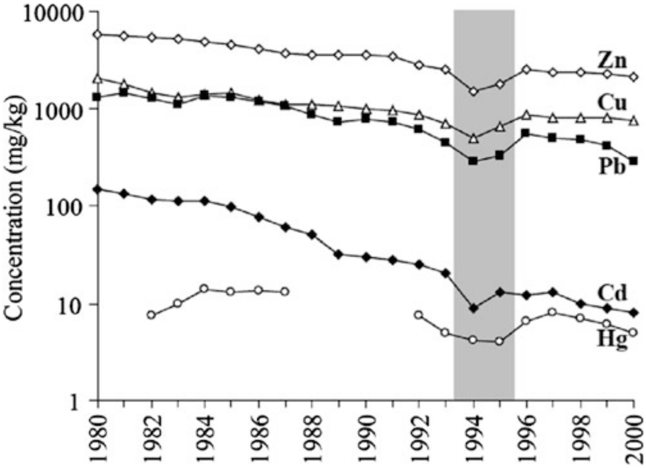


Fig. 10.1 Temporal variations of trace element contents (mg kg^{-1}) in treated sewage sludge from the Seine Aval treatment plant in Paris, France (eight million people). The Cd concentrations decrease faster than Zn concentrations, likely due to reduction in use of Cd products and lower Cd concentrations in galvanised structures such as roof sheets. The *shaded period* represents the time of metro line construction [26]

Table 10.3 Total anthropogenic Cd emissions in the EU-16 (tons y^{-1}) from Cd/CdO industry and its downstream users and diffuse Cd emissions from other sources estimated in 2002 [19]

	To air (t year^{-1})	To soil (t year^{-1})
Cd/CdO production and processing	4.7	–
Other non-ferrous metals production	9.7	–
Production of iron and steel	31	–
Oil/coal combustion	54	–
Processing phosphates	0.7	–
Municipal waste incineration	3.2	–
Other (cement, glass prod., traffic, municipal wastewater)	>20.7	–
Phosphate fertilisers		231
Sludge application on soil		>13.6
Totals	**>124**	**>244.6**

Emissions to air largely return to soil via atmospheric deposition, i.e. a considerable fraction of the 124 t Cd y^{-1} must be added to the emissions to soil

shift in use towards batteries that are increasingly recycled has generally decreased fugitive Cd emissions to water and to sewage sludge in the western world. For example, Cd concentrations in the sewage sludge from the world's second largest sewage treatment plant of Seine Aval (Paris) have decreased >tenfold between 1980 and 2000 while Zn concentrations decreased to a much smaller extent in the same period (Fig. 10.1) [26].

The emission of Cd from Cd/CdO producers and processors only form a minor part of the total emissions of Cd as illustrated for the European data (Table 10.3).

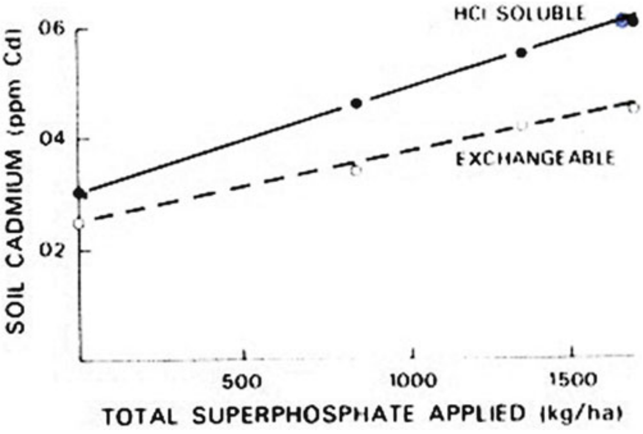


Fig. 10.2 Soil Cd increases with cumulative application of P-fertilisers in experimental plots in Australia. The HCl soluble Cd increases from 0.03 to 0.06 mg kg^{-1} soil [62]

Current emissions of Cd from the Cd/CdO producing industry and its downstream users (including recycling plants) have strongly reduced in EU since estimates of about 20 years ago. The major sources of the net Cd input at the large scale are P fertiliser application, production of iron and steel and oil combustion. Table 10.3 suggests that the EU average ratio of Cd input in soils via P fertiliser (231 t year^{-1}) to that by atmospheric deposition (124 t year^{-1} air emission) is about 2:1. The contribution of P-fertiliser to the accumulation of Cd in soil is well established, with earliest records in Australia (Fig. 10.2) where soil Cd of experimental plots was found to increases with cumulative P applications to the plots [62]. Numerous long-term studies in UK, Denmark, France and Australia have demonstrated the gradual build-up of Cd in soil with typical increases of 0.1–0.3 mg Cd kg^{-1} soil over >100 years (Table 10.4 and see [19] and for a compilation). Such concentration changes are only detectable in long term (>50 years) observations due to analytical and sampling error.

The contribution of P-fertilisers to soil Cd has logically led to proposals to limit Cd in P-fertilisers. Mass balance modelling has been used to estimate allowable fertiliser Cd concentrations, i.e. concentrations at which annual losses balance the input and at which soil Cd concentrations are not further increasing. A considerable fraction of European fertilisers has Cd concentrations >60 mg kg^{-1} P_2O_5 (Fig. 10.4). Table 10.4 illustrates the input-out Cd balance of Europe in 2002 and Fig. 10.3 illustrates the estimated trends for different proposed Cd limits in Europe based on mass balance modelling for different EU countries with site specific information. This assessment showed that 100 years of ongoing use of P-fertilisers with an average Cd/P ratio of about 140 mg Cd kg^{-1} P (60 mg Cd kg^{-1} P_2O_5) would increase soil Cd by 20% with the 90th percentile of the scenarios predicting up to 60% increase. This would also increase food chain Cd by about the same factor since added Cd does not show pronounced Cd fixation (see below Sect. 10.4).

Table 10.4 The Cd input-output (in g Cd ha^{-1} $year^{-1}$) balance in European agricultural soils estimated for 2002 [19]

	Range	EU average
Input		
P fertiliser	1.1–4.5	2.5
Atmospheric deposition	0.6–3 (measured)	0.4 (assumed net deposition)
Animal feed	0.05–0.1	0.05
Total		**2.95**
Output		
Crop offtake	0.3–0.8	0.5
Leaching	0.1–5.7	2.0
Total		**2.5**
Soil Cd	0.30 mg kg^{-1}	0.32 mg Cd kg^{-1}
	Current	After 60 years with 2.95–2.50 = 0.45 g Cd ha^{-1} $year^{-1}$ net input

Input of Cd via compost and animal manure was not considered as a net source of Cd on the regional scale (in contrast with field scale) although import of animal feed represents a small net source of Cd.

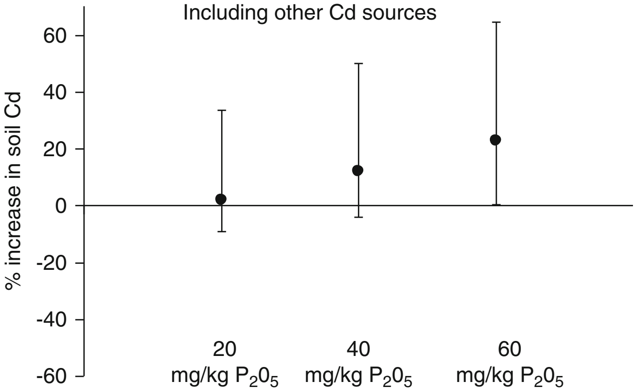


Fig. 10.3 Predicted change in soil Cd in European soils after 100 years at three concentrations of Cd in inorganic P-fertilisers. Means (10–90th percentile) of different EU scenarios that assume various values of fertiliser rates, soil properties, climatic condition and included other diffuse Cd sources. This mass balance calculation was made by this author based on the EU-wide questionnaires on fertiliser Cd risks and was used to propose limits of Cd in EU (not yet adopted in 2011)

10.4 The Fate of Cadmium in Soils

10.4.1 Soil Chemical Reaction Mechanisms

Cadmium in soils is almost invariably present in soil at the Cd(II) oxidation state. The Cd^{2+} cation has an electronic configuration of Pd° with completely filled d-shell ($4d^{10}$), i.e. Cd is not a transition metal. However, the electron cloud of this cation is polarizable and is considered as a class B metal in Schwarzenbach

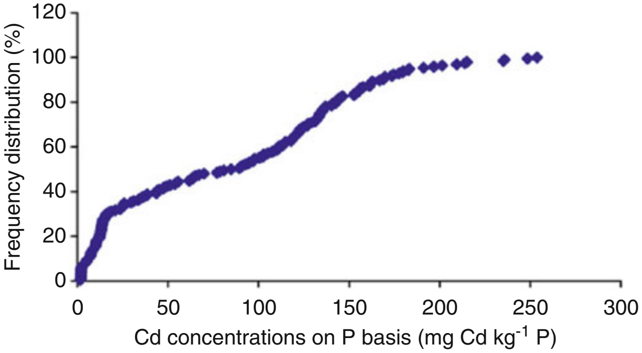


Fig. 10.4 Frequency distribution of Cd concentrations in European fertilisers expressed per unit P (Note: 137 mg Cd kg^{-1} P is equivalent to 60 mg Cd kg^{-1} P_2O_5, the latter being a proposed generic limit in EU but not yet adopted in 2010 [48])

classification of metal (A = hard as Ca^{2+}, C = soft as Cu^{2+}), therefore Cd^{2+} participates in covalent binding with surfaces and is, therefore, less soluble than harder cations. Class B cations such as Cd^{2+} form inner spheres complexes with high selectivity onto surfaces whereas harder cations may bind as outer sphere cations. Below we will illustrate that Cd^{2+} forms definitively stronger bounds with soil particulates or soil colloids than Ca^{2+}, however these bounds are not as strong as for transition metals such as Cu^{2+}.

Soil solution Cd concentrations in uncontaminated (total Cd ~0.2 mg Cd kg^{-1}), pH neutral soils range <0.1–5 μg l^{-1} ([12] and Sect. 10.4.3). This means that only a very small fraction of total Cd is present in soil solution and that annual losses of Cd by leaching are generally negligible. The precise binding mechanisms of Cd in soil are almost impossible to detect with current spectroscopic techniques at environmentally relevant concentration. Therefore, solubility data or chemical extraction data are used to indirectly infer Cd binding mechanism. Christensen [14] suggested that sorption and not precipitation controlled solution Cd in the environmentally relevant concentration range in soil (0.1–10 mg Cd kg^{-1} soil); the solution Cd increases almost proportionally to Cd addition (Fig. 10.5) whereas precipitation reactions would infer constant solution concentrations with increasing Cd additions. Precipitation is unlikely to control Cd solubility unless at excessive Cd contamination and at pH values >7.0. For example, the solubility product of $CdCO_3$ ($K_{sp} = 10^{-12}$), the most insoluble possible Cd form in aerobic soils, predicts that Cd precipitates in calcareous soil at pH 7.5 only above 55 μg Cd^{2+} L^{-1}. Sorption and solution complexation reactions in whole soil (see below for some data) typically reduce Cd^{2+} at that pH to $<$ 10 μg l^{-1} for soils up to 10 mg Cd kg^{-1}. This means that soil Cd concentrations should exceed >100 mg Cd kg^{-1} for this precipitation reaction to occur, clearly beyond the range of soil Cd concentrations.

Further empirical evidence on Cd *sorption* revealed that soil texture has a weak effect on Cd sorption (somewhat more sorption on sandy loam than loamy sand, Fig. 10.5), that sorption strength at low Cd concentrations is markedly larger than at

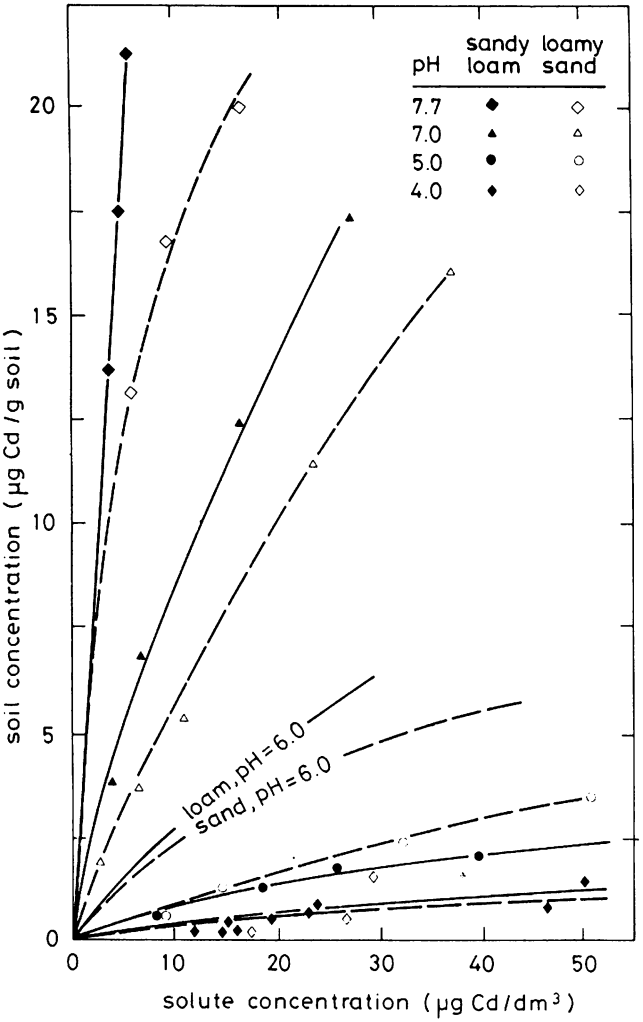


Fig. 10.5 Sorption isotherms of Cd determined in 10^{-3} M $CaCl_2$ for two soils at different pH values. The soil Cd concentrations (*Y-axis*) cover the range from background (<1 mg Cd kg^{-1}) to contaminated soils (1–10 mg Cd kg^{-1}). The typical soil solution Cd concentrations are also illustrated: <10 μg l^{-1} for soils above pH = 6 and up to 50 μg l^{-1} in contaminated, acid soils (From [14])

high concentrations (site-heterogeneity), and that pH has a marked effect on Cd sorption (factor 3–5 stronger sorption per unit pH increase [14, 17]) whereas a tenfold increase of solution Ca^{2+} (almost the spectrum of contrasting soils) decreases Cd^{2+} sorption only by factors 2–3. Cadmium solubility data in contrasting soils reveal that pH is generally the primary statistical factor associated with Cd concentrations in solution (often more important that total Cd), followed by soil organic matter content [7, 17].

Table 10.5 The sorption strength of Cd^{2+} and other metals at trace levels on isolated humic acid and Fe-oxides at pH = 6 and a background Ca^{2+} of 10 mM typical for an agricultural soil

	Humic acids		Fe-oxides	
	$\log K_{MA}$	K_d (l kg^{-1})	$\log K_{MH}$	K_d (l kg^{-1})
Ca^{2+}	0.7	100	−7.3	0.6
Cd^{2+}	**1.3**	**20,000**	**−4.0**	**1,000**
Zn^{2+}	1.5	80,000	−3.8	1,600
Cu^{2+}	2.0	3.E+08	−1.8	2.50E+05

The K_d is the solid-liquid concentration ratio (mg kg^{-1} divided by mg l^{-1}). The K_{MA} is the average sorption constant on free sites of humic acids and the K_{MH} is sorption constant on Fe-oxides in competition with H^+. Cadmium binds stronger than Ca^{2+} but much weaker than Cu^{2+} and organic matter is the preferred sorbent for Cd at pH = 6. At pH >7, oxides become more preferential adsorbents (not shown). Constants and calculation made with WHAM 6 speciation code

Soil organic matter, oxyhydroxides of Fe, Al and Mn and clay minerals are the three main Cd adsorbents in soil. Numerous sorption data on these isolated soil constituent have been collected and are now embedded in speciation codes. Protons are the main competing cations for Cd^{2+} sorption on organic matter or oxyhydroxides because Cd^{2+} binds to surface oxygen atoms of carboxylic or phenolic groups of humic substances or to surface hydroxyl groups on oxyhydroxides. A general sorption equation reads:

$$\mathrm{S{-}OH} + \mathrm{Cd}^{2+} = \mathrm{S{-}OCd}^{+} + \mathrm{H}^{+} \tag{10.1}$$

in which S–OH is the surface hydroxyl group. This simplified equation already predicts that increasing H^+ decrease sorption drastically. The sorption constants of Cd^{2+} to humic acids (major sorptive phase of soil organic matter) and Fe-hydroxides are shown in Table 10.5 and illustrates that Cd^{2+} binds orders of magnitude more selective than Ca^{2+} (example: about 200-fold on humic acids at environmental conditions) but somewhat less than Zn^{2+} and orders of magnitude less than Cu^{2+}. Note, however, that Ca is present at 10^{-3}–10^{-2} M whereas Cd is present at 10^{-9}–10^{-7} M, i.e. Ca^{2+} is a competing cation for Cd^{2+} sorption despite the pronounced Cd:Ca selectivity. The Cd^{2+}:Ca^{2+} selectivity for sorption on clay minerals is typically less than five at relevant conditions [21], therefore clay minerals are unlikely to be important adsorbents for Cd in most soils. Speciation modeling predicted that the majority of Cd is bound to organic matter in soils with $pH < 6.5$ whereas Fe-oxides become most important adsorptive constituent at pH >6.5 [10].

Cadmium may form complexes in solution with soluble ligands, i.e. inorganic ligands or dissolved organic matter (DOM). These complexes have reduced charge and mobilize Cd in soil. A well known example of that is the increases Cd solubility in saline soils if chloride (Cl^-) or, to a lesser extent, sulfate salinity is present. The formation of $CdCl_n^{2-n}$ complexes increase Cd mobility by more than a factor 5 at 120 mM Cl^- compared to corresponding non-saline soils [53]. In non-saline soils, solution speciation data and modeling shows that more than half of Cd is present as the free cation unless at high pH where Cd-DOM complexes contribute to increased Cd mobility (Fig. 10.6). Hence, DOM transport is not a major route by which Cd is mobilized from soils to ground- or surface water.

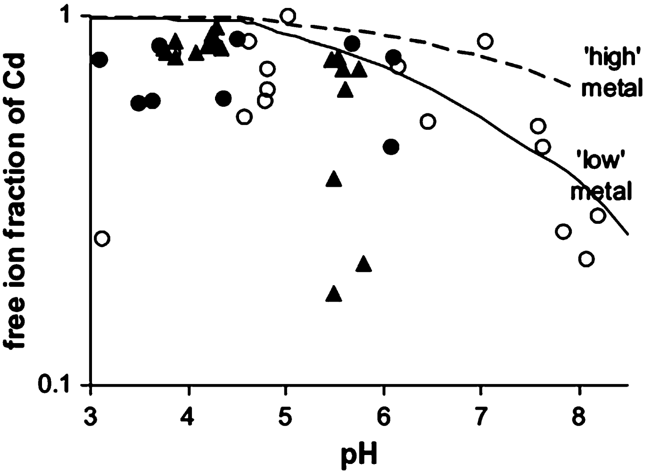


Fig. 10.6 Free-ion fractions of Cd, i.e. Cd^{2+} concentrations relative to total dissolved Cd concentrations, in soil solution measured with Donnan dialysis (*symbols*; different authors) and values predicted by modeling for uncontaminated and contaminated soils (*lines*). Most data and model predictions show >50% free Cd in solution unless at pH > 7.0 (From [17], Data do not include saline soils where Cd complexation can be significant)

10.4.2 Slow Reactions

Slow reactions and/or sorption irreversibility have a large environmental consequence for Cd since these reactions may gradually lower Cd bioavailability and counteract the ongoing diffuse Cd emissions to soil. Laboratory studies have shown that Cd sorption in soil reaches equilibrium within hours [14] and that sorption is quasi fully reversible, even after >1 year ageing after adsorption [13]. This pronounced reversibility may be related to the relative large ionic radius of Cd^{2+} (0.95 Å) that limits intraparticle diffusion in oxyhydroxides and that does not allow isomorphic substitutions in octahedral sites occupied by the smaller Al^{3+} or Fe^{3+} cations in minerals. However, long-term sorption data are always difficult to interpret since small changes in pH may already explain changes in mobility. Isotopic exchange has been subsequently used to more sensitively detect the reversibility in soils to which Cd has been added for longer periods. This method is based on the addition of a Cd^{2+} isotope (e.g. radioactive $^{109}Cd^{2+}$) that is equilibrated for a short period (1–7 days) after which the specific activity (SA) of Cd in solution is measured. The SA is the $^{109}Cd/Cd$ ratio. If this ratio is larger in solution than in the entire soil, then a fraction of the Cd in soil has not equilibrated with the freshly added ^{109}Cd, i.e. some (old) Cd is bound stronger than (freshly added) ^{109}Cd. The Cd in soil that is fully isotopically exchangeable is also termed labile Cd and is the fraction of total Cd that is equally mobile (available) as freshly added Cd. Hence, isotopic exchange allows detecting which fraction of long-term added Cd has been immobilized with slow reactions and which fraction remains

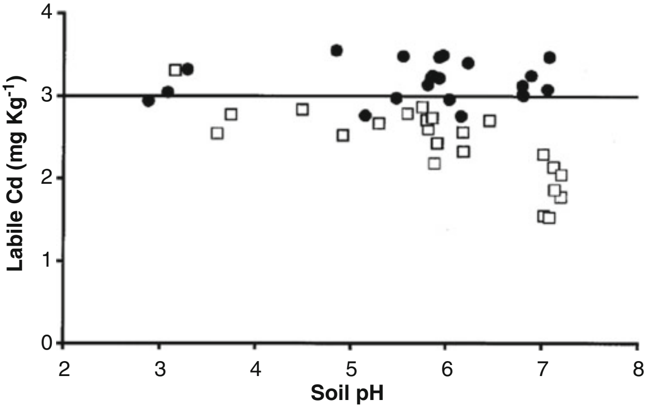


Fig. 10.7 Long-term reactions of Cd in soil: the concentration of radio-labile Cd after 11 (•) and 818 (□) days of incubation in 23 soils amended with 3 mg Cd kg^{-1} at day 0. Note that ageing does not reduce Cd availability more than about 20% unless at pH > 6.5 [58]

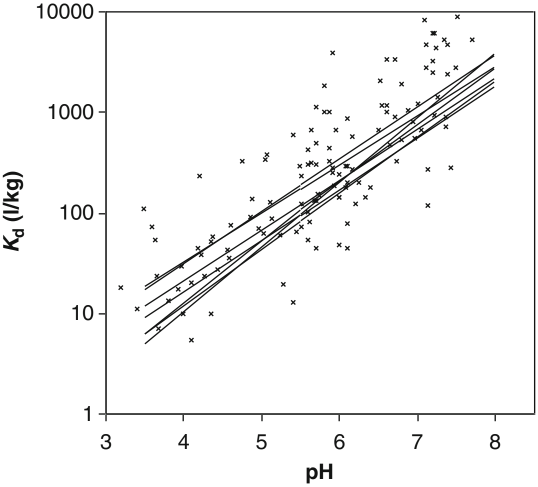
reversible. In a study of 23 contrasting soils, amended with Cd and aged for >2 years, the labile Cd was >80% of added Cd at pH <6.5 but was lower at higher pH (Fig. 10.7), hence ageing reactions are unlikely environmentally relevant unless at large pH [58].

10.4.3 Models and Data of Cadmium Solubility in Aerobic Soils

The number of data on Cd concentration in soil solution (*in situ* data) are much less documented than that of Cd concentrations in soil extracts. Soil extracts with dilute salts (e.g., $CaCl_2$ 0.01 M) may be used as a surrogates but give somewhat lower concentrations due to dilution of ligands than mobilised Cd [17]. The *in-situ* data, therefore, match soil extract based sorption models reasonably well (Fig. 10.8).

Sorption of Cd is quasi linear with almost no intercept within the environmental concentration range (Fig. 10.8). Therefore, Cd solubility data in soil can be normalised to total soil Cd in the K_d expression, i.e. the ratio of total concentrations of Cd in soil (mg kg^{-1}, typically dry weight based) to the concentration in soil solution (mg l^{-1}). The range of K_d values is 10–5,000 l kg^{-1} in soil, and mainly depends on soil pH. At an average background soil Cd concentration of 0.2 mg kg^{-1}, the soil solution concentrations hence ranges 0.2/10–0.2/5,000 mg l^{-1}, i.e., <0.1–20 μg Cd l^{-1} and 0.4–200 μg l^{-1} in contaminated environments. Such data, combined with solution speciation data predict that Cd^{2+} activities in soil solution range 10^{-9}–10^{-7} M in non-contaminated soils, increasing one or maximally two orders of magnitude in strongly contaminated soils, i.e. 10^{-9}–10^{-5} M is the almost widest range that can be observed [58]. Recently, a review was made about Cd solubility in soils and the different empirical or multi-surface models were evaluated [17]. It was concluded that empirical models are more

Fig. 10.8 Symbols: *in situ* K_d values of Cd [15, 16] and McGrath (personal communication) and lines from various empirical adsorption studies reviewed in [17]



calibrated than the multi-surface model, and a best fit empirical model for different independent data reads:

$$\log K_d = -1.04 + 0.55\ \text{pH} + 0.70\log(\%\text{OC}) \tag{10.2}$$

in which OC is the organic carbon content in %. This equation predicts a $K_d = 300$ l kg^{-1} at pH = 6 and 2% OC and that the K_d increases about factor 4 ($=10^{0.55}$) per unit pH increase.

Numerous claims have been made that Cd added by biosolids such as sewage sludge or compost is less available than Cd salts because sludge particles also carry sorption sites [4]. Cadmium salts are non-environmentally relevant sources, but are often used to identify dose-response data for risk assessments. Figure 10.9 illustrates that this claim is not justified for Cd solubility (in contrast to bioavailability, see below), at least not for the initial years after biosolid application where *larger* solubility is found in sludge amended soils [44]. The larger solubility is attributed to higher concentrations of competing cations (e.g., trace metals). Equation 10.2 also predicts that the effect of %OC on K_d is indeed relatively weak: increasing soil organic C from 2.0% to 2.5% by adding biosolids (requiring large doses!) increases the K_d only from 300 to 350 l kg^{-1}. This means that increasing organic matter (OM) doses does not immobilise Cd strongly, unless in soil where the %OM is extremely low.

10.4.4 Fate of Cadmium in Reduced Soils

Soil pH increases upon waterlogging soils and this may explain immobilisation of Cd when soils are submerged. Sulphides that form in strongly reduced soil may

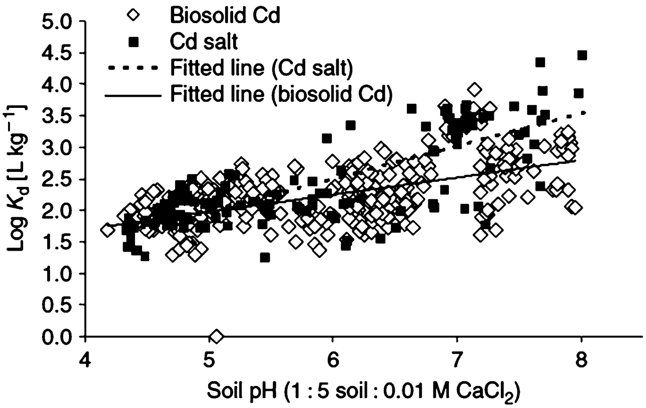


Fig. 10.9 The K_d for Cd (soil Cd to soil solution Cd concentration ratio) in soil amended with Cd^{2+} salts or biosolids (sewage sludge…) across several experimental field sites in Australia. The fitted lines were significantly different and show that biosolid Cd was surprisingly *more* soluble than Cd salts, a factors that was attributed to higher concentrations of competing cations in biosolid amended soils [44]

precipitate Cd^{2+} as CdS and render solubility well below 0.1 $\mu g\ l^{-1}$, concentration that can never be lowered by sorption [3]. These sulphides are rarely present as pure sulphides and it is more likely that mixed Zn/Cd sulphides are formed. Solid solution theory predicts a lower solubility for Cd substituted in ZnS than for pure CdS. Despite lower solubility of CdS than ZnS, the oxidation rate of Cd is much faster than that of Zn by several hours. Rice plants growing in a submerged soil have an aerobic rhizosphere where such CdS may oxidize readily. Oxidation kinetics show that high Zn:Cd sulphides (i.e. Zn:Cd molar ratio >4), are relatively resistant to oxidation [3].

10.5 Cadmium in Agricultural Crops

10.5.1 Soil-Plant Transfer of Cadmium

Cadmium has no known physiological role in higher plants, but is readily taken up from soil and is translocated to above ground plant tissues. Figure 10.10 illustrates soil-plant relationship of Cd for rice grown in the area where the Cd related human health impact was first identified (see also Sect. 10.1). Figure 10.10 is selected to illustrate three main features of Cd uptake.

1. *relatively large bioavailability*. In this case, crop Cd concentrations are 0.5-fold soil Cd concentrations. Dry weight based Cd concentrations of other crops/plant tissue range 0.05-fold to 2-fold the total Cd concentrations of soil (Table 10.6).
2. *unregulated uptake*. Zinc is the chemical analogue of Cd, and Fig. 10.10 shows that Zn concentrations in tissues are relatively constant in contrast

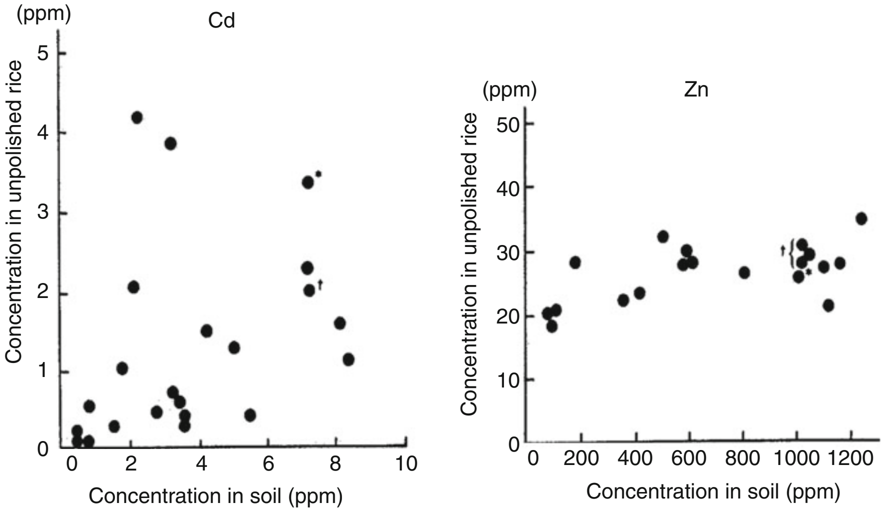


Fig. 10.10 Effect of soil Cd and Zn concentrations, on Cd and Zn in brown rice grain grown at Toyoma, Japan. Note that grain Zn was not increased by high soil Zn, but Cd had large increase [23]

Table 10.6 Crops differ in Cd concentrations. A summary of average (or median) crop Cd concentrations of different surveys and compilations

Plant	Fresh weight (μg kg^{-1})	Dry weight (μg kg^{-1})	Notes
Non-durum wheat	22–80	25–92	Means/medians of five surveys (n = 1,733) [20]
Green bean (pod)	7	67	n = 47 [33]
Durum wheat	~90	~100	[40]
Grassland (mainly drygrass)	14	116	n = 900 [33]
Potatoes	23	117	n = 239 [33]
	15–32	75–160	Means/medians of three surveys (n = 296) [20]
Fodder maize (entire shoot)	23	195	n = 197 [33]
Leek (edible part)	20	200	n = 139 [33]
Tomato (fruit)	10	210	n = 57 [33]
Onion	13	270	n = 83 [20]
Carrots	31	282	n = 172 [33]
	32–44	290–400	n = 191 means/median of two surveys [20]
Lettuce	39	780	n = 170 [33]
Spinach	76	850	n = 95 [33]

If soil Cd data and/or soil pH data were available, crop Cd were calculated for a soil Cd concentration of 0.40 mg kg^{-1} (= 400 μg kg^{-1}) and pH = 6.5. Crops are sorted in increasing order of dry weight based concentrations

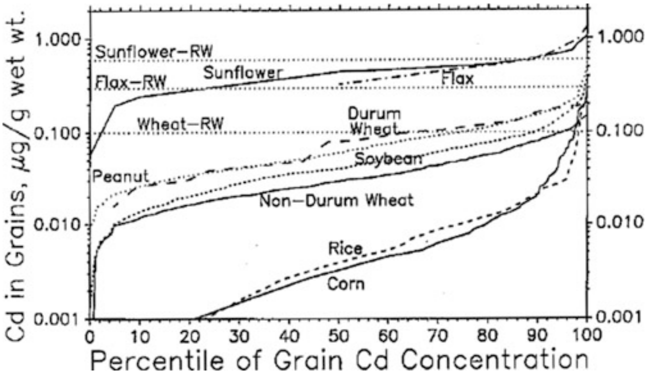


Fig. 10.11 Statistical distribution of cadmium concentration in grain crops [40]. The German *Richtwert* (RW) for crops shown with horizontal dotted lines. The limits of the FAO codex alimentarius are 0.1 µg g^{-1} for cereal grains and 0.4 µg g^{-1} for polished rice (CODEX, 2010)

with those of Cd. This is because Cd uptake is not regulated by physiological limits (plant demand) and the Cd uptake does increase with increasing soil Cd concentrations. Experimental studies in which Cd is administered as a Cd^{2+} salt show that uptake increases linearly with soil Cd provided that all other soil properties remain constant [8].

3. *Cd bioavailability varies largely and total soil Cd concentrations poorly predict Cd uptake*. At identical total soil Cd, crop Cd varies typically >tenfold. Total soil Cd typically explains less than 50% of the variance of crop Cd concentrations in surveys and country-wide surveys show that crop Cd concentrations typically vary more than tenfold (Fig. 10.11). This means that total soil Cd concentrations are poor predictors of Cd risks.

10.5.1.1 Soil Cadmium Bioavailability

Surveys of crop Cd concentrations and associated soils generally show that crop Cd concentrations increase with increasing total Cd and with decreasing pH and, in some cases, with decreasing %OM at constant total Cd (example: [18]). Chloride salinity markedly increases crop Cd concentrations [39, 42] above about 50 mM Cl^- in soil solution (about 500 mg Cl^- kg^{-1} soil). Zinc deficiency stimulates Cd uptake [41]. Such information has assisted the development of countermeasures to reduce Cd in plants, i.e. soil liming, organic matter amendment and Zn fertilization. The successes of these countermeasures are variable as will be discussed below.

Soil chemical and plant physiological studies have revealed the major mechanisms explaining the variable Cd bioavailability among soils. These mechanisms have recently been reviewed [45] and will be briefly summarized without reference to the original studies. Short-term ion uptake studies with roots demonstrate that Cd is actively absorbed and follows a concentration-dependent pattern similar to enzyme kinetics. Since most Cd concentrations are below the so-called Michaelis constant, uptake increases almost proportionally with increasing solution concentrations. Similarly, plant tissue concentrations rise as soil concentrations rise. This pattern is the basis of using the *BioConcentration Factor (BCF)* concept (also termed '*Transfer Factor*' concept) in risk assessment, i.e. a constant plant tissue:soil concentration relationship. In the environment, BCFs vary because of different bioavailabilities of Cd. Variable bioavailability is related to differences in metal or metalloid speciation, interionic effects on ion uptake from pore water and indirect effects of soil properties on translocation within the plant. The general paradigm on metal uptake from soil is that roots absorb elements through pore water and the concentration of the dissolved elements affects the uptake rate. This would suggest that soil Cd bioavailability increases as the K_d decreases, for example as pH decreases. While decreasing soil pH indeed increases Cd bioavailability as mentioned above, the relative effects are generally smaller than that what can be expected from a pure chemical point of view. Indeed, recent large-scale surveys of plant metal concentrations and speciation of metals in the associated soils demonstrated that pore water Cd concentrations or free ion activities of the Cd did *not* explain the crop concentrations [12, 31]. Two processes may be invoked here that complicate the analysis in practice, i.e. *rhizosphere processes* that alter the pore water composition compared to the solution that can be sampled, and *ion competition* effects which affect the uptake rate of the free ion. Concentrations gradients of Cd in the rhizosphere are the result of the balance between the ion uptake rate and resupply by the uptake of water. Simple calculations have illustrated that Cd is strongly depleted in the rhizosphere because the root uptake rate exceeds the transport to roots by mass flow and diffusion [45]. Under such conditions, Cd bioavailability is controlled by the maximal transport which is a complex function of solution Cd concentration, labile Cd on the solid phase (the dynamic buffer pool) and the tortuosity of the water filled pores. Cadmium ion uptake is furthermore affected by *interionic effects*, i.e. the uptake rate of the ion decreases or increases as the concentration of an ion competing with the same uptake site is increased or decreased, respectively. Solution culture studies have shown that Cd uptake increases when H^+ activity is lowered (pH increases), for example shoot Cd increased factors of 4–13 in unbuffered nutrient solution between pH 5–7 for ryegrass, lettuce, cocksfoot (*Dactylus glomerata*) and watercress [28]. This ion interaction effect counteracts the soil chemical effect: the soil chemical interactions predict that soluble Cd decreases by about a factor of 12 between pH 5–7 whereas the ion interaction reduce uptake of Cd^{2+} by factors of 4–13. These counteracting interactions were also found in a pot trial with contrasting soils grown by ryegrass and showed that the soil chemical reaction slightly outweigh the ion uptake reactions, i.e. the net effect of increasing soil pH on decreasing crop Cd is smaller than a factor of 1.5 per unit pH increase [31]. Field data on Cd uptake by numerous plants also show that the net effect of increasing soil pH on reducing cadmium bioavailability is, on average among plants, only a factor of 1.6 per unit pH increase [45].

10.5.1.2 Variability in Crop Cadmium Concentrations Among Different Crops

Plants differ in Cd concentrations when grown in similar soils (Fig. 10.10 and Table 10.6). Grain and potato Cd concentrations have received considerable attention because of their large impact on the dietary Cd intake by humans. For example, a daily consumption of 300 g wheat grain products at 40 μg kg^{-1} contributes 12 μg Cd whereas one daily portion of leafy vegetables such as lettuce of 100 g fresh weight (5 g dry weight) at 800 μg kg^{-1} dry weight only contributes 4 μg. Grain Cd contributing to the diet is typically largest for durum wheat (about twofold above bread wheat, see Fig. 10.11) and agricultural products that exceed limits are often durum wheat, sunflower kernels and peanuts. Translocation is an important process in determining trace metal concentrations in plant tissues and explains genotypic variations in crop Cd concentrations. For instance, it was shown that the root-to-shoot Cd translocation via the xylem is the major process determining shoot and grain Cd accumulation among rice cultivars for which >tenfold variation exists in rice Cd concentrations when grown in identical conditions [60]. That study explained the generally higher Cd concentrations in indica cultivars than in japonica cultivars in rice. The transport from leaves to other plant tissues (e.g., grains, tubers) can occur in phloem only. For instance, Cd in potato tubers is not directly taken up from the soil, but is first transported in the xylem to the shoot, and then back down through the phloem [51]. A compilation of shoot-root Cd concentration ratios [45] revealed that Gramineae (maize, barley, oat, ryegrass, cocksfoot, rice) are often shoot cadmium excluders (shoot: root concentration ratio <0.05), with some exceptions. For instance, some maize inbred lines or rice cultivars show large cadmium translocation to shoot (shoot: root concentration ratios >0.25). Also for the Leguminosae (pea, beans, etc.), the translocation of cadmium to the aerial parts is usually small, whereas the Solanaceae (potato), Asteraceae (lettuce) and Brassicaceae (watercress) show in general relatively large translocation to the shoot (shoot:root concentration ratios >0.25). Recently, a gene (OsHMA3) was described that explains low Cd translocation to the above-ground parts of rice by coding for a transporter that sequesters Cd in root vacuoles [59]. This transporter is present, but is not functional, in high grain Cd cultivars. Similarly, genotypic effects of Cd concentrations in durum wheat cultivars are related to a single gene that is responsible for root-shoot translocation [25].

Plant-breeding can be an important tool to reduce the concentrations of Cd. Low-Cd durum wheat cultivars and sunflower hybrids have been developed [25]. The high and low Cd near-isogenic lines of durum wheat differ about a factor 2.5 in grain Cd concentrations when grown at the same location. This selection helps to achieve crop Cd concentrations below legal limits without yield loss or effects on grain quality, including grain Zn concentrations when grown in Zn deficient soils [25].

Table 10.7 A sensitivity analysis of predicted atmospheric contribution to plant Cd concentrations, using current air Cd concentrations in rural and contaminated areas

AAF ($m^3\ g^{-1}$)	BCF (-)	Air conc ($ng\ m^{-3}$)	Soil metal conc ($mg\ kg_{dw}^{-1}$)	Predicted plant metal conc ($mg\ kg_{dw}^{-1}$)	Airborne (%)
20	1.5	0.2	0.2	0.3	1
20	1.5	20	0.2	0.7	57
20	1.5	0.2	2	3.0	0.1
20	1.5	20	2	3.4	12

The assumed air accumulation factors (AAF: plant:air concentration ratio, $m^3\ g^{-1}$ dry weight) and soil-plant bioconcentration factors (BCF, dry weight based) for lettuce are based on experimental data of [27]. The four scenarios of soil and air concentrations are based on expert judgement, reflecting current air concentrations in rural areas in EU and background soil concentration for lowest values, and air concentrations near metal smelters and contaminated soils, for high concentrations. Adapted from [45]

10.5.2 Uptake of Cadmium from Air

A fraction of Cd that is measured in plants is airborne, even after washing, in below-ground parts and in plants that have been grown in rural areas away from air pollution. Cadmium is associated with small particulates (<10 μm) that can be deposited on plants. These *aerosols* may adsorb to plants or eventually also be absorbed. A recent compilation of the restricted number of studies show that the fraction airborne Cd in plant Cd varies <4–60% with some remarkable numbers that 20% of grain Cd of wheat grown in rural areas (air Cd <1 ng m^{-3}) is airborne [45]. Based on this compilation, a prediction was made on the fraction airborne Cd. This fraction is obviously larger when air Cd concentrations are higher and when soil Cd concentrations are lower (Table 10.7). The contribution of airborne Cd to crop Cd is often neglected, but may explain the weak association of crop Cd with soil properties. In addition, risk of historic air Cd pollution may be still detectable in humans (biological half life is about 20 years) but may not be reflected any more in crop Cd concentrations, obscuring relationships between human biomonitoring and food chain Cd (see Sect. 2.3.2.1).

10.5.3 Models and Data of Cadmium Concentrations in Crops

Average Cd concentrations in crops, based on worldwide compilations, are given in Table 10.6 and soil factors explaining these crop Cd concentrations have been removed by modeling. Models on crop Cd uptake from soil range from empirical (statistical) ones that relate crop Cd with soil properties (e.g. [18]) to fully mechanistic ones, coupling soil chemistry, rhizosphere transport and ion uptake/translocation studies [56]. The latter models are undoubtedly most challenging and reveal the rate limiting factor, however they are complex to use and have less validation than the former. The most simplest empirical model is the normalization of crop Cd

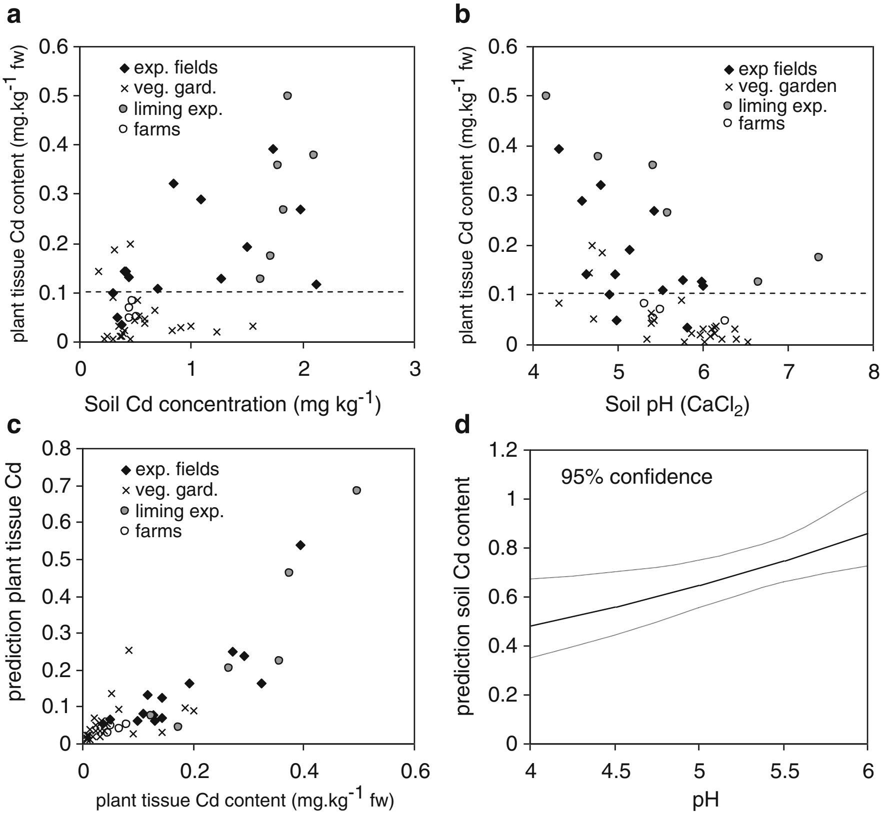


Fig. 10.12 Concentrations of Cd in leek (*Allium ampeloprasum* L.) as a function of soil cadmium concentration (0.43 M HNO_3 extraction) (**a**), as a function of soil pH (**b**), predicted versus measurements (**c**), and predicted soil concentrations (Eq. 10.3) as a function of pH where the limit value for cadmium in leek is exceeded (**d**). Results are from several studies in The Netherlands. The *dotted line* is the European limit value for cadmium in leek (Adapted from[45])

concentrations to soil Cd concentrations, yielding the BCF expressed as the ratio between the Cd concentration in the vegetable (mg kg^{-1}) and that in soil (mg kg^{-1}). To account for soil factors explaining the BCF and for non-linearity between soil and crop Cd, Freundlich type function are often used instead, i.e.

$$\log\left[\mathrm{Cd_{plant}}\right] = a + b\log[\mathrm{Cd_{soil}}] + c[\mathrm{pH}] + d\log[\%\mathrm{OM}] \tag{10.3}$$

with Cd_{soil} the total Cd concentrations in soil and OM the organic matter content in soil. Most compilations show that $b < 1.0$, i.e. there is some non-linearity, that c is only 0.05–0.40 and that d is often not statistically significant [20, 45]. Predictions of these models and the 95% confidence intervals of the mean predictions are illustrated for leek in Fig. 10.12.

10.6 Ecotoxicity of Cadmium in Soil

The toxicity of Cd on soil dwelling biota is generally found at higher soil Cd concentrations than those at which human health is being affected (see Sect. 10.1). Therefore, the ecotoxicological risk of Cd to plants and soil invertebrates or microbiological processes is somewhat less document than the foodchain risk and, arguably, less relevant. It is logical, however, that risk of soil Cd to mammalian wildlife species that are exposed via the foodchain may be as large as human health risk since the long half-life of Cd in mammalians also leads to a gradual increase of body-burden of Cd on the long-term.

A compilation of toxicity thresholds of Cd for soil dwelling biota (higher plants, invertebrates and soil microbial processes) was made in Europe. Most of the thresholds were estimated based on laboratory tests in Cd^{2+} salt spiked soils. Adverse effect concentrations in laboratory and field tests are found at total Cd concentrations between 2.5 and >1,000 mg kg^{-1} with a tendency to find lowest thresholds for plants grown in potted soil applied with Cd^{2+} salts. About 160 toxicity tests were reviewed and reliable highest No Observed Effect Concentrations (NOECs, i.e. the largest soil Cd concentration at which the biota were unaffected) were collated. A soil Cd limit (PNEC = Predicted No Effect Concentration) to protect soil organisms was proposed in Europe in 2007 [19] as the fifth percentile of the NOEC values yielding PNEC = 2.3 mg Cd kg^{-1} (Fig. 10.13). Quite in contrast are the ECOSSLs (Ecological Soil Screening Limits) that have been derived

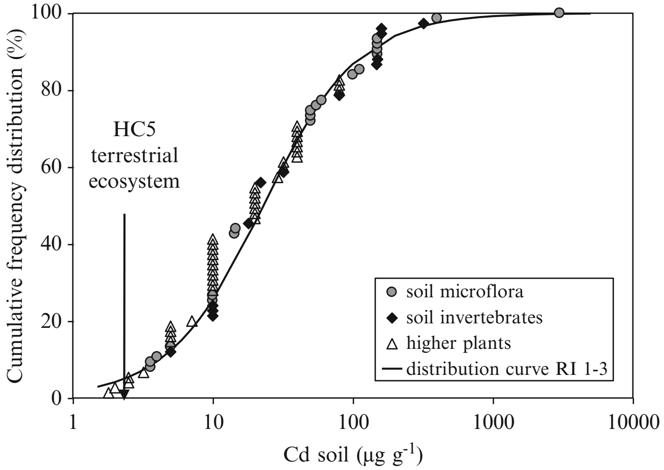


Fig. 10.13 The cumulative frequency distribution of the highest No Observed Effect Concentrations values of Cd toxicity tests of soil microflora, invertebrates and higher plants. Observed data and logistic distribution curve for the whole RI 1-3 data (a high quality data group) fitted on the data. The 'safe' soil Cd concentration is defined as the 5th percentile of the species sensitivity distribution (HC_5, indicated) and is 2.3 µg g^{-1} (= 2.3 mg kg^{-1}). Figure extracted from the European risk assessment of Cd-metal [19]

by US-EPA in 2005 that are 32 mg Cd kg^{-1} (plants) and 140 mg kg^{-1} (invertebrates). The differences between the EU and US-EPA limits are mainly related to the data treatment and not the underlying data themselves.

Risk of soil Cd to mammals and birds via the food chain is difficult to assess in the environment. Wildlife has a wide foraging habitat and cause-effect relationships are always unclear for wildlife. There is currently only little field evidence that attributes pathological injury in wildlife to Cd [6]. Tissue Cd concentrations such as kidney Cd concentrations have suggested risk to moles, shrews and beavers in highly contaminated soils (see [19]). In predators such as owl and kestrel, kidney Cd concentrations are below assumed limits. White tailed ptarmigan (*Lagopetus leucurus*) have been found with kidney Cd concentrations up to about 200 μg g^{-1} fresh weight (as observed in a mining area in Colorado, U.S.A.) which is twofold above the toxic threshold and is a known case of Cd poisoning to birds [38]. The risk assessment for Cd to protect wildlife typically estimates the effects indirectly from feeding tests in the laboratory with surrogate species and with an estimated food chain model. Without going into detail, it is of note that the relaxed ECOSSLs described above for plants and invertebrates are remarkably stringent for mammals (0.4 mg Cd kg^{-1}) and birds (0.8 mg Cd kg^{-1}). In the European Cd risk assessment of 2007 [20], standard assessments predicted risk at soil Cd concentrations more than tenfold below soil background values. An alternative approach for terrestrial wildlife was proposed based on measured tissue residues in field collected mammals and on renal thresholds yielding a generic critical soil Cd concentration to protect mammals of 0.9 mg Cd kg^{-1} dry weight. This soil limit is triggered by data on moles and shrews (both carnivorous) dwelling in acid soils. Excluding data from soils with pH <4.2, a critical soil Cd of 3.3 mg ${kg_{dw}}^{-1}$ was derived.

10.7 Risk Assessment of Cadmium and the Management of Cadmium-Contaminated Land

There is a myriad of soil Cd limits that are in place in various legislations and limits differ in the risk pathways considered, in the margins of safety adopted (e.g. soil screening values<soil clean-up values) and limits may be affected by political choices. Table 10.8 illustrates the wide range of soil limits that are found.

To illustrate a risk assessment, some background information is given about the risk assessment of Cd in Europe [19-20] which led to the conclusion that current exposure of Cd in the EU is above acceptable limits and that countermeasures have to be taken to reduce exposure. The most stringent risk pathway is the human health assessment. In theory, the risk assessments has to evaluate the entire chain: emissions-environmental concentrations-human exposure via the environment (including food chain)-transport and disposition inside the body-concentrations in target organs. This long and variable chain has been circumvented by contrasting current human biomonitoring data in humans (urinary Cd concentrations, Cd–U in

Table 10.8 A selection of soil Cd limits (mg kg^{-1}) and their basis

Legislations	Protection goal	Limit (mg Cd kg^{-1} soil) and name	Note
US-EPA-2005	Mammals	0.4 ECOSSL	[61]
US-EPA-2005	Birds	0.8 ECOSSL	[61]
EU-risk of chemicals -2007	Human health	0.6–1.3	Range reflecting different EU regions with different soil Cd availability and dietary habits[19]
EU-risk of chemicals-2007	Mammals+birds	0.9	[19]
EU-risk of chemicals-2007	Plants, invertebrates, soil microorganism	2.3PNEC	[19]
Belgium (Flemish region)-2009	Human health	1.3–4.4 clean up value	Range for different soil pH values affecting food chain risk[19]
EU countries, Switzerland, USA and Canada	Mainly human health	0.4–37 clean up values for soils or residential areas	[50]
EU-sewage sludge limits 86/278/EEC	Unknown	1–3	Valid for soils with pH 6–7
US-EPA 1993 (biosolids)	Human health	39 kg Cd ha^{-1} (about 13 mg Cd kg^{-1})	Cumulative sludge loading limit

Ecological Soil Screening Limits (ECOSSLs) or predicted no-effect concentrations (PNEC) are derived to evaluate current emissions and should not be considered as clean-up values since the degree of protection is large (i.e. conservative limits).

μg Cd g^{-1} creatinine) to acceptable limits. The bone and kidney tissues are considered as the most sensitive target organs for the general populations exposed to Cd. For reference, population mean Cd–U values are about 0.2–0.3 μg g^{-1} creatinine for the non-smoking population. The Cd–U values are most importantly affected by smoking (doubled for smokers compared to non-smokers), gender (women>men) and age (concentrations peak at age 50). Adverse health effects on bone or kidney function due to Cd in the general population have been identified at 1–3 μg Cd g^{-1} creatinine. There is, however, a lingering scientific debate about the health significance of the changes observed at Cd–U levels <5 μg g^{-1} creatinine and this was reflected in the contrasting views expressed during the evaluation for this EU risk assessment. For example, The Lowest Observed Adverse Effect Level (LOAEL) for Cd–U was agreed at 2 μg Cd g^{-1} creatinine in the EU risk assessment while the latest JECFA(WHO) evaluation of Cd for the general population used a threshold of 5.2 μg Cd g^{-1} creatinine to derive tolerable dietary Cd intake [34]. The ratio of actual concentrations of Cd–U to the LOAEL is called the Margin of Safety (MOS). A MOS value >3 was considered acceptable for the European assessment, leading to risk when Cd–U exceeds 0.67 (=2/3) μg g^{-1} creatinine. When confronted with the measured data in the general population, the amplitude of the MOS appear >3 for more than 90% of the population, but risk could not be excluded for smokers and iron-deficient individuals (based on the theoretical scenarios) as the latter have higher Cd uptake from food [20].

Derivation of a limit value for Cd in soil is far more complex than assessment direct biomonitoring, as it requires an evaluation of food chain transfer (e.g. models as Eq. 10.3), dietary preferences of the general population and of highly exposed individual and the food Cd bioavailability issues (not covered here but also variable by at least factor 2). The variability (not uncertainty) of the transfers soil-plant, plant-diet and diet-body burden are factors 2–10 for the general environment and conservative evaluations that multiply worst case estimates, yield soil Cd limits below background. For site-specific assessments, human biomonitoring may be defensible to circumvent the uncertainties, i.e. if Cd–U<limit values, risk may be excluded. However; it must be realised the Cd–U values reflect life-time intake and, given the half-life of 15–20 years in humans, there is always a considerable delay between external exposure and body-burden. Blood Cd reflects current exposure, however no generally accepted reference values exist.

10.7.1 Managing the Risk of Cadmium

Reducing diffuse Cd emissions will only yield effects on reducing food chain Cd in the very long-term as the residual effects of soil Cd is prevalent. For example, Cd concentrations in P-fertilisers do not generally affect crop Cd concentrations in the first years after application [46]. From a theoretical perspective, smoking is the first factor that should be regulated to lower human exposure to Cd. Daily smoking of 20 cigarettes contributes 0.5–2 μg Cd d^{-1} for systemic uptake, which is at least equivalent to the daily Cd uptake via the diet at background. Reducing food Cd bioavailability by managing the Fe status of consumers is probably the second best theoretical option, given that Fe status is the second factor explaining interindividual Cd–U values in the general population [5]. Managing smoking and Fe-status (food habits!) are not directly possible for regulators and, therefore, options to reduce Cd emissions such as fertiliser Cd limits or sludge Cd limits have been proposed (Fig. 10.3) or are in place (Table 10.8). For site-specific cases, i.e. managing contaminated land, land use is probably the most efficient way to lower food chain risk. For example, food crops may be replaced by non-food crops (biofuel, cotton) or cropping systems in which transfer to consumers is limited (sugar cane and even dairy farming). Soil liming has surprisingly no consistent effects on crop Cd concentrations [55] although the effects are generally beneficial if crop Cd concentrations are high, such as in high Cd or very low pH soils [30, 49]. Removal of Cd by phytoremediation is only an option in the very long-term. For example, a field trial in a Cd contaminated, pH neutral soil (soil Cd about 2 mg Cd kg^{-1}) with different plant species yielded annual above-ground Cd removal with harvested crop ranging between 1 and 179 g Cd ha^{-1} $year^{-1}$, the largest flux found for the Cd hyperaccumulator *Thlaspi caerulescens* [35]. The plough layer contains about 7,000 g Cd (0–25 cm, density 1.4 kg dm^{-3}), i.e. annual removal is less than 5% of the total stock. Numerous studies have shown successes of soil Cd immobilisation strategies by, for example, addition of organic matter, Fe or Mn-oxyhydroxide based products can be effective in high Cd contaminated environments. Control of soil pH is known to be a critical factor in all such studies [9].

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Chapter 11
Chromium and Nickel

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Abstract Nickel (Ni) and chromium (Cr) are elements naturally present in all rock types and present in the pedosphere in a range from trace amounts to relatively high concentrations, as compared to other trace elements. Particularly high Ni and Cr concentrations are found in serpentine rocks and soils, originating from this rock type and colonized by a specialized flora that may present some curious species capable of hyperaccumulating extraordinary high concentrations of Ni in their above-ground parts. In recent decades, the large release of Cr and Ni by industrial activities, mainly the manufacture of stainless steel, as well as the use of sewage sludge as soil amendment in agricultural soils, have caused an impressive increase in the levels of these two metals in the pedosphere and other environmental matrices. This has led to increasing environmental concern as, while relatively low concentrations of Ni and Cr are essential for plants and other living organisms including humans, both the elements are toxic for all living organisms if present in excessive concentrations. This chapter reviews the distribution and the geochemical behaviour of Ni and Cr, their main dynamics in the soil environment, with regards to the natural and anthropogenic sources. The relationships of Ni and Cr with the plants, in particular with some Ni hyperaccumulator species are also discussed.

Keywords Nickel • Chromium • Solubility • Pollution • Ultramafic rocks • Serpentine • Hyperaccumulators

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11.1 Introduction

Nickel (Ni) is positioned between cobalt (Co) and copper (Cu) in Group 10 of the periodic table, the so-called ‘iron–cobalt–nickel’ group of metals. Ten isotopes of Ni exist in nature and the most abundant stable isotope has atomic number 28, atomic mass of 58.71 g mol^{-1}, electron configuration $[Ar]3d^8 4s^2$, electronegativity value of 1.8, density of 8.9 g cm^{-3} at 20 °C, ionic radius of 0.069 nm for $Ni(II)^+$ and 0.06 nm for $Ni(III)^+$, van der Waals radius of 0.124 nm, standard potential −0.25 V and melting and boiling points at 1,453 °C and 2,913°C, respectively. Normally, the Ni oxidation states are 0 or +2, although the +1 and +3 states can exist under certain conditions. The dominant inorganic species is Ni(II) throughout the pH and Eh range of most natural waters as it readily loses two electrons and, in any case, Ni(I) and Ni(III) ions are not stable in aqueous solution [3].

Elemental Ni is a silvery white, hard, malleable metal. Even though the use of Ni can be traced back to the beginning of the Bronze Age in Mesopotamia in 3500 BC, the identification of Ni as an element is relatively recent. In 1751 the Swedish chemist and metallurgist Axel Fredrik Cronstedt isolated a white metal from minerals originating from a Cu–Co mine, while he was attempting to extract Cu. The Ni containing mineral, from which Cronstedt extracted this metal, was probably now called Niccolite (NiAs). The name nickel was derived by the German word ‘kupfernicke’ used for Niccolite, meaning ‘Devil’s copper’ or ‘St Nicholas’s (Old Nick’s) copper’. Although the aspect of Niccolite is that of a Cu mineral, no Cu can be extracted from it and for this reason the Saxon miners had named the mineral according to the spiteful dwarf ‘Nickel’, who had apparently turned the Cu in the ore into a non-available form.

Nickel is a transition element with a broad range of applications in modern industry, being used in everything from coins to automobiles to jewellery. The largest Ni use by far is the manufacture of stainless steel, an alloy consisting of 8% Ni, 18% Cr and 74% Fe. Moreover, Ni is an excellent catalyst for many reactions and so it is used for a large number of industrial and research applications alone or in combination with other metals.

A primordial, but still conserved today, role of Ni in a different scenario, that is the biological one, accounts for the industrial chemistry of this metal. In fact, some industrial processes, such as hydrogenation, desulfurization, and carbonylation are based on some chemical properties of Ni just as the corresponding Ni-dependant enzymes, i.e., hydrogenase, carbon monoxide dehydrogenase, and methyl-coenzyme M reductase [81]. So, Ni is well known as an essential trace element for plants and cyanobacteria [77, 118]. Furthermore, Ni can be regarded as a “catalyst of early life” [65]. In fact, the environment in which life began was most likely electron-rich, and gases, such as H_2 and CO_2, and metal sulphides were available [97, 98]. Thus, special catalysts were needed to handle these gases and so this element was employed for a rich biochemical role by early-life forms [84]. The mineral greigite [Fe_5NiS_8], an Fe–Ni sulphide, could be regarded as a possible candidate for an early Ni catalyst as its molecular structure is very similar, for example to that of the thiocubane [4Fe–4S] unit of the ferredoxins [96]. The relative importance of Ni for primordial forms of life most likely decreased following the changes in the atmosphere's chemical composition, particularly the massive photosynthetic O_2 production [35].

While Ni is essential in certain bacteria, plants, and domestic animals, its essentiality for humans is still not very clear and the toxicity and carcinogenicity of high doses of Ni are well documented and depend mainly on its potential to damage proteins and nucleic acids [58].

Chromium (Cr) was first discovered in a Siberian red lead (Pb) ore in 1798 by the French chemist Louis Nicholas Vauquelin, who obtained metallic Cr from crocoite ($PbCrO_4$). Chromium is a steel-grey, lustrous, hard, brittle metal of Group 6 of the transition series.

The most abundant stable isotope has the following physico-chemical properties: atomic number of 24, atomic mass of 51.996 $g.mol^{-1}$, electronic configuration $[Ar]3d^5 4s^1$, electronegativity value of 1.6, density of 7.19 g cm^{-3} at 20°C, an ionic radius of 0.061 nm (Cr III) or 0.044 nm (Cr VI), a van der Waals radius of 0.127 nm, standard potential −0.71 V (Cr III/ Cr), and melting and boiling points at 1,907°C and 2,672°C, respectively. The trivalent Cr(III) and the hexavalent Cr(VI) species are the stable forms of this element, other oxidation states can transiently exist in living organisms [107].

The origin of the name comes from the Greek word "chroma" meaning color as many of its compounds are intensely and variously colored. Its use can be dated back to the third century BC from the analysis of weapons found in some Chinese burial pits from more than 2,000 years ago. Such archaeological finds showed no sign of corrosion, because the bronze was coated with Cr.

Chromium is used on a large industrial scale including metallurgy, electroplating, production of paints and pigments, tannery, wood preservation, chromium chemical production, and pulp and paper production. Due to its high corrosion resistance and hardness, chromium is largely used to form stainless steel. This application and electroplating are currently the highest volume uses of the metal. Wastes from Cr industries (e.g., sludge, fly ash, slag, etc.) have been employed as a fill material at numerous locations [100] at which leaching and seepage of Cr(VI) from the soils into the groundwater poses a considerable health hazard. Water resources can also be contaminated instead by Cr mainly from the tanning industry [25].

Chromium(III) is essential for humans and Cr deficiency can have detrimental effects on the metabolism of glucose and lipids (e.g., impaired glucose tolerance, elevated fasting insulin, elevated cholesterol and triglycerides, and hypoglycaemic symptoms) [5, 6]. On the other hand, ingestion of large amounts of Cr(III) may cause health problems such as lung cancer [34, 121]. Cr(VI) is toxic to biota at concentrations in the order of 10–100 times lower than Cr(III) [59], being a carcinogen and may cause death to animals and humans if swallowed in large doses [110]. Human exposure to Cr-containing substances includes ingestion of food and water, inhalation of airborne particulates, and contact with numerous manufactured items containing Cr compounds [110]. The limit concentration for drinking water established by the World Heath Organization is 50 μg L^{-1} of Cr(VI) . This value can be often exceeded in drinking waters of areas with ophiolitic rocks such as California, Italy, Mexico and New Caledonia [44].

This chapter describes the main natural and anthropogenic sources of Ni and Cr in soil, their main chemical forms and reactions, and the interactions of these two elements with plants, with special emphasis on the so-called nickel-plants, peculiar plant species adapted to serpentine soils and also used for phytoextraction and phytoremediation of Ni contaminated soils.

11.2 Origin of Nickel and Chromium in Soils (Geochemical and Contamination Sources)

The environment reservoir of Ni is the Earth's Fe–Ni molten core (10% of global Ni), followed by the Ni dissolved in the sea (ca. 8 10^9 t). Considerable amounts of Ni are also present in coal and oil. The abundance of Ni in the Earth's crust is about 80 mg kg^{-1} [3] and it is generally distributed with other siderophilic elements, such as Co and Fe. Nickel is located in the igneous rocks and it can be found associated with all the geochemical phases of mineralogical cycles, i.e. metamorphic and sedimentary rocks, soils and sediments [113].

Geochemically, Ni is siderophilic and also has great affinity for sulphur (S); this leads to the formation of many different sulfides, arsenides as well as antimonides in nature, such as millerite (NiS), niccolite (NiAs) and breithauptile (NiSb). Nickel can be also associated with carbonates, phosphates, and silicates.

The ionic properties of Ni allow it to substitute for several alkaline and metallic cations, such as Mg, Al, Li, Fe(II), Fe(III), Mn(II), Mn(III), Cu, in primary minerals [75]. Nickel in minerals can substitute for Fe even in pyrite. However, among the metallic rock forming elements, the Ni isotopic fractionation has been relatively less studied as compared to other elements.

In igneous rocks, Ni forms mainly octahedral coordination in silicate minerals such as olivine, hornblende, augite and biotite and magnetite. Such minerals are poorly stable and undergo rapid weathering. For this reason, Ni in developed soils is generally associated with clays such as vermiculites and chlorites, saponite in the serpentine soils, and Fe or Mn (hydro)oxides and concretions, and its concentrations decrease with increasing acidity of rocks down to 5–15 mg kg^{-1} in granites [57]. Sedimentary rocks contain Ni in the range of 5–90 mg kg^{-1}, with the highest range being for argillaceous rocks and the lowest for sandstones.

Nickel contents are particularly high in ultramafic rocks (in the order of 2,000 mg kg^{-1}). The two main types of commercially exploitable Ni deposits are laterites, where the principal ore minerals are nickeliferous limonite (Fe, Ni)O(OH) and the hydrous Ni silicate garnerite ($(Mg,Ni)_3(OH)_4[Si_2O_5]$) formed during tropical weathering, and sulfide ores, with pyrrhotite, pyrite and chalcopyrite and especially pentlandite ($(Ni, Fe)_9S_8$) as the main Ni-containing minerals.

The total content of parent rocks greatly affects the Ni content in soils, although the concentration of Ni in surface soils also depends on soil-forming processes and pollution. The Ni content of the pedosphere varies within a broad range, mainly from 0.2 to 450 mg kg^{-1}, with a calculated world mean of 22 mg kg^{-1} [104], or a range of 0.2 and 5,000 mg kg^{-1} and an average value varying between 20 and 50 mg kg^{-1}, if ultramafic soils are included. However, the concentration ranges found the in literature depend on the surveyed areas, and also on the soil texture, with clay soils being richer in Ni than coarser textured soils [69].

In a comprehensive report on the metal background concentrations of European soils on the basis of the parent material and independently on the soil use, Utermann et al. [114] reported Ni background values ranging between 3 and 48 mg kg^{-1}, with the lowest concentrations in soils formed on sandy materials and higher values in soils originating from volcanic rocks. Nickel concentrations in the soil depend more on its concentration in the parent material in the less developed soils, whilst its concentration in the most developed soils depends on the predominant pedogenic factors [112]. In particular, high intensities of leaching and erosion deplete soils in Ni. In natural ecosystems, soil enrichment with Ni occurs in alluvial soils or in soils subjected to the deposition of volcanic ashes. Total Ni concentrations up to 7,000 mg kg^{-1} can be found in ‘ultramafic; soils originating from igneous ultramafic rock [18]. Clay and loamy soils, e.g. rendzinas, cambisols, and kastanozems, typically contain total Ni concentrations in the upper range of the mean values quoted above. Relatively high Ni concentrations have been also found in soils originating from basic and volcanic rocks, in some organic-rich soils and in soils of arid and semi-arid regions.

Anthropogenic sources of Ni have resulted in a significant increase in the Ni content of soils. Main Ni sources are emissions from metal processing operations and fumes from combustion of coal and oil. The application of sludges and phosphate fertilisers also may be important sources of Ni in agricultural soils. Nickel concentrations in the rain have been reported to vary between 0.17 and 17 μg L^{-1} [10], representing an annual input of 0.002–0.2 mg kg^{-1} in the topsoil of areas with 1,000 mm of annual rainfall [113].

Nickel in sewage sludge, where it is present mainly in organic chelated forms, is readily available to plants and therefore may be highly phytotoxic. Nickel concentration in the solution of heavy metal polluted soils is generally higher and it can be in the order of mg L^{-1}, depending on the soil total concentration, Ni source and age of pollution.

Chromium presents an average concentration of 100 mg kg^{-1} in the Earth’s crust [41] whereas the concentration range in soil is between 1 and 3,000 mg kg^{-1} [61]. Chromium is mainly associated with mafic and ultramafic rocks in which it can reach values of 3,000 mg kg^{-1}. Acid igneous and sedimentary rocks display much lower Cr contents, commonly ranging from 5 to 120 mg kg^{-1}, with the highest content in argillaceous sediments.

Chromium (III) has ionic properties close to those of $Fe(III)^+$ and $Al(III)^+$ and therefore similar geochemical properties. Chromium substitutes for Fe or Al in chromite ($FeCr_2O_4$), the primary geological source for Cr. Chromite is relatively resistant to weathering, diagenesis, and metamorphic reactions [85]. Under progressive oxidation, the chromate ion ($CrO_4{}^{2-}$) is formed; this form of Cr is more mobile and also readily sorbed by clays and hydrous oxides. Though native Cr deposits are rare, some metallic Cr has been discovered in the Russian mine Udachnaya Pipe that is a kimberlite pipe rich in diamonds, where the reducing environment helped produce both elemental Cr and diamonds.

The main source of Cr in natural soils is the weathering of their parent materials. Total Cr concentration in soil varies from 0.5 to 250 mg kg^{-1}, with average values varying between 40 and 70 mg kg^{-1}, depending on the surveyed areas [33, 93]. The Cr background concentrations of European soils on the basis of the parent material and independently on the soil use, are in the range 5–68 mg kg^{-1}, with the lowest concentrations in soils formed on sandy materials and higher values in soils originating on volcanic rocks [114]. Higher Cr concentrations, up to 10,000 mg kg^{-1}, are present in soils formed from mafic and volcanic rocks. In fact, in mafic and ultramafic rocks the Cr concentrations can be higher than 3 g kg^{-1}, typically in the form of chromite, associated with variable amounts of MgO, Al_2O_3 and SiO_2.

Sandy soils and organic-rich Histosols usually show low Cr concentrations, containing an average of 47 and 12 mg kg^{-1}, respectively. Total Cr concentrations are generally positively correlated with the fine granulometric fractions [57]. Chromium total concentrations higher than the local background values originate from atmospheric fallout and inputs of Cr from Cr-rich sludge and wastes from industrial activity incorporated into soils.

Chromium in natural soils from the weathering of the parent material is present mostly as insoluble $Cr(OH)_3$ or as Cr(III) adsorbed to soil colloids [12]. The most common Cr form is $Cr(OH)_2^+$, bound to clays and humic substances, which are negatively charged at pH >5.5 [94]. In neutral-alkaline soils, with pH values >7.0, Cr precipitates as $Cr(OH)_3$, also in combination with alkaline metals and heavy metals. In strongly acidic soils (e.g. pH <4), $Cr(H_2O)_3^{+6}$ is the predominant Cr form.

The Cr(VI) is typically associated with oxygen as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) oxyanions. The Cr(III) is less mobile, less toxic and is mainly found bound to organic matter in soil and aquatic environments [107]. The relation between Cr(III) and Cr(VI) strongly depends on pH and oxidative conditions, but in most cases, the Cr(III) is the dominating species [61].

High concentrations of about 2,000 mg kg^{-1} of both Ni and Cr can be found in the so-called "serpentine" soils [18]. Serpentinization is a geological low-temperature metamorphic process, in which low-silica mafic and ultramafic rocks are oxidized and hydrolyzed into serpentinite. The process can be described by the following reaction:

$$6[(Mg_{1.5}Fe_{0.5}SiO_4)] + 7H_2O \leftrightarrows 3\left[Mg_3Si_2O_5(OH)_4\right] + Fe_3O_4 + H_2. \qquad (11.1)$$

In this process, Ni may be released from the olivine and co-precipitate with magnetite. However, when layered silicates or trioctahedral lattices are present (e.g. saponite, chlorite), Ni may preferentially react with them.

The name derives from the Latin word *serpens* meaning ‘snake’ as serpentine-rich rock has an olive greenish-grey colour, striped in different shades, that looks like the skin of a snake [15]. Serpentine soils are derived from the weathering of ultramafic rocks (“ma” stands for Mg and “f” for ferrum, or Fe), igneous or metamorphic rocks that comprise at least 70% hydrous Mg Fe phyllosilicate, or mafic, minerals with the general formula $Mg_3Si_2O_5(OH)_4$ and including antigorite and chrysotile [18, 63]. Serpentine rocks originate from metamorphic alterations of peridotite and pyroxene with water and they may form in the upper part of the earth mantle or near the earth’s surface during subduction events.

The strong enrichment in siderophile (Fe-loving) elements, such as Cr and Ni, of ultramafic rocks derives from the fact that the ionic radii of $Ni(II)^+$ and of $Cr(III)^+$ are respectively very close to those of $Mg(II)^+$ and of $Fe(III)^+$, so that ionic substitution easily takes place into Mg-rich minerals, such as olivine and pyroxene which are dominant in these rocks [18]. Even though Ni and Cr concentrations in serpentine soils are often similar, Cr is less soluble than Ni. Although only about 1% of the total Ni in soils is available to plants, this far exceeds the percentage of available Cr [18].

Apart from their anomalously high concentrations of Ni and Cr, serpentine soils are characterized also by elevated levels of Fe and Co, they also contain low Ca: Mg ratios and are often deficient in essential plant nutrients such as N, P and K [18]. These peculiar chemical properties, along with elevated soil temperatures and drought, make serpentine soils particularly toxic and unsuitable for most plant species [17, 31, 63] and for many microorganisms [70]. Ultramafic rocks and serpentinites of ophiolite complexes constitute about 1% of the terrestrial landscape [86]. Nevertheless, their study allows a better understanding of Ni and Cr enrichment of surface water and Ni and Cr transfer to living organisms.

11.3 Chemical Behaviour of Nickel and Chromium in Soils

Nickel has a relatively high affinity for soil organic matter (SOM), with 5% of total soil Ni being generally associated with this soil component. The main SOM electron donors are O, and N and S to a lesser extent, with Ca, Mg and Cu as main competitors. Nickel(II) organic complexes in soil can be formed with low molecular weight organic ligands (LMWOLs), humic substances or particulate organic matter. Association of metals, including Ni to humic substances has been mainly studied by chemical extractions with strongly alkaline solvents (e.g. NaOH) [109]. These data are questionable because Ni solubility strongly depends on pH, with maximum ionic $Ni(H_2O)_6^{2+}$ concentration at pH values below 6, whereas at alkaline pH, Ni may precipitate as hydroxides such as $Ni(OH)_3^-$ or $Ni_4(OH)_4^{4+}$, with very limited solubility. Extractions with strong alkaline solutions followed by acidification and classical SOM fractionation may also cause artefacts due to Ni re-distributions among the various SOM fractions. However, currently no chemical extraction method distinguishes between the forms of metals in soil.

Anyway, complexes with LMWOLs are labile, whereas formation of inner sphere complexes with soil solid phases form less reversible complexes. Among the identified organic complexes, Ni has been reported to be present also in porphyrin-like compounds, likely originating by reactions of Ni with chlorophyll and co-factors of methanogenic bacteria [29].

Due to its high affinity for organic and inorganic ligands, Ni concentrations in the soil solution are relatively low. Nickel concentrations in the solution of uncontaminated soils are in the range of 0.03–51 μg L^{-1}, whereas in serpentine soils from various locations the range is in the order of 500–900 μg L^{-1} [55].

Chromium can exist in oxidation states varying from 0 to VI, but only Cr(III) and Cr(VI) are sufficiently stable in the soil environment, whilst Cr(IV) and Cr(V) are generally unstable intermediates in Cr(III) oxidation and Cr(VI) reduction reactions. Reduction of Cr(VI) depends on its high positive redox potential in both acidic and alkaline solutions [36] in the presence of electron donors, according to the following chemical equations:

$$\mathrm{HCrO_4^-} + 7\mathrm{H^+} + 3\mathrm{e^-} \leftrightarrows \mathrm{Cr^{3+}} + 4\mathrm{H_2O} \text{ and } \mathrm{CrO_4^{2-}} + 4\mathrm{H_2O} + 3\mathrm{e^-} \leftrightarrows \mathrm{Cr(OH)_3} + 5\mathrm{OH^-} \tag{11.2}$$

However, as the Cr(VI) oxidizing capacity decreases on consumption of H^+ and also on the $Cr(OH)_3$ hydrolysis forming $Cr(OH)_2{}^+ \cdot H_2O$ and $Cr(OH)_2{}^+ \cdot H_2O$ [78], its oxidation potential in soil normally deviates from the theoretical Eh/pH diagrams [61].

Chromium chemical reactivity in soil varies as a function of soil pH , redox potential, presence of potential electron donors and Cr adsorption on colloids. In neutral or sub-neutral soil pH and natural Cr concentrations, both Cr(III) and Cr(VI) may form various hydrolysis and deprotonated products, which may dominate over the others. In fact, although the $Cr(OH)_3$ is sparingly soluble at pH 5.5–12.0 [90], the dominant species of Cr(III) should be the product of the hydrolytic product $Cr(OH)_2{}^+$. However, with increasing Cr(III) concentration, polynuclear hydrolytic products (e.g., $Cr_2(OH)_4{}^{2+}$, $Cr_3(OH)_5{}^{4+}$ and $Cr_4(OH)_6{}^{6+}$) may also be formed [90]. In acidic (e.g. pH value <5.5) and strongly acidic soils (e.g. pH value <4), $Cr(OH)_2{}^+$and $Cr(H_2O)_6{}^{3+}$, respectively, may be the predominant forms of Cr(III) [94].

The hydrolysis products of the Cr(III) are commonly adsorbed onto clay minerals, and the strength of this adsorption generally increases upon alkalinization of the soil pH, also due to the increase of negative charge on the clay surfaces and deprotonation of organic ligands such as humic substances [53], whereas at neutral-alkaline pH precipitation of $Cr(OH)_3 \cdot H_2O$ prevents the organic Cr complexation.

Hexavalent Cr in soils may naturally originate from chromite weathering processes in the presence of Mn minerals (e.g. birnessite), which may act as potential oxidants of the released Cr(III) [86]. For Cr(VI), the relative proportions among the various forms mainly depend on soil pH and total Cr(VI) concentration, being the $HCrO_4{}^-$ and $CrO4^{2-}$ the prevailing forms at acidic and alkaline pH values, respectively. Condensed dichromate ($Cr_2O_7{}^{2-}$) may be formed at Cr concentrations higher than 10^{-2} M [78]. In neutral-alkaline soils, the Cr(VI) may form soluble Na or K chromates or less soluble Ca and Ba chromates [53].

Hexavalent Cr can be lost from soil by leaching, or be retained in soil by adsorption onto Fe (hydro)oxides such as goethite, Al oxides and other positively charged colloids, whereas in acidic soils, chromate is soluble and is more easily leached [54]. It has been reported that adsorption of Cr(VI) onto Al- and Fe-oxides causes a kinetic ^{53}Cr/^{52}Cr isotope effect between the soluble and the adsorbed species [40], and that the microorganism-mediated dissimilatory Cr(VI) reduction discriminates between ^{53}Cr and ^{52}Cr isotopes, reducing preferentially the ^{52}Cr(VI) isotope [108].

Chemical oxidation of Cr(III) to Cr(VI) can occur in the presence of Mn oxides (e.g. buserite), involving Mn(III, IV) (hydr)oxides, reduced to Mn(II) [11]. This reaction depends also on the redox conditions, soil pH and presence of intermediate reducers [54]. Chemical reduction of Cr(VI) to Cr(III) by magnetite and Fe(II)-containing minerals has been reported [39]. The Cr(VI) reduction by hematite and biotite over a wide range of pH has been reported by Eary and Rai [38], in the presence of dissolved Fe(II), not necessarily occurring with solid Fe-bearing phases. For the above mentioned ionic properties, Cr in soil is strongly retained by the solid phases, and is generally poorly soluble and not mobile. However, soil acidification, as well as increase of Cl^- or F^- concentrations may drastically increase Cr solubility [102]. Increase of Cr(VI) in soil pore water by phosphate following P fertilisation of ultramafic soils of New Caledonia, possibly due to a Cr(VI)-phosphate ligand exchange mechanisms has been reported [13].

Trivalent Cr forms complexes with organic and inorganic ligands containing the electron donors O, N, S such as ammonia, urea, ethylenediamine, sulphide. However, partition of organo-Cr(III) complexes between the soil solid and solution phases depends on the molecular dimensions of the ligand. Relatively small ligands such as LMWOLs, increase the Cr solubility, whereas relatively large or particulate organic ligands such as humic substances may immobilize Cr(III). Relatively high abundance of fulvic acids or LMWOLs such as citrate may promote the Cr redistribution among goethite, FeO(OH), Al oxides and other soil colloids, through the formation of soluble Cr(III) complexes and transient oxidation to Cr(VI) [53].

In the soil environment, the Cr(VI) chemical reduction by S_2^- can be increased in the presence of clay minerals such as montmorillonite and kaolinite [22]. Lan et al. [66] reported that in the presence of sulphide, illite promoted the Cr(VI) reduction, Al oxides had no effect, whereas kaolinite, montmorillonite, amorphous SiO_2 prevented the Cr(VI) reduction. The reason for the kaolinite to prevent the Cr reduction was the elemental S sorption onto its surface.

11.4 Soil – Plant Relationships

Nickel has been proven to be essential for the fundamental metabolism of soil bacteria, fungi and algae, although its precise function has not always been elucidated [71]. A fundamental role of Ni in microbial metabolism may be the function of Ni in the synthesis of urease. Theoretical calculations by Zantua and Bremner [119] demonstrated that ultra-trace amounts of Ni (in the order of 2 μg kg^{-1}) are sufficient to let the soil urease activity work at the maximum velocity, therefore Ni total content cannot be considered a limiting factor for soil urease activity.

Nickel is an essential element for plants, ranging generally from 0.05 to 10 mg kg^{-1} DM [67, 81]. Nickel deficiency is very rarely found in plants, due to the very small amount needed for normal metabolism, whereas, with increasing Ni contamination, excess Ni is more commonly found in these organisms [28]. Symptoms of Ni deficiency, such as leaf tip necroses [42, 43], interveinal necrosis and patchy necrosis of younger leaves [21] are a result of the lack of urease, which leads both to urea accumulation to toxic levels and to N deficiency.

With regard to Ni toxicity, threshold concentrations are commonly reported to be less than 100 μg g^{-1} [3, 80]. Responses to toxicity differ significantly according to plant species, growth stage, cultivation conditions, Ni concentration and exposure time [57, 67]. In general, critical toxicity levels are >10 μg g^{-1} DM in sensitive species and >50 μg g^{-1} DM in moderately tolerant species (as reviewed in Chen et al. [28]). Among the toxic effects of high Ni concentrations in plants, retardation of germination, inhibition of growth, reduction of yield, induction of leaf chlorosis and wilting, disturbance of photosynthesis, inhibition of CO_2 assimilation and diminution in stomatal conductance [28] are the most frequently reported.

Soil Ni toxicity thresholds to plants are difficult to predict because, as for all the other elements, only a small fraction of the total metal is bioavailable, and the phytoavailability of Ni varies greatly depending on soil properties [65]. Soil toxicity threshold concentrations for Ni are commonly reported to be in the order of 100 mg kg^{-1} [3, 80]. In view of this, the maximum admissible Ni concentration established for agricultural soils on the basis of the 86/278/EEC directive of 30 mg kg^{-1} for acidic soils and 75 mg kg^{-1} for neutral alkaline soils seems to be protective for plants.

Nickel is quickly taken up by plants from soils in the form $Ni(H_2O)_6^{2+}$ and, until toxic concentrations in plant tissues are reached, this absorption is positively correlated with the soil Ni concentrations [57].

The solubility of Ni in the rhizosphere may be affected by the release of LMWOLs by plant roots [32, 67]. There are several examples showing that the presence of particular compounds in the substrate can either increase or decrease Ni uptake, depending on their quantity, quality, and the characteristics of the plant in question. The presence of organic acids or inorganic ligands in soil solution results in the formation of Ni complexes with different characteristics that may inhibit or enhance root uptake [81]. In this context, Molas [74] showed that Ni(II)-EDTA was less toxic and less accumulated than Ni(II)-citrate or Ni(II)-Glu in hydroponically-grown cabbage plants.

In contrast to animals, the essentiality of Cr for plant metabolism has not been definitively proven, although stimulatory effects on plant growth and yield from the addition of small amounts of Cr have been reported [120]. The positive effect of Cr(III) on plant growth was suggested to be related to influence on the levels of plant growth hormones, such as cytokinin, interaction with nucleic acids or chromium-induced increase in polyamine levels [88].

Chromium concentrations in shoots of plants living on non-contaminated soils are usually in the range of 0.02–0.2 mg kg^{-1} DM and rarely higher than 5 mg g^{-1} DM [57, 120]. These very low Cr concentrations are mainly due to the relative immobility of this element in both soils and plants, probably because of the predominance of the more insoluble $Cr(III)^+$ form. The low Cr availability, from 0.01 to 4 mg kg^{-1}, also leads to poor correlation between Cr concentrations in plant tissues and soils [120]. Plant Cr uptake in non-contaminated soils may be partially explained by natural Cr(III) oxidation in the presence of Mn-rich minerals, particularly due to the peculiar reactivity (e.g. metal concentration, acidification) in the rhizosphere [79]. Nevertheless, different plant species show differences in their ability to accumulate Cr in their tissues, being the highest in members of the cabbage family (Brassicaceae). These plants, known to be sulfurophile, if supplied with $CrO_4{}^{2-}$, can accumulate large amounts of Cr, possibly due to the chemical similarity between chromate and sulfate ions [120]. However, Cr concentrations in edible plant parts are so low that they rarely meet the nutritional requirements for the human diet.

In most plants the range of critical leaf Cr concentrations is 1–10 mg g^{-1} DM [120]. Stunted growth, poorly developed root system, curled and discoloured leaves [89], leaf chlorosis, narrow leaves [52], chlorotic bands [57], yield reduction [50] are the most common visual symptoms of Cr toxicity in plants. Under field conditions, Cr is hardly ever toxic to plants, with a few exceptions [3], and 75–100 mg kg^{-1} is thought to be the total soil Cr concentration above which plant toxicity can occur [117]. It is noteworthy to underline that while the 86/278/EEC directive established no maximum limits for total Cr concentrations, individual member states included maximum values or concentration ranges for total Cr for agricultural soils in their national statutory values. The range of total Cr permitted in various EU Countries varied from 30 (Netherlands) to 300 (Portugal) and 400 (United Kingdom) mg kg^{-1}, although the British limit was not statutory. The Italian legislation established limits for Cr(VI) at 1 μM. As for the available form, 1–5 mg kg^{-1} of available Cr estimated by soil extractions with various electrolytes, is supposed to be toxic for most plant species [2]. Factors such as soil properties, plant species, soil characteristics, and Cr species may greatly affect the level at which Cr is phytotoxic; for example Cr is more toxic to plants growing on sandy soils compared with peat soils [73].

11.4.1 Serpentine Soils

Both Cr and Ni are present at phytotoxic concentrations in serpentine soils. In fact, although these soils are characterized not only by a high metal content, but also by other unfavorable conditions (e.g. low water retention) for plant growth, they are colonized by plant species adapted to survive in such an extreme environment [17].

These species have often become endemic to such substrates and actually the tight relationship between serpentine soils and its flora was documented as long ago as the sixteenth century [115]. In fact, serpentine endemic plants can act as flag species, faithfully indicating the presence of such mineralized substrates and thus have been used for mineral prospecting already from a long time [19].

The relationship between serpentine soils and plants finds expression not only in a particular flora composition, but also in the so-called ‘serpentinomorphoses’ [82], which are unusual and characteristic features showed by serpentine species, such as xeromorphic foliage, development of a large root system, dwarfism, plagiotropism, glabrescence or pubescence, glaucescence and erythrism [17, 116], that concur to plant adaptation to the serpentine factor [63].

Metal tolerant plants are often excluders [7], limiting uptake and root-to-shoot translocation of trace metals. They are more rarely accumulators, concentrating metals in their tissues [7]. Serpentine plants evolved a variety of physiological strategies to accumulate and tolerate a wide range of concentrations of Ni and Cr in their tissues, from typical values of the non serpentine plants to values far higher than the typical toxicity thresholds [see for example 60, 87, 106]. Among accumulators, a group of bizarre plants shows extraordinarily high metal concentrations in their above ground parts, exceeding 2,000 μg g^{-1} DM [8], and they are the so-called “hyperaccumulators” [20]. Whatever the reason for the evolution of this particular phenomenon was, probably a defense strategy against natural enemies [16], metal hyperaccumulators can surely be one of the most representative emblem of the indissoluble relationship between serpentine soil and plants because of their inability to compete in non-serpentine environments.

The term metal “hyperaccumulator” was first coined by Brooks et al. [20] to define plants living on serpentine soils with Ni concentrations higher than 1,000 mg kg^{-1} DM in their above-ground parts. The discovery of a large number of taxa (more than 400) that accumulate Ni in their tissues suggested that the concentration of this metal can be one of the main factors in determining the flora and vegetation in many serpentine areas [18, 95, 115], whereas no serpentine plants are known that hyperaccumulate Cr [18, 30, 95]; which is likely to be due to its low solubility in these soils.

The first metal hyperaccumulator discovered was the Tuscan nickel plant *Alyssum bertolonii* [72] and the well-known connection between serpentine soil and this cruciferous plant was already recorded in the sixteenth century by Cesalpino [24]. The soil-plant relationship for *A. bertolonii* is peculiar as, to our knowledge, so far it is the only hyperaccumulator plant that is not only a faithful indicator of serpentine soils for geobotanical prospecting, but also a useful tool for biogeochemistry as it is representative of the degree of Ni mineralisation of the soil [47].

In metal hyperaccumulator plants the metal is quickly taken up by roots, rapidly transported into shoots and leaves, and sequestrated in the vacuole [62]. For this reason, these plants have been used as solar-driven ion-pumps for removing the metal from polluted soils in phytoextraction experiments [92, 99]. The benefits of this ‘green’ technology relies on the low costs of growing and harvesting crops, and low impact compared to the ‘dig and dump’ approach to soil remediation [26].

Phytoextraction, also protects polluted soils from erosion [105] and may provide financial returns thanks to ‘phytomining’ practices [91], which is the recovery of metals from hyperaccumulator plants. Phytomining of Ni has more potential than other metals [27] because most of the known hyperaccumulators are able to concentrate 1–3% Ni in dry matter, providing 12% to >20% in the ash; these values are an order of magnitude higher than lateritic ores [37], which, based on the Ni economic value, may balance the costs of crop production.

11.5 Soils Contaminated with Nickel and Chromium

Nickel contamination of soils is a serious problem as a result of anthropogenic activities. Generally, localised Ni contamination occurs near to a smelter or plating works or is associated with mining activity [4]. A significant source of Ni in soil can be represented also by the use of both P -containing fertilisers and wastes, such as sewage sludge and pulverised fuel ash. For example, coal can contain up to 70 mg kg^{-1} Ni which can become highly concentrated in ash residues [4]. Moreover, the burning of oil and coal account for the widespread atmospheric deposition of Ni. Worldwide production of Ni has increased from about 20,000 t $year^{-1}$ in 1930 to about 800,000 t $year^{-1}$ in 1985 [103] and to about 1.25 Mt $year^{-1}$ in 2000 [49].

In both naturally rich and Ni contaminated soils, Massoura et al. [68] through isotope equilibration experiments reported that the labile fraction ranged between 0.1% and 50% of total soil Ni. The Ni solubility in contaminated soils is likely to be controlled by the contents of crystalline Fe oxides [46]. A large body of literature exists on the occurrence and importance of slow reactions between Ni and Fe oxides (e.g. goethite), due to the slow diffusion towards the interior of the goethite particles [76], although the formation of Ni-enriched phases cannot be excluded [101]. In a recent experiment, Fischer et al. [45], reported that slow reactions of Ni and Cr with goethite have a different dynamic as compared to those of Cd, Co, Cu, Hg, Mn, Pb, and Zn. This experimental evidence highlights the importance of the Fe–Al bearing minerals in controlling sorption in Ni–Cr contaminated soils.

As for the bioavailability of Ni in soils polluted by long term sludge application, Hooda et al. [51] reported that the potential phytoavailable Ni estimated by the DGT technique in ten consecutive deployments, accounted for 0.7% of total Ni (56 mg kg^{-1}), which was a higher proportion as compared to Cd, Co, Cu, Pb, but lower than that of Zn (3%) in the same soil.

Soil Cr contamination arises mainly from the uncontrolled emissions from metallurgical industries, improper disposal of dye, tannery and textile industrial wastes, and incorporation of sewage sludge into agricultural soils [83]. Chromium production worldwide has increased from about 500,000 t $year^{-1}$ in 1930 [103] to about 3 Mt $year^{-1}$ in 1985 and to about 4.5 Mt $year^{-1}$ in 2000 [49]. Although the predominant industrially emitted form is Cr(III), significant levels Cr(VI) have been detected in soils of various world regions (e.g. India, China), especially where no soil protection legislation is enacted. A particular form of Cr contamination is found at former wood treatment plants where chromated copper arsenate (CCA) has been used for decades as a wood preservative. In these peculiar industrial sites, the Cr accumulation into the surface soil may vary depending on the pedo-climatic conditions. In a sandy acidic CCA polluted soil from northern Sweden, Kumpiene et al. [64] reported soil Cr total concentrations in the range of 3–4,000 mg kg^{-1} (plus As and Cu in the order of 5–6,000 and 1,500 mg kg^{-1}, respectively), whereas in a sandy neutral French soil, Bes and Mench [14] reported no Cr and As accumulation, but only Cu enrichment (1,500–2,600 mg kg^{-1}) of topsoil from a wood impregnation plant.

The presence of Cr(VI) in soils incorporated with Cr-rich residues may be due to mineral-mediated (e.g. Mn oxides) chemical oxidation described in the previous paragraph. Notwithstanding the extensive research on the speciation of Cr in soil, the complex behaviour of the various Cr species in different forms still results in a high level of uncertainty on the prediction of Cr mobility and potential risks for humans and ecosystems posed by Cr contamination of soils.

In volcanic soils affected by repeated Cr-polluted river flooding, Adamo et al. [1] reported that among the several trace elements (Cu, Ni, Zn) exceeding the local background values, Cr soil contamination was the only metal clearly related to flooding events, and was mainly associated with short-range-order aluminosilicates and organo-mineral complexes, and progressive Cr insolubilization with ageing was also observed. In this study, soil micromorphology/SEM/WDS analyses also revealed Cr and Cu enriched silt and clay coatings in surface and subsurface soil horizons, suggesting a transfer of metal-rich sediments along the soil pore network with water movement [1].

While Cr forms in contaminated wastewater have been characterized, less information is available on Cr in the atmosphere. It is known that both Cr(III) and Cr(VI) are generally present in the atmosphere in which Cr is dissolved in aerosol or associated with particles of various radii. In the atmospheric aerosol, the main Cr forms are: $Cr(H_2O)_3^{6+}$, $Cr(OH)^{2+}$, $HCrO_4^-$ and $Cr_2O_7^{2-}$. Therefore, the air-borne Cr is expected to be the form of chromium that undergoes to major transformations in the soil environment.

In an interesting comparative experiment, Jones [56] evaluated the sorption of Cr with that of other trivalent ions (Y, Rh, La, Pr, Gd) in two acidic soils with different soil organic matter content. The main result of the study was that more than 99% of the metals were associated with the exchangeable phase, and that the main factors controlling the Cr solubility were the $Al(III)^+$ release at acidic pH (<4.5) and the organic matter dissolution at pH >5.0. In the same study, the competitive binding of carboxylic acid was also shown [56]; this may have implications for the assessment of Cr phytoavailability in contaminated soils, due to the relatively high concentrations of bi- and tri-carboxylic acid in the rhizosphere.

In a survey of six French soils polluted by atmospheric metal inputs, Gandois et al. [48] reported that among several measured heavy metals Cr was larger than Ni contamination, whereas Ni was more soluble than Cr using 0.01 M $CaCl_2$ as extractant, with soil pH and dissolved organic matter having the most significant effect on Ni and Cr partitioning. This paper also well illustrates the differences in the chemical behaviour of Ni and Cr in terms of solubility in relation to soil pH. In fact, for acid soils soluble and exchangeable Ni, but not for Cr, was negatively correlated with soil pH [48].

An important emerging aspect of soil pollution by trace elements is related to the properties and environmental behaviour of the so called ‘nanoparticles’, i.e. discrete entities with size in the order of 10^{-8}–10^{-7} m, today largely used for production of new materials such as polymers, textiles, fuel and solar energy cell liners, composite materials, biomarkers, diagnostics and sensors. Nanoparticles behave differently from elements or polynuclear molecular aggregates, due to their surface physico-chemical properties and reactivity.

Nickel and Cr nanoparticles are produced in large amounts mainly by manufacturing and smelting activities. Their inhalation can lead to asthma, pulmonary fibrosis and ultimately lung cancer [23].

Nickel in bimetallic commercially available Ni/Fe nanoparticles, has been demonstrated to have catalytic properties towards LMWOCs and chlorinated organic xenobiotics, mainly altering the reducing capacity of Fe in aqueous solutions [111]. However, information on the stability of these bimetallic nanoparticles in soil and the eventual Ni leaching and toxicity is still poor. Among the fundamental properties, Cr containing nanoparticles of 20–200 nm size may exhibit a net magnetic moment at the surface [9], which influence their behaviour in the soil environment, where magnetic minerals are largely present. Even for Cr-containing nanoparticles, knowledge of their reactivity and stability in the soil environment is still scarce.

11.6 Concluding Comments

Nickel and Cr concentrations in soils and sediments have increased worldwide during the last century due to mining, smelting and industrial activities. So, a continuous research effort is needed not only to check the spread of these metals in the environment, but especially to assess their real environmental mobility. In this context, the study of the mechanisms responsible for the transfer of Ni and Cr from environmental matrices to living organisms has fundamental importance in order to clarify metal exposure routes to all biota and predict the relative consequences. Furthermore, much research has to be dedicated both to the reduction of emissions of Ni and Cr into the environment during anthropogenic activities and to the remediation of metal polluted soils, taking into account of the great advantage of the availability of the naturally evolved Ni hyperaccumulating plants.

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Chapter 12
Cobalt and Manganese

Nicholas C. Uren

Abstract Cobalt (Co) and manganese (Mn) are closely associated in soils because they have similar chemical properties. The main forms of Mn in soil are the water-soluble and exchangeable forms of Mn(II) and the insoluble Mn oxides, mainly Mn(IV) and to a lesser and more uncertain extent as Mn(III). The concentration of water-soluble plus exchangeable Mn(II) (WS+Exch Mn) is determined by the relative rates of the chemically independent and physically separate reactions, the microbial oxidation of Mn(II) and the chemical reduction of the Mn oxides (by organic matter). The solubility and availability of Co to plants is influenced greatly by the activity of the Mn oxides and the reactions which affect Mn. The Mn oxides also participate in sorption and oxidation reactions which impact on soil health in that the former affects the availability of trace metals and the latter oxidises organic moieties, of which some are phytotoxic.

Keywords Cobalt • Manganese • Attenuation • Biogenic Mn oxides • Microbial oxidation • Soil health • Sorption

12.1 Introduction

Cobalt (Co) and manganese (Mn) are two heavy metals which have little of the notoriety afforded to other heavy metals such as lead (Pb), for example. Their lack of notoriety is a result of their lower potential to exert any toxic properties that they may have and to the lack of appropriate situations, particularly in soils. Nevertheless, the ability of Mn oxides to sorb preferentially heavy metals and to act as oxidants means that they play significant roles soil health. Sometimes though their role as oxidants of arsenic (As) and chromium (Cr) may be deemed good (oxidation of As(III) to As(V))

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or bad (oxidation of Cr(III) to Cr(VI)). The close association of Co with Mn oxides in soils is illustrated strikingly in electron micrographs of Mn accumulations in soils (e.g. [88, 108]).

Rarely is Co of concern in the environment other than in agricultural situations where its low availability in soils leads to disorders in ruminant livestock [153]. On the other hand, both Mn deficiency and toxicity occurs in plants and Mn may be of environmental concern in a few situations associated with water quality and the mining of Mn ores. Both Co and Mn are closely associated in primary minerals, soils and sediments, but not so closely associated in biological systems although both are essential to some organisms, Mn to nearly all and Co for animals and prokaryotes; Co is still regarded as a beneficial element for plants [116].

This chapter will concentrate on some aspects of the behaviour of these two elements in soils and on practical aspects in relation mainly to the environment and plant growth.

12.2 Geochemical Occurrence

In igneous rocks both Co and Mn are present in the divalent state and are found mostly in the ferromagnesian minerals where their respective divalent radii allow them to substitute readily for Fe(II) and Mg(II) [41]. As a result, the concentrations of Co and Mn are greatest in the ultrabasic and basic rocks such as serpentine and basalt respectively and least in acidic rocks such as granite (Table 12.1).

During the weathering of igneous rocks and soil development, the Co(II) and Mn(II) are released concomitantly as soluble Co^{2+} and Mn^{2+} from the ferromagnesian minerals early in the weathering cycle following the oxidation of Fe(II) and acid attack on the silicate framework. Under some soil conditions, e.g., poor drainage, their mobility is relatively high and they may be transported by leaching to depth in the developing soil profile or lost in drainage waters. Thus, some Co and Mn may move into groundwater and subsequently into streams and eventually the oceans, although some Co may be retained in resistant minerals such as ilmenite and magnetite [98]. However, predominantly both the Co^{2+} and Mn^{2+} are retained in soil in association with layer silicates, organic colloids and mostly in oxides of Mn, although the smaller ratio of Co to Mn in soil than in igneous rocks (Table 12.1) suggests that Co is less well retained during soil formation than Mn.

In sedimentary rocks the concentrations of Mn and Co are highly variable, but as a rule they are highest in fine-grained sediments e.g., shales, and lowest in coarse-grained sediments e.g., sandstones. The variations in concentrations of Mn and Co in metamorphic rocks are as great as those in the parent rocks and so the variations are as great as those found in igneous and sedimentary rocks.

Ultimately deficiencies of both elements are found primarily on sandy soils and some peats whereas toxicities of Mn occur on soils derived from rocks which contain high proportions of ferromagnesian minerals. The occurrence of Co deficiency in ruminant livestock grazing pastures on pumice soils in New Zealand is a

Table 12.1 Total concentrations (mg kg^{-1}) of Co and Mn in soils and rocks

	Earth's crust	Ultramafic	Basic	Granodiorite	Granite	Shale	Limestone	Soil
Co	25	150	50	10	1	20	4	1–40
Mn	950	1,300	2,200	1,200	500	850	1,100	850
Co/Mn ratio	0.026	0.12	0.023	0.0083	0.002	0.023	0.00036	0.00012–0.0047

From Levinson [65]

unique situation but not surprising since the most recent showers of rhyolitic pumice contain mainly glass (>95%) and only traces of ferromagnesian minerals [136].

In soils, pedogenic accumulations of Mn occur as stains, cutans, nodules and concretions, often in association with Fe and usually in soils which are poorly drained or have been exposed to excessive wetness in a previous age. Thus, nodules are complex objects, of which some are relics formed in a previous age, others are forming while others may be dissolving; as Taylor and Pohlen [138] commented "Some have had a long and complicated history." Some aspects of their formation and the Co associated with them shall be discussed later (Sect. 12.6).

12.3 Forms of Cobalt and Manganese in Soils

The forms and associations of both Co and Mn with phases of soil have been summarised in Table 12.2.

12.3.1 Soluble Forms of Cobalt and Manganese

The hydrated ions of $Mn(H_2O)_6{}^{2+}$ and $Co(H_2O)_6{}^{2+}$ are the primary forms of interest in the soil solution where they tend to form labile outer sphere complexes with various ligands as the pH increases (Table 12.2). The ligands include the usual anions found in the soil solution (e.g. OH^-, Cl^-, $HCO_3{}^-$ etc.) and low molecular weight organic moieties. The molar ratio given in Table 12.3 indicates the severe competition that Mn^{2+} faces with respect to Ca^{2+} and Mg^{2+} as the pH increases even though the dissolved organic carbon increases with increasing pH and the tendency of Mn^{2+} to form complexes increases; the same applies to Co^{2+}.

$$Mn^{2+} + H_nL \leftrightarrow (MnL)^{2-n} + nH^+ \tag{12.1}$$

The soluble forms of Co in the soil solution form labile outer sphere complexes in the same manner as Mn (Table 12.4); little or no evidence of soluble Co(III) exists [7, 171].

Table 12.2 Forms and associations of Co and Mn with phases of soil

Phase of soil	Form or association	Notes
Soil solution	Soluble $M(H_2O)_6^{2+}$, MOH^+, $M(L^{n-})^{(2-n)+}$	pH dependent
Organic	Exchangeable M^{2+} (Ca^{2+})[a]	Outer sphere
	Nonexchangeable M^{2+} (Ca^{2+}); exchangeable M^{2+} (Cu^{2+})[b]	Outer sphere and inner sphere respectively
	Nonexchangeable M^{2+} (Cu^{2+}):	Inner sphere
	Mixture of Mn oxides and microbial cells	Includes EPS[c]
Inorganic	Exchangeable M^{2+} (Ca^{2+})	
	Nonexchangeable M^{2+} (Ca^{2+}); exchangeable M^{2+} (Cu^{2+})	
	Nonexchangeable M^{2+} (Cu^{2+}): lattice forms (occluded)	
	Primary minerals: danaite (Fe,Co)AsS, cobaltite CoAsS, olivine, pyroxenes, amphiboles, biotite, ilmenite, magnetite	
	Secondary minerals: hydrous oxides of Fe and Mn	

M represents both Co and Mn where appropriate

[a] Exchangeable with respect to Ca^{2+}

[b] Exchangeable with respect to Cu^{2+}

[c] Extracellular polymeric substances (EPS)

Table 12.3 Effect of soil pH on concentrations of Mn, Ca, and Mg in the soil solution of a sandy loam [50, 51]

Soil pH (1:5 H_2O)	Mn Soil solution (mM)	Mn Removed by Chelex 100 (%)	Dissolved organic C (mg L^{-1})	Ca (mM)	Mg (mM)	Molar ratio $\left(\frac{(Mn)}{(Ca)+(Mg)}\right)$
4.5	217	52	94	15.3	9.4	9×10^{-3}
4.9	32	50	84	19.0	8.6	1×10^{-3}
5.6	3.1	83	96	19.5	6.6	1×10^{-4}
6.7	0.41	91	196	27.6	6.1	1×10^{-5}
7.5	0.34	95	245	32.4	6.2	9×10^{-6}

Table 12.4 Effect of soil solution pH on concentrations of Co in soil solutions displaced from a sandy loam [124, 125]

pH	Dissolved organic C (mg L^{-1})	Co (mM)	(Co^{2+})/(Co) ratio
4.75	35	0.13	0.5
5.40	45	0.05	0.5
5.80	59	0.07	0.2
6.15	70	0.06	0.1
6.60	75	0.03	<0.05

12.3.2 Insoluble Forms of Cobalt and Manganese

Exchangeable and non-exchangeable forms of Co^{2+} and Mn^{2+} are, in essence, insoluble forms. The readily exchangeable Co^{2+} and Mn^{2+} are associated with colloidal layer silicates and organic matter; one expects that their behaviour is not greatly different to that of Ca^{2+} and Mg^{2+} [23, 38, 112]. McBride [80] agrees although he believes that Mn forms inner sphere complexes with surface groups on organic matter at high pHs. Also, Tiller [145] discussed the specific adsorption of Co^{2+} on layer silicates and although there is a propensity for it to occur as the pH increases, implying less competition from H^+ and an increasing tendency for $CoOH^+$ to be adsorbed, the Mn oxides would seem to take over in soil.

12.3.2.1 Oxides and Hydrous Oxides of Manganese

Most of the oxides of Mn which have been identified in soils are macroscopic forms and are relatively unreactive towards mild reducing agents. The more finely divided Mn oxides are more reactive towards mild reducing agents, but these oxides are difficult to identify because of the low concentrations and because they tend to be amorphous. Of the identifiable oxides and hydroxides of Mn which are found in soil, the two most common forms are birnessite [$(Na_{0.7}Ca_{0.3})Mn_7O_{14}.2.8H_2O$] and vernadite [$\delta$-$MnO_2$] [39, 91]; there are others, e.g. lithiophorite [$(Al, Li)MnO_2(OH)_2$], but they are less common.

Few of the naturally occurring oxides contain high proportions of Mn(III) and most Mn present is Mn(IV); for soils the most common Mn oxides, birnessite and vernadite, contain primarily Mn(IV) [91]. Although Mn(III) appears to be an essential intermediate in the pathways of both the microbial oxidation of Mn(II) and the reduction of Mn(IV), its persistence and behaviour in natural compounds and environmental systems has been ignored [74].

The zero points of charge, ZPCs, of these Mn oxides are generally low, about 3 or even less for δ-MnO_2 while the specific surface area (SSA) ranges widely from values as low as 1 or 2 and may be as high as between 130 and 300 m^2g^{-1} for δ-MnO_2 [139]. Tebo et al. [141], in summarising the properties of microbial Mn oxides produced in cultures, state that they are "typically high average oxidation state [i.e., structural Mn(IV)] layer-type oxides with very high specific surface areas and poor crystallinity, most closely resembling δ-MnO_2 or H^+-birnessite." Thus, it would seem that given time and persistence the product of microbial oxidation in soils changes to more crystalline versions. For an extensive review of the mechanisms of formation and properties of biogenic Mn oxides the reader is referred to Tebo et al. [140].

In the context of this chapter, as indicated earlier, there are two forms of Mn oxides which can be crudely divided into chemically reactive and unreactive. The former oxides are a valuable source of Mn to plants while the latter are unreactive towards mild reducing agents (e.g., quinol) and reducible in stronger reducing agents (e.g., dithionite), but nevertheless of great interest for example as sinks for heavy metals. The reducibility of Mn oxides depends upon their crystallinity, SSA, degree of hydration and composition [166]. These physicochemical attributes in the synthetic oxides are determined by the way in which they are prepared, where wet way preparations are usually reactive while dry way preparations are of low reactivity [87]. Since a main interest in Mn oxides is their ability to oxidise organic compounds, i.e. their reducibility, a standard test of their reducibility under standard conditions as suggested by Fatiadi [33] would be appropriate.

12.4 Behaviour in Soils

Probably for too long the strict adherence to predictions afforded to us by thermodynamics have let us down when it comes to the behaviour of Mn in soils. The predictions are indications of what might happen given time, but they do not give any indications of reaction rates, catalysed or not. Also, molecular oxygen (O_2) in spite of its high redox potential is a sluggish oxidant such that in soils soluble reducing agents persist but may react with Mn oxides. The competition between O_2 and Mn oxides in soils is between a mobile gas with low solubility and low diffusion rate in water and an insoluble but strong oxidant.

12.4.1 Oxidation

The oxidation of Mn(II) can occur through either abiotic means – either auto-oxidation or catalytic oxidation, or by microbial processes. Morgan [100] has estimated that the relative half-lives of the disappearance of Mn(II) at pH 8 in aqueous systems are (a) 10 h for bacterial oxidation, (b) 30 days for oxidation by surface catalysis, and (c) 400 days for auto-oxidation; a relative order of 1:72: 960, i.e. auto-oxidation is about 1,000 times slower than the rate of microbial oxidation. Although the primary stable form of Co in the environment is Co^{2+}, its oxidation to Co^{3+} can occur; the Co^{3+} readily hydrolyses and is rendered insoluble.

12.4.1.1 Auto-Oxidation

The best representation of the reaction is probably:

$$Mn^{2+} + 0.5(x - 1)O_2 + H_2O \rightarrow \mathbf{MnO_x} + 2H^+$$

where $1 < x \leq 2$. The Mn oxide (bold print) is insoluble while the other species are in solution. The thermodynamic prediction is such that one expects oxidation of Mn^{2+} to occur readily down to pHs around 4, but because the activation energy of Mn(II) oxidation is high it doesn't proceed as readily even in the presence of molecular O_2 [139]. In general, reactions with molecular O_2 at ambient temperatures of the environment generally proceed very slowly [32], and because of this both Mn^{2+} and organic reducing agents persist in soils of acidic and neutral pHs when one would otherwise expect them to be oxidised by O_2 [83].

Even when alkali is added to a solution of a Mn(II) salt nothing happens to the faint pink solution until the first signs of precipitation of Mn hydroxide occurs, but once the buff coloured hydroxide appears at a pH of about 8 or more it very quickly turns brown due to oxidation by O_2 from the solution and the atmosphere. It would seem, that in the absence of the Mn hydroxide, O_2 is an incompetent oxidant, but when the Mn hydroxide forms, the O_2 is transformed into a competent oxidant, which may due to the sorption of the O_2 molecule and its conversion into a much more aggressive oxidant such as atomic O [32]. The primary product of autoxidation of Mn(II) in oversaturated solutions is commonly found to be manganite (γ-MnOOH) [56, 101] and measurable rates of oxidation are observed in such solutions, but the rates are slow when compared with oxidation catalysed by microbes and some surface catalysts [31, 100].

12.4.1.2 Catalytic Oxidation of Mn^{2+}

The catalytic oxidation of Mn^{2+} in soil may occur because of the presence of the diverse array of surfaces, but since humic substances have been found to decrease the rate of catalytic oxidation of Mn(II) on a variety of surfaces [174], it becomes a problematic proposition and almost impossible to resolve.

12.4.1.3 Microbial Oxidation of Manganese (II)

A wide range of microorganisms such as bacteria, fungi, microalgae and even spores of bacteria, in a wide range of environments, are able to catalyse with ease the oxidation of Mn(II) such that biogenic Mn oxides are formed rapidly from Mn(II) at all pHs of environmental systems greater than 4. The mechanism by which microbes oxidise Mn(II) has been discussed in detail by Tebo et al. [140]. In all cases the Mn oxide is found outside the cell, sometimes on the cell or in the biofilm of EPS surrounding the cell [150], and in some cases Mn oxides are observed in agar culture quite remote from the site of microbial growth (e.g. [20]). In the former cases similar extracellular enzymes have been identified for a number of different species of bacteria, while in the latter case a mobile oxidant or promoter of oxidation has diffused into sterile regions of the agar and caused oxidation, but nothing is known about the oxidant responsible. Nevertheless, it is likely that such a compound is rapidly reduced in the soil environment and so any impact it might have would be near its source.

Because soil is a different and more complex system than water alone, and surfaces may catalyse Mn(II) oxidation, some doubt has been expressed about the role of microorganisms in the oxidation of Mn in soils (e.g. [82, 120]). Nevertheless, the weight of evidence for microbial oxidation is strong [36].

Abiotic oxidation of Mn^{2+} is favoured, one would expect, by (a) increasing the activity of Mn^{2+}, (b) increasing the pH, and (c) increasing the partial pressure of O_2. Respectively, there is much evidence (a) that the microbial oxidation of Mn^{2+} is inhibited by high concentrations of Mn^{2+} in cultures (e.g. [15]) and agar (e.g. [62]); (b) that microbial oxidation for a Mn-oxidising microbe from soil usually has an optimum pH for oxidation so that increasing the pH can inhibit microbial oxidation of Mn^{2+} (e.g. [16, 17]) which may explain the seemingly incongruous result where liming increases Mn availability on a Mn deficient soil of neutral pH [52, 53]; and (c) that microbial oxidation in soils and other environments has been observed in microaerophilic environments near an oxic/anoxic interface (e.g. [143, 161]).

Ross and Bartlett [120] claim that there are few cases where successful re-inoculation of an isolated Mn-oxidising microbe has been recorded. There are a few reasons why that may be so. Firstly, the introduction of microbes into soil is not favoured with a high rate of success [4], and secondly, autoclaved soils are no longer the soils they used to be [128]. Nevertheless Thompson et al. [143] successfully re-inoculated an autoclaved soil with a Mn-oxidising fungus isolated from the same soil and were able to observe vigorous and extensive deposition of Mn oxides around the hyphae. They also found that the optimum temperature for oxidation by fungi in soil was 21°C, while oxidation was totally inhibited at 3°C and 52°C.

Thus, it is known that the oxidation of Mn(II) in soils:

(a) is brought about by a diverse array of Mn(II)-oxidising microbes;
(b) occurs at all soil pHs even as low as 4;
(c) is inhibited by soil sterilisation with poisons, desiccation, dry heat, steam, and irradiation;
(d) produces a poorly crystalline form of layered Mn oxide, similar to birnessite or vernadite (δ-MnO_2), with a high SSA and oxidation state (i.e. x in $\mathbf{MnO_x} \leq 2$);
(e) produces an insoluble oxide which is a strong oxidant and easily reducible;
(f) produces an oxide which is enveloped with a mass of cells in a biofilm or matrix of EPS; and
(g) produces an oxide which has a strong capacity to sorb trace metals.

The presence of EPS or biofilms has been noted in some investigations [37, 149, 164], but what may happen in soil has not been considered. The highly hydrated EPS would shrink considerably on drying, drawing the oxide particles together. The reversibility of rehydration and swelling and the biodegradability of the EPS are significant issues also.

Further, no attention has been given to the fact that microbial oxidation of Mn (II) in soil would be restricted to soil pores large enough to accommodate the colonies of Mn-oxidising microorganisms and where conditions are favourable to their existence. This means that the microbial Mn oxides will be found predominantly in mesopores (3–30 μm) and on the surfaces of macropores such that the oxides are unevenly distributed throughout soil and tend to be found between aggregates and on their surfaces, a situation which would favour availability to plant roots (see Sect. 12.7).

However, with time and in certain situations, Mn oxides accumulate in relatively unreactive forms, the mechanism of which is uncertain. The longer a biogenic Mn oxide persists, the less reactive it is likely to become because of ageing, a process associated with increasing crystallinity, decreasing hydration, decreasing SSA and progressive exclusion and replacement of metals with less affinity for sites within the lattice than others such as Co [166]. The first step in this process may be a decrease in SSA associated with microbial oxidation and accumulation at select spots [157], the relatively lower SSA decreases reducibility which then allows the physico-chemical processes of ageing to proceed; only strong reducing agents (e.g. dithionite) or waterlogging can release the Mn from such forms. When autolysis occurs and enzymes and cell constituents are released, some products may reduce the Mn oxides.

12.4.2 *Reduction of Manganese Oxides*

The general reaction for the reduction of insoluble Mn oxides is:

$$\mathbf{MnO_x} + 2xH^+ + 2(x-1)e^- \rightarrow Mn^{2+} + xH_2O$$

where $1 < x \leq 2$ and in soil the source of electrons (e^-) could be any appropriate reducing agent, usually an organic moiety such as a phenol, or reducing agents produced by microbes, or microbes utilising the $\mathbf{MnO_x}$ as an alternative electron acceptor in their metabolism. The latter reaction is only of significance in poorly drained anoxic situations where O_2 and other alternative electron acceptors such as NO_3^- are scarce.

The form of the Mn oxide will determine its reducibility. The microbial Mn oxides, because they are usually poorly crystalline and have a high specific surface area, are readily reducible. Other forms are less easily reducible and require stronger reducing agents (e.g. dithionite) and conditions (e.g., anaerobiosis) to be reduced and for the Mn to come into solution as Mn (II).

In soil, the organic compounds which can reduce Mn oxides range from low molecular weight compounds such as pyruvate to large polymeric compounds. The range of phenolic compounds in soils is extensive and mostly are chemically bound to surfaces [132] so that their reducing capability with respect to reactive Mn oxides is only expressed when they desorb into the soil solution. More complex oxidative polymerisation of polyphenols by Mn oxides has been investigated by many (e.g. [131]), and discussed at length by Whelan et al. [173], such that one appreciates the important role that the microbial oxidation of Mn(II) plays in the regeneration of Mn oxides. The fact that insoluble Mn oxides can oxidise organic compounds in the passive presence of molecular O_2 illustrates their effectiveness as an oxidant.

The situation is complex, probably far beyond what we can imagine, because for example, products of the reduction reaction e.g. polymerised products and adsorbed Mn^{2+}, inhibit further reduction [76] in “mixed batch reactors”. In soil, the same inhibitions may occur but the extent will depend on conditions such as activities of reactants, products and ambient electrolytes, and the physical access of the

Mn oxides and their reactivity. Although many organic compounds identified in soils have been shown to reduce Mn oxides, the forms of organic matter actually present in the soil solution have not been explored with respect to their ability to react with Mn oxides. However, with GCMS and HPLC one could easily investigate the forms in the soil solution, particularly with respect to their relative reducing ability and the products which are formed; the same changes could be investigated with root exudates.

Other organic molecules with reducing ability are produced by roots in solution cultures [159]. For example, Park et al. [110] isolated root exudates of sunflowers (*Helianthus annuus*) and found hydroquinone, vanillic acid, caffeic acid and other organic compounds capable of reducing Mn oxides. Most allelochemicals are largely phenolic and are oxidised by Mn oxides [64, 81] and so their effectiveness and persistence in soil may be determined by the status of the Mn oxides in soil; also many phytoalexins are phenolic compounds [106] and would probably behave in the same way. The volatile organic compounds (VOCs) produced by soils and their proclivity to react with Mn oxides have not been investigated. One hundred VOCs were derived from [28] soil and 12 litter samples from a wide range of ecosystems in the USA [63]. A study of their oxidation by Mn oxides at ambient temperatures would be interesting and may indicate whether or not VOCs contribute to the release of Mn^{2+} when soils are air-dried.

The reduction of Mn oxides can be brought about by microbes by indirect means, most commonly by the production of acid and reducing agents [36]. Under waterlogged conditions, where the pH usually rises, the Mn oxides are reduced by metabolic by-products from microbial metabolism and by their use as an alternative electron acceptor in microbial respiration. Much is known about the microbial reduction of both Fe and Mn in those environments where anaerobic respiration is active [73, 103].

The reduction of Co(III) has not been studied with respect to soil but presumably its chemical reduction is brought about by similar compounds and in similar circumstances to the reduction of Mn oxides, perhaps less easily.

12.4.2.1 Redox Potential

The redox potential of a soil is discussed often as if it is a significant property and that it represents a delicately poised equilibrium between the oxidised and reduced species present. Well it might be except that there are a few problems which make it difficult to have much faith in it, so much so that one cannot regard measured redox potentials as little better than ball park figures and that “They are useful to classify soils as oxic, suboxic, or anoxic, but little beyond that.” – Sposito [135]. Part of the problem is that molecular O_2 as discussed above is a feeble oxidant of both Mn^{2+} and organic reductants, and that some of the significant couples are of soluble and insoluble species e.g. $Mn^{2+}/\mathbf{MnO_x}$.

12.4.3 "Equilibrium"

$$\mathrm{Mn}^{2+} \underset{\text{Reduction}}{\overset{\text{Microbial oxidation}}{\rightleftarrows}} \mathbf{MnO_x}$$

The "equilibrium" between microbial oxidation and reduction in soils is best represented as above where the microbial oxidation of Mn^{2+} (forward reaction) is favoured by increasing pH whilst the reduction of $\mathbf{MnO_x}$ (back reaction) is favoured by decreasing pH. In a moist and aerobic soil under a certain set of circumstances, say field capacity and at a constant temperature, there is a balance between the rates of microbial oxidation and reduction by organic moieties; the reactions, as depicted earlier, take place simultaneously and somewhat independently of one another, particularly in space. The concentration of water-soluble plus exchangeable Mn^{2+} (WS+Exch Mn) remains constant and it is an average concentration of many independent microsites that contribute upon extraction. One cannot call it an equilibrium in a true chemical sense since the reactions are independent of each other particularly in space where reduction of Mn may be occurring in pores of all sizes including those which are too small to accommodate microbes including Mn-oxidising microbes. If either reaction is favoured over the other, the balance will be affected and the concentration of WS+Exch Mn will change appropriately.

The temporal variation in the concentration of WS+Exch Mn in the field arises from various causes [25, 133, 134], but primarily from changes in water potential and temperature insofar as they affect microbial activity [24]. Reduction is favoured by the addition of both acid and readily biodegradable organic matter and by waterlogging. Also, anything which inhibits microbial oxidation such as drying will favour reduction and the WS+Exch Mn will increase. Much less is known about what factors favour microbial oxidation other than it occurs most rapidly at near neutral pHs under constant conditions of moderate temperatures, although oxidation has been measured in acidic soils down to pHs of 4 and down to a temperature of 10 [133]. The complexity is high because several different species of microbes may be responsible, each of which has its own set of optimal conditions for oxidation with respect to factors such as pH, temperature and ambient O_2 supply.

Air-drying of paddy soils, both in the laboratory and in the field, has shown concomitant increases in WS + Exch forms of Co and Mn, whereas Cu was not affected greatly [77, 78]. Li et al. [68] also found that air-drying of soils increased the concentration of Co extracted by 0.05 M $\mathrm{CaCl_2}$ but air-drying did not affect the concentration of Co extracted by 0.02 M EDTA (pH 7). The apparent discrepancy can be explained by the fact that the $\mathrm{CaCl_2}$ extracted largely WS+Exch Co which increases on air-drying as a result of the reduction of easily reducible Mn oxides, whereas EDTA (pH 7) does not discriminate between Co associated with easily reducible microbial Mn oxides [18] and the WS+Exch Co in the air-dry soils and in the field moist soils.

Air-drying usually leads to increased concentrations of WS+Exch Mn(II) measured upon extraction. Logically, during desiccation the physical disruption of cells and release of contents is proceeding, but in the virtual absence of water and of volatile reactive compounds, there is no opportunity for the potential reactants to move and so physical separation prevents change. Upon extraction as soon as water is added to the soil the potential reactants can move and, aided by the mixing that occurs upon extraction, the Mn oxides are quickly attacked by what reactants are there, albeit in limited amounts. Since Ross et al. [121, 122] found, using x-ray absorption near edge structure spectroscopy (XANES spectroscopy), no difference between single scans of moist samples and their air-dried (3 weeks) counterparts then it would appear that the reduction takes place on re-wetting when the air-dry soil is extracted. Whether or not the technique is sensitive enough to detect the relatively small changes in Mn(II) concentrations on air-drying is uncertain, although Guest et al. [43] claim that the method gives a semi-quantitative measure.

Complete or partial sterilisation by steam, heat, drying, γ-irradiation, biocides, fumigants etc. cause an increase in WS+Exch Mn(II) because each of these treatments inhibit the microbial oxidation of Mn(II) while at the same time chemical reduction by organic matter continues at various rates determined by the conditions in the soil imposed by the treatment. For example, some fumigants not only inhibit the microbial oxidation of Mn(II) but also are reducing agents in their own right. Upon air-drying, as discussed above, drying inhibits the microbial oxidation of Mn(II) but reduction is favoured in the short time it takes for extraction.

12.5 Oxidation of Cobalt (II) to Cobalt (III)

Auto-oxidation of Co^{2+} does not occur readily, but observations suggest that some Mn oxides oxidise Co^{2+} to Co^{3+} [86]. McKenzie [90] observed that the colour of Mn oxides changed from brown to black after adsorption of Mn^{2+} and Co^{2+}, a change which can be interpreted as a change in oxidation state. Crowther et al. [28] confirmed by X-ray photoelectron spectroscopy that sorption of Co^{2+} by a synthetic birnessite was accompanied by the oxidation of the Co^{2+} to Co^{3+} by Mn(IV), possibly by way of the reaction:

$$2Co^{2+}{}_{(aq)} + 2MnO_{2(s)} + 3H_2O_{(l)} \rightarrow 2CoOOH_{(s)} + Mn_2O_{3(s)} + 4H^{+}{}_{(aq)}.$$

The oxidation occurred at pHs from 4 to 7 while at pHs of 8 and 10 $Co(OH)_2$ precipitated on the oxide surface.

Biogenic Mn oxides have been shown to oxidise Co(II) to Co(III) with incorporation of Co(III) into the lattice [102, 126]. In soils the Co associated with oxides of Mn is most likely trivalent so that both concomitant reduction of the Mn oxides and the Co(III) needs to occur before Co and Mn are in divalent forms which plants can use.

12.6 Nodular Forms of Manganese

Nodular forms of Mn that are found in soils have been studied with increasing vigour in recent years because they represent sinks for heavy metals and because now the combined use of synchroton-based analytical techniques offer a lot with respect to the study of Mn accumulations in soils with greater analytical and crystallographic resolution than in the past (e.g. [79]). As a result, much is now known about Fe–Mn nodules, their morphology, composition and mineralogy but little is known about their formation other than they form in soils under alternating periods of waterlogging and drying, reduction and oxidation respectively. The concentric rings in the cross-sectional view of so many Fe–Mn nodules represent periods of oxidation of Mn^{2+} and Fe^{2+} mobilised from insoluble oxides during the periods of waterlogging (e.g. [71, 109]).

It is difficult to devise a satisfactory theory which explains the formation of relict nodules. The only satisfactory dating of Mn oxides requires the use of ^{40}Ar–^{39}Ar ratios which in turn is based on the decay of naturally occurring ^{40} K to ^{40}Ar [27]. However, of the Mn oxides only cryptomelane has sufficiently high K concentrations and since it is not a common Mn oxide found in soils [91], the usefulness of this method of dating is restricted. Also, because many relict nodules have formed under conditions which existed in paleoenvironments [42] the uncertainty is high. However, assuming that contemporary Mn accumulations develop in the same way as the relict nodules then one would expect that the greatest degree of certainty about mechanisms and processes of formation could come from systematic investigation of the formation of Mn accumulations in paddy soils where cycles of wetting and drying have been regulated for centuries. These redoximorphic soils are no older than about 2,000 years old, their history and recent pedologic evolution are known, and much of the uncertainty surrounding dating should not arise.

Studies of the pedogenic evolution of the paddy soils coupled with the analytical techniques referred to above and other studies of the microbial populations inside Mn nodules and the surrounding soil [19, 20, 45, 176] provide an opportunity to advance the science of the genesis of nodular concretions. Because they are sinks for heavy metals, their formation represents perhaps a means by which remediation of soils polluted with heavy metals may be achieved.

The subject of the sorption and associations of trace metals by and with Mn oxides respectively is too large to review here (the topic with respect to microbial Mn oxides has been reviewed recently [99, 165]), and so only the association between Co and Mn oxides will be discussed. Tiller [144] observed the strong association between Co and Mn in krasnozems (ferrosols) formed on dolerite in Tasmania; in some profiles Mn and Co were found in pockets and veins of lithiophorite. Further investigations of manganiferous accumulations in a diverse array of Australian soils by Taylor and McKenzie [137] showed that about 80% of the total Co in the soils was associated with Mn oxides, primarily lithiophorite and birnessite. Similar investigations have found the association to be strong in most Fe–Mn nodules (e.g. [22]), some soils [35] and less obviously so in some others (e.g. [49, 68]). However, in a study of soil nodules McKenzie [88] found that although all high concentrations of Co were associated with moderate to high concentrations of Mn, there were many spots with high concentrations of Mn which had low concentrations of Co. The close association between the total Mn concentration in soils and Co uptake of applied Co by clover further confirmed the connection and the indicated the practical problem of fixation of recently applied Co [2, 89].

12.7 Availability of Manganese to Plants

In the field, both Mn deficiency and toxicity occur throughout the world [119, 127], but in a practical sense deficiency is easily dealt with by the use of tolerant species and varieties, foliar sprays and fertilisers [44]. Similarly, Mn toxicity is found worldwide on acidic soils, either naturally or induced, and is managed by the selection of tolerant species and varieties and by the application of lime; where episodes of infrequent waterlogging lead to Mn toxicity liming may not be sufficient to overcome the toxicity and some measures to improve drainage may be required.

Despite the apparent simplicity of the solutions to the practical problems of Mn deficiency and toxicity, there are issues of understanding which need to be resolved with respect to availability and some of these are dealt with below.

12.7.1 Factors Influencing Manganese Availability

A simplified representation of the basic transformations of Mn in soils and uptake by plant roots is given thus:

$$\underset{\text{Insoluble \& Reducible}}{\mathbf{MnO_x}} \quad \overset{\text{Reduction} \rightarrow}{\longleftarrow \text{ Microbial oxidation}} \quad \underset{\substack{\text{Water-soluble}\\ +\text{ exchangeable}}}{Mn^{2+}} \overset{\text{uptake}}{\dashrightarrow} \text{Roots}$$

The main soil factors which have been shown to influence the availability of Mn are WS+Exch Mn(II), reactive Mn oxides, structure and pH (Table 12.5). While the plant factors are less clear, it is well known that some plant species are better at deriving Mn from soils and some genotypes of the same species are better at deriving Mn from the same soils. The situation is made even more complex by the impact of environmental factors, particularly those that affect plant growth and microbial activity such as temperature and rainfall.

The uptake of Mn from soils by plants is dominated by the effect of pH on the solubility of Mn^{2+} in the soil solution and as a readily exchangeable cation. The forms utilised by plants depend strongly upon pH [155, 158]. At neutral to alkaline pHs where the concentrations of WS+Exch Mn are low and bear no relationship to availability, Mn uptake takes place by a mechanism called contact reduction [61, 162],

Table 12.5 Factors influencing the availability of Mn (and Co) to plants growing in soil

Soil	pH	Sorption of Mn^{2+} (and Co^{2+}) Oxidation of Mn^{2+} (and Co^{2+}) Reduction of $\mathbf{MnO_x}$ (and Co^{3+}) Microbial activity
	Reducibility of Mn oxides	Specific surface area Crystallinity Composition Hydration
	Structure	Contact Aeration
	Water potential	Aeration
Plant	Species	Variety
	Root growth and surface area	Length Thickness Total surface area
	Reducing capacity of roots	
Environmental	Climate	Rainfall: amount and distribution Temperature

where roots contact and reduce Mn oxides to Mn^{2+} under “the right set of circumstances” [162]; the Mn^{2+} thus formed then moves through the mucilage at the soil-root interface and is absorbed by the root. As the soil pH decreases, the concentration of WS+Exch Mn increases, and Mn uptake by contact reduction occurs but it is increasingly overtaken quantitatively by uptake by diffusion and convection (mass flow). At strongly acidic pHs, where Mn toxicity may occur, uptake by convection predominates. In the soils where uptake by convection and diffusion predominate measures of WS+Exch Mn such as 0.01 M $CaCl_2$ give reasonable estimates of availability.

When Jones and Leeper [54, 55] started to investigate the role of Mn oxides in plant nutrition they realised quickly that there were many different oxides of Mn, so that adding a Mn oxide to a Mn-deficient soil was not necessarily guaranteed to be successful. The Mn oxides prepared by wet way methods (e.g. δ-MnO_2 usually) were found to be the most effective sources of Mn because they are most reactive whereas dry-way preparations (e.g. β-MnO_2usually) were ineffective.

The optimal rates of Mn applied to deficient soil of neutral to alkaline pH, either broadcast or banded, range from 5 to 50 kg ha^{-1} [119]. Apart from Walter [169] there has been little interest in the development of fertiliser forms of Mn because of the rapid fixation/attenuation in soils of high pH, particularly calcareous soils. The fertiliser forms of Mn, which are usually soluble sources of Mn^{2+}, are quickly oxidised microbially to insoluble oxides and they lose their usefulness with time such that a new addition needs to be made with the next crop. For example, Brennan et al. [14] found that the residual value of previously applied Mn to two acidic sands in Western Australia was not as effective as current soil applications to prevent split seed in lupins, and that the effectiveness decreased with increasing time. In contrast, the residual value of Cu and Zn on similar soils may be 10 years or more [12, 13].

Attenuation of soluble Mn(II) applied to soil may simply be due to the conversion to an insoluble oxide of Mn and subsequent ageing processes. However, because reactive Mn oxides added to soil can cure Mn deficiency [54, 55] there must be processes in addition to microbial oxidation which contribute to the decrease in availability. The tendency of Mn to accumulate in spots [157] will decrease the surface area available to roots much more than if the oxides were evenly distributed throughout the soil. Although the presence of a hydrated biofilm surrounding a biogenic Mn oxide appeared not to interfere with the reductive dissolution of the oxide [149], dehydration and shrinkage of the biofilm, particularly if not readily reversible, may cause a decrease in the surface area available to reducing agents and hinder the reaction. Also, the shrinkage of the biofilm may withdraw the Mn oxide into pores that are physically inaccessible to root surfaces and thus decrease the opportunity for contact reduction. Repeated cycles of wetting up and dehydration are likely to lead to an increase in crystallinity and anhydrous character of the Mn oxides, which in turn lead to lower reactivity.

Apart from foliar sprays, fertiliser application and appropriate selection of Mn efficient species and genotypes, the severity of Mn deficiency can be overcome to some extent by the use of seeds with a high Mn content. For example, Longnecker et al. showed that barley with an increased Mn content in the seed can increase grain yield under conditions of extreme Mn deficiency [72].

12.7.2 Estimation of Plant Availability

The estimation of plant availability is not easy because of the numerous factors involved (Table 12.5). Nevertheless with an understanding of the factors involved and armed with appropriate soil and plant analyses, the experienced farmer or agronomist can manage Mn deficiency and toxicity with relative ease. The same also applies to Co deficiency.

12.7.2.1 Plant Analysis

Availability of an element in a soil to plants can only be measured properly by the total uptake of that element by the plant in the soil in question i.e. uptake = total yield × concentration. However, because the whole plant cannot be sampled for analysis (e.g. perennial plants), compromises are made and for the most part a particular plant tissue (e.g. youngest expanded leaf blade, petiole) at a certain stage of growth can be used as a fairly reliable indicator of the need or otherwise for Mn fertilisation, usually by foliar sprays and soil application [40, 119].

12.7.2.2 Routine Soil Analysis

Soil tests are really a very crude estimate of availability, albeit quick and easy [118]. This seemingly unsatisfactory situation arises because the availability of Mn is a function of the interaction between plants, roots in particular, and soils, such that the situation cannot be solved simply by soil analysis alone [158]. The inadequacy of soil tests on their own is well illustrated by the fact that some varieties show no deficiency symptoms on some soils, whereas on the same soil other varieties are deficient; also an abnormally high rainfall event may cause the onset of Mn toxicity in a crop. The soil factors which most influence Mn solubility in soils are pH, microbial activity, and the reducibility of Mn oxides, yet factors such as soil structure are known to affect availability [40, 113]. The routine sampling and testing of soils disregards the significance of structure and the localisation of Mn oxides in mesopores as discussed above. It should be noted here that any shortcomings of soil tests with respect to Mn will be equally relevant with respect to Co in lieu of their close association, chemistry and behaviour.

12.7.2.3 Sequential Fractionation Schemes

Sequential fractionation schemes have been used to chemically identify various forms of elements and their associations (e.g. [75, 146, 147]). However, there are difficulties that arise from the conflict between the different aims (e.g. chemical speciation vs. bioavailability) and the level of understanding, particularly of the forms and behaviour of Mn. Also, the schemes are criticised (e.g. [59, 84]) because they are indirect, resorption can occur with some extractants, and they can have limited specificity when compared with physical techniques such as microprobe analyses and X-ray absorption spectroscopy. Beckett [9] clearly indicated many problems associated with the choice of extractants, and how an extractant such as sodium pyrophosphate, because it acts as a complexing agent, a peptizing agent and a solvent, it solubilises soil organic matter which in turn acts as a reducing agent [97]. In spite of all these shortcomings and its lack of specificity, sodium pyrophosphate continues to be used.

Other issues that are commonly overlooked in both routine soil tests and fractionation schemes are: (i) extraction with a simple salt such as $CaCl_2$ causes desorption of H^+ which gives rise to a decrease in pH and may increase the concentration of WS+Exch Mn(II) because the pH decrease favours the reduction of readily reducible Mn oxides by organic matter; (ii) 0.05 M Na_2H_2EDTA at pH 4.6 will dissolve Mn oxides and as the pH increases less Mn is dissolved, but even at pH 7 dissolution still occurs [18]; (iii) H_2O_2 can reduce reactive Mn oxides in mildly acidic media (e.g. [60]); (iv) Na hypochlorite can dissolve reactive Mn oxides by oxidising Mn to permanganate [5, 60, 163]; (v) 0.5 M $CuSO_4$ at pH 3 [43] will dissolve soil active Mn oxides through reduction by soil organic matter, a reaction facilitated by the displacement of Mn^{2+} by Cu^{2+}; and (vi) sodium acetate at pH 5, as used by Tessier et al. [142] and many others, will displace H^+ from most soils, cause reduction of readily reducible Mn oxides, and thus release metals associated with the oxides, not just “carbonate bound”.

A continuous-flow sequential extraction scheme was used by Tongtavee et al. [151] to evaluate the chemical associations between Co and Mn, but unfortunately the first two extractants they used are 0.01 M $Ca(NO_3)_2$ and 0.11 M CH_3COOH, both of which would acidify the suspension and cause the reduction of active Mn oxides and the release of Mn and associated elements into solution. Otherwise the method shows promise to investigate relationships between elements.

12.8 Other Availability Issues

12.8.1 Vesicular Arbuscular Mycorrhizae

There is evidence which suggests that inoculation of sterilised soil with vesicular arbuscular mycorrhizae (VAM) may decrease the acquisition of Mn by plants [24], although the effect may only be observed in some soils, with some plant species and with some, but not all VAM [6, 10, 57, 107]. Because the VAM inoculum used may contain propagules other than spores, and may contain contaminating microbes capable of oxidising Mn(II), it is likely that oxidation occurs and alleviates Mn toxicity that may have arisen from the sterilisation procedure. The outcome is that the apparent success of VAM to stimulate plant growth in some experimental systems is not necessarily due to improved P nutrition, for example, and the possibility of Mn toxicity was not considered to have an impact on the growth of the plant species under consideration.

In much research into the effects of VAM on plant growth, every attempt is made to obtain an inoculum of spores free of contaminating microorganisms [148], but such stringent requirements may be superfluous since VAM have been found to contain endobacteria [11]. The species of endobacteria present represent a wide range including species from the genera *Bacillus, Burkholderia, and Pseudomonas*. All of these genera contain species capable of oxidising Mn(II), and Cahyani et al. [20] recently found *Burkholderia* species were the most common bacterial strains isolated from Mn nodules from paddy subsoils. It would seem that it is impossible to produce a reliable inoculum of a VAM free of other microbes.

12.8.2 Zinc-Induced Manganese Deficiency

Zinc-induced Mn deficiency has been observed in a number of situations where soils have become contaminated with Zn [30, 114, 152, 154]. When a strongly acidic sandy loam was limed and up to 400 mg kg^{-1} of Zn as $ZnSO_4$ was added, symptoms of Mn deficiency in oats were found in plants at pH 6.1 (1:2 H_2O) and with 100, 200 and 400 mg kg^{-1} of added Zn; no symptoms were observed in any plants at higher or lower pH or with less Zn than 100 mg kg^{-1} added [154, 160]. The mechanism of the interaction is not an obvious one but it deserves further investigation. Most cases are associated with former sewage farms where high concentrations of Zn exist and where the soils have been depleted of active Mn through leaching with high BOD water. If the soils are limed to overcome the potential toxicity and mobility of the heavy metals that have accumulated over the years, then Zn-induced Mn deficiency may arise.

12.8.3 Mundulla Yellows

A dieback disorder of *Eucalyptus* species and other native Australian plants called Mundulla yellows (MY) is found along limestone roads in the south-east of South Australia. Awareness of MY arose in the 1990s when it was believed to be caused by biotic agents, herbicide residues, global warming etc., but it was not long before these agents were discounted. The disorder is found in the same area where Samuel and Piper [123] investigated what was known locally as "road take-all", a disorder found in oats growing along limestone roads in the region and which proved to be Mn deficiency. Other trace element deficiencies occur in pine forests alongside roads in the area [46] and it would seem that MY is caused by multiple trace element (Cu, Fe, Mn and Zn) deficiencies caused by the addition of finely divided limestone dust to the roadsides and nearby paddocks [111].

12.9 Cobalt Availability, Deficiency, Contamination, Toxicity and Remediation

Because of the close association between Mn and Co and their decreasing solubility with increasing pH, one might be excused from thinking that the availability of Co closely follows that of Mn [35]. However, there are four scenarios where the low availability of Co in soils can arise: (i) inherited deficiency through low concentrations in the parent material such as on the pumice soils in New Zealand, and peats in Ireland [168]; (ii) acquired deficiency through losses as a result of pedological processes over the ages (e.g., granitic soils) and accelerated by hydromorphic influences [168]; (iii) derived deficiency through its strong association with Mn in well-drained soils with high Mn status [144]; and (iv) acquired deficiency through the application of lime to acidic soils covered by the former three situations. The availability of Co closely follows that of Mn in those soils which tend to be poorly drained [1] and are in the pedological process of becoming deficient, but where the Mn status of a soil is high then Co availability tends to be low. The Co/Mn ratios in soils (Table 12.1) tend to be less than parent rocks which suggests that Co is relatively more mobile than Mn and relies upon the retention of Mn for its own retention.

The mechanisms of Co uptake are most probably the same as described above for Mn, so that as the pHs of soils decrease from neutral pHs the total uptake increases strongly, and the proportion of Co uptake from contact reduction barely increases while the contributions from diffusion and convection increase.

12.9.1 Cobalt Availability and Deficiency

Cobalt deficiency refers to the scarcity of Co in soils in so far as it affects N fixation by rhizobia in legumes and the health of grazing ruminants (sheep and cattle), a situation which occurs when pasture concentrations fall below 0.08 mg kg^{-1} both in Scotland and New Zealand where most research has been carried out (e.g. [68, 69, 70, 92, 93, 129, 130]). Any Co applied to soil as $CoSO_4·7H_2O$ will initially dissolve and the Co^{2+} will distribute between the solution and solid phases including Mn oxides where it will be oxidised to Co^{3+} and retained within the oxide lattice [28]. If the Co associates with Mn oxides that are difficult to reduce then its availability will be very low whereas in association with an easily reducible Mn oxide its availability is virtually parallel to that of Mn. It would appear that once the total Mn concentration in soil exceeds a certain limit the usual application rate of 350 g of $CoSO_4·7H_2O$ ha^{-1} is inadequate because of immobilisation of the additional Co in Mn oxides; a limit of 1,000 mg kg^{-1} was proposed by Adams et al. [2] for some Tasmanian soils and Li et al. [70] came to the same conclusion based on an investigation of a wide range of soils from New Zealand.

The extractants which have been used to evaluate the availability of Co in soils have met with mixed results. In Australia where deficiency in ruminants may occur mostly in the southern states, soil tests are not carried out because those tested have proved unreliable [115]. On some occasions some extractants gave promising results but recently Li et al. [70] found that both 0.05 M $CaCl_2$ and 0.02 M Na_2H_2EDTA at pH 7 were poor predictors of Co availability to ryegrass in a glasshouse trial involving 18 grassland soils from New Zealand. Because 0.02 M Na_2H_2EDTA at pH 7 will extract Mn from reducible forms of Mn oxides [18] and therefore, Co, it is unreasonable to suggest that Co associated with soil organic matter is probably an important source of Co in soils. When Co^{2+} is added to soil it would first form predominantly readily exchangeable forms with both inorganic and organic colloids, then there would be a gradual transfer to the Mn oxides which would involve desorption from the colloids and sorption, and possible oxidation, by the Mn oxides. One would expect that if the association of added Co with Mn took place rapidly then it would be unlikely that organic forms would play a significant part whereas the latter may play a role if the transfer was relatively slow, but either case does not support the contention that Co was associated soil organic matter in soils either with or without added Co. Certainly in experimental soils containing high concentrations of Mn, either naturally or added, the sudden decrease in Co uptake suggests a rapid association with Mn [2, 89].

Since Co^{2+} is the form taken up by plants, any extractant needs to mobilise WS+Exch forms as with Mn, and thus would probably have some success in soils of low pH. At higher pH, plants can rely less on the WS+Exch Co in that the concentrations are less and they must derive Co from the Mn oxides with which the Co is associated, most probably as Co^{3+}. For success at near neutral soil pHs, any extractant must reduce reactive Mn oxides and the Co^{3+} associated with them, and a mild reducing agent like quinol may be suitable. The limited success of both $CaCl_2$ and acetic acid is due to the acidity associated with their action, desorption of exchangeable acidity and acidity *per se* respectively, which combined with the mild reducing property of soil organic matter releases not only exchangeable forms but also readily reducible forms of Co and Mn. The variable reducing powers of organic matter between soils contributes to inconsistent results.

12.9.2 Cobalt Contamination and Toxicity

The occurrence of Co contamination of soils is rare, while Co toxicity is even more so except in highly contrived circumstances. Where contamination does occur it most probably does so by the addition of either an oxide, or a hydrous oxide or a sulphide of Co or an arsenide. These forms have not been used in contamination experiments, but if they had been used then one would expect that no immediate effect is likely. For example, any oxide of Co may persist for a considerable time and be unlikely to dissolve rapidly enough to cause toxicity. At the same time, attenuation of the Co (see below) is likely to be taking place, so that well-drained soils may be able to cope with high rates of addition of these forms of Co, particularly in the presence of reactive Mn oxides and accompanying applications of lime. Where smelting of sulphidic ores containing Co causes acidification of surrounding soils, such as near Sudbury in Canada [47], plants etc. will suffer immediately and greatly from the acidity *per se* as well as toxicity from the other metals present in the ore.

In experiments on Co toxicity the main sources of Co used were soluble salts such as $CoSO_4$. The same salts are used in fertiliser applications to pastures to cure Co deficiency in grazing ruminants where rates of the order of about 5 kg ha^{-1} are used and are never likely to have toxic effects. In many experiments investigating Co toxicity, rates of addition, intended to mimic contamination of soils near industrial sources, between 50 and 400 mg kg^{-1} Co as Co nitrate were used [117], many times more than the rates used in Co deficient situations. Similarly in more recent work even higher rates of application of soluble salts of Co (160–2,400 mg kg^{-1}) have been added and assays for Co toxicity carried out after only 7 days equilibration [67, 96]; such experiments, even though they may give some idea of soil solution concentrations that are toxic to plants in the short term, must be regarded as unrealistic. Also, in similar, but not quite so unrealistic experiments with the same soils, concentrations of up to 3,281 mg Co kg^{-1} were used and in contrast the soils were allowed to equilibrate for up to 1 year [171, 172]. It is likely that the addition of Co^{2+} salts at such high rates would reduce Mn oxides, inhibit the microbial oxidation of Mn^{2+}, and decrease the soil pH. Such changes and the impact on the Mn status are relevant where such levels of contamination with soluble forms of Co^{2+} occur, but as pointed out above Co contamination is rare and when it occurs it is usually with insoluble compounds.

12.9.3 Cobalt Remediation and Attenuation

After trace metals such as Co, Cu, Ni and Zn are added to soils in soluble forms they gradually lose their availability to plants through reactions with soil constituents giving rise to forms of lower solubility and availability. Such attenuation is desirable when considering a potentially toxic metal such as Cd, but clearly undesirable with respect to trace metals added as fertiliser.

In the case of Co, Barrow [8] found that, along with Ni and Zn, it became less soluble more quickly than Cd, and he attributed the observed decreases in solubility to micropore diffusion into various soil constituents. Probably, with respect to Co the most effective treatment of polluted soils is to increase the soil pH [172] and to increase the Mn concentration. Initially the decrease in availability is due to stronger and increasing association with organic matter, layer silicates as interlayer sorption as $CoOH^+$, and with Mn oxides. With time, the lattice incorporation of Co(II) into Mn oxides as they form and its oxidation to Co(III), the attenuation proceeds and effectively decreases the availability of the applied Co to plants, although Bakkaus et al. [7] appear somewhat doubtful about the role of Mn oxides.

If phytoremediation by some hyperaccumulator is to be effective then it would be best to maintain a high state of availability by using acidifying N fertilisers; but once the Co concentration had been decreased to an acceptable one then, if the acidification had occurred, liming would probably be necessary.

The failure of a “very finely ground crystalline reagent-grade MnO_2” up to concentrations of 2,000 mg kg^{-1} of MnO_2 to have any effect on the uptake of Co from two soils contaminated with 400 mg kg^{-1} [117], is almost certainly due to the likelihood that the reagent grade of Mn oxide that was used was pyrolusite with a very low SSA and very high degree of crystallinity; most reagent grade Mn oxides are pyrolusite which are notoriously unreactive. The addition of the same amount of Mn as $MnSO_4$ would probably have been much more effective since the microbial oxidation of Mn(II), and the production of an amorphous highly reactive Mn oxide would provide an active sink for the fixation of Co. If the concentration of added Co was high enough to inhibit the microbial oxidation of Mn, the addition of an active Mn oxide such as birnessite may have had an effect, but even then it might be temporary since the reduction reaction would prevail; ultimately the Mn-oxidising microbes might recover.

12.10 Role of Manganese Oxides in Soil Health

Waksman [167] drew attention to what was known as “soil sickness”, which at the time was a term used for every ailment of soil-grown plants which could not be explained by conventional wisdom at the time. “Organic complexes” were believed to be involved and in more modern times allelochemicals and similar entities have been implicated. As indicated earlier, Mn oxides are capable of oxidising alleged allelopathic compounds and so active Mn oxides in soils may be more significant than is commonly appreciated.

The remediation of polluted soils has been investigated extensively, but it would seem that what happens in the laboratory and the glasshouse does not necessarily happen in the field and that the balance between successes and failures in the field may be in favour of the latter [94]. With respect to the use of Mn oxides, they are added usually either to oxidise organic pollutants or to sorb toxic metals. The success of the former relies not only on destruction of the pollutant, but also the regeneration of the Mn oxides by microbial oxidation, whilst the success of the latter requires that the oxide retains its sorption activity in the initial sorption phase and that subsequently the oxides lose their reducibility such that the metals are locked away in an unreactive phase. The failure of pure reactive oxides to achieve successful remediation, as expected from laboratory experiments with pure oxides, may occur through the adsorption of organic matter, phosphate, silica or become saturated with metals [84]. Such loss of desired activity may be more likely for Fe oxides than for Mn oxides although sorption of metals on Mn oxides can decrease their reducibility and polymerised products from the oxidation of catechol adsorbed on the surface of a Mn oxide may inhibit further oxidation [76]. The loss of activity via reduction is unlikely to occur for Fe oxides in well-drained situations whereas the Mn oxides may be quickly reduced and the Mn quickly involved in the Mn cycle of oxidation and reduction.

12.10.1 MnO_x as an Oxidant

Reference has already been made to the oxidation by reactive Mn of naturally occurring phytotoxic organic compounds in soil. There are other oxidation reactions that may have some importance: (i) sorption of atmospheric NO_2 by soil and its oxidation to NO_3^- [3]; (ii) sorption of atmospheric SO_2 and its oxidation to SO_4^- [156]; (iii) oxidation of xenobiotic organic compounds [173] such as aromatic amines where Li et al. [66] have shown that Mn oxides oxidise polyaromatic amines (e.g. a-naphthylamine) with concomitant polymerisation such that both the mobility and bioavailability are decreased; (iv) oxidation of oestrogens in water at acidic pHs by synthetic δ-MnO_2 [175] may occur in soils receiving secondary sewage effluent; and (v) oxidation of Cr(III) and As(III).

The ability of soils to both oxidise Cr(III) and reduce Cr(VI) [48, 58] may appear contradictory because reactive Mn oxides and reductants good enough to reduce Cr(VI) probably could not co-exist in soils. Much of the research investigating the oxidation of Cr(III) has been carried out in dilute suspensions of soil or Mn oxides in water to which acidic solutions of Cr(III) are added. If there was preferential adsorption of Cr^{3+} onto the surface of Mn oxides then the test may be useful. However, since hydrolysis and sorption of Cr^{3+} onto any surface available are most likely to be rapid, comparable to Al^{3+}, the Cr^{3+} may not stay in solution long enough to be effective. Thus, the oxidation of Cr^{3+} in these tests is as much to do with the hydrolysis and sorption of Cr^{3+} as the reducibility of the Mn oxides.

Further, the standard net Cr(III) oxidation test as a measure of the activity of Mn oxides is an unnecessary and complicated diversion because of the uncertain fate of Cr^{3+}, and particularly since simple reductants like quinol are available and are chemically similar to those reductants already present in soil. For example, the use of Cr(III) as an alternative reductant to quinol, makes interpretation of results unnecessarily complicated [104, 105] and add little to the understanding of the behaviour of Mn in soils.

Similarly, experiments where Fe–Mn nodules were ground and the resulting powder's ability to oxidise As(III) to As(V) determined [21], may provide evidence of just that, but have little relevance with respect to the role that such nodules play in the behaviour of As in soils.

12.10.2 Sorption and Attenuation

The literature is replete with evidence that Mn oxides have exceptional ability when it comes to the sorption of trace metals. Much of this evidence, is based on sorption studies in dilute suspensions of Mn oxides, synthetic and natural, which nevertheless shows that enrichment of many elements occurs in nodular and concretionary forms of Mn oxides. For example, Palumbo et al. [109] found that the nodules from two alfisols are significantly enriched in most trace metals relative to the host soil, with Mn, Co, Ce, Pb, Ba, Cd, and Ni more enriched than Fe, V, La, Cu, S, and Zn. The enrichment of Cd was surprisingly high in this case and it is possible that its sorption behaviour has been overlooked since the sorption of Cd on biogenic Mn oxides exhibited comparable sorption when compared with the sorption of other heavy metals [34, 95].

The likely steps in the attenuation of Co and other metals are (i) co-precipitation as the oxide forms, (ii) structural re-organisation during recrystallisation of the oxide, and then (ii) micropore diffusion. The process is favoured by increasing pH and by continued integrity of the oxide. The addition of a synthetic Mn oxide to remediate a Co contaminated soil will bypass the first step but nevertheless it may rapidly “fix” Co [89]. However, because biogenic Mn oxides have been shown to sorb two to three times as much Ni^{2+} and Zn^{2+} as synthetic Mn oxides [170], it may be more effective to add soluble Mn(II) to soil, allow microbial oxidation, and presumably co-precipitation, to proceed. If an unreactive (but stable) oxide such as pyrolusite is added to soil then the only way that it can bring about attenuation is by micropore diffusion and probably only to a limited extent.

However, as shown by McBride and Martinez [85], it is not as simple as just adding an oxide and some thought has to be given to the potential reversibility of the sorption process, the persistence of the oxide in both the short and long term, and how to overcome annealing of the oxide surface brought about by the sorption of polymeric organic compounds, and the processes involved in the aging process and their impact on the reactivity of the oxides [166].

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Chapter 13
Copper

Koen Oorts

Abstract Background copper (Cu) concentrations in soil depend on geology and typically vary between 2 and 50 mg Cu kg^{-1}. The widespread use of Cu has resulted in significant anthropogenic inputs to topsoils through atmospheric deposition and agricultural practices (fertilisers, pesticides, sewage sludge etc.). Copper mainly occurs in its divalent state (Cu^{2+}) and has high affinity for binding to organic matter. Sorption processes control the solubility of Cu under most environmental conditions, but Cu precipitates can form in alkaline soils. The solid-liquid partitioning of Cu in soil is largely controlled by the soil pH and organic matter content, with higher solubility at low pH and low organic matter content. Except for acidic soils, most (>90%) of the dissolved Cu in soil is complexed with dissolved organic matter. Copper is an important essential element for all living organisms and deficiency in plants and ruminants occur in soils with low available Cu. Copper concentrations in plant shoots typically range between 4 and 15 mg Cu kg^{-1} dry matter (DM) and are well regulated over a wide soil Cu concentration range. Elevated soil Cu concentrations cause toxic effects in all terrestrial organisms (plants, invertebrates and micro-organisms). The toxicity of Cu largely depends on soil properties, which control the bioavailability of Cu in soil through their effect on precipitation, sorption and complexation processes. Predicted no effect concentrations (PNECs), protecting 95% of all species or microbial processes, vary between approximately 10 and 200 mg Cu kg^{-1} soil and increase with increasing cation exchange capacity, clay and organic matter content.

Keywords Copper • Adsorption • Bioavailability • Ageing • Deficiency • Toxicity • Critical concentrations

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13.1 Introduction

Copper, with atomic number 29, is the first element of group Ib of the periodic table of elements. It ranks 26th in abundance in the lithosphere. The average abundance of Cu in the earth's crust is 60 mg Cu kg^{-1} [42] and concentrations in soil typically vary between 2 and 50 mg kg^{-1}. Copper was known to some of the oldest civilizations, and has a history of use that is at least 10,000 years old. The name 'copper' refers to the island of Cyprus, where Cu was principally mined in the Roman era. The first signs of Cu smelting, i.e. the refining of Cu from simple Cu compounds such as malachite or azurite, date back to 5000 before Christ (BC). Copper smelting appears to have been developed independently in several parts of the world: in the Balkans by 5500 BC, in China before 2800 BC, in the Andes around 2000 BC, in Central America around 600 BC, and in West Africa around 900 BC. Alloying of Cu with zinc or tin to make brass or bronze was practiced soon after the discovery of Cu itself. The use of bronze became so widespread in Europe approximately from 2500 BC to 600 BC that it has been named the Bronze Age.

Although Cu has been in use at least 10,000 years, more than 95% of all Cu ever mined and smelted has been extracted since 1900. Measured by weight, Cu is the third most important metal used by man. The total global demand for Cu in 2007 was approximately 24 Mt [27]. About 35% of all Cu used by industry originates from recycled Cu. The world production of Cu reached more than 15 Mt $year^{-1}$ in 2008. Copper is mainly used in electrical applications (65%), and construction (25%). Other uses are transport (7%) and coins, sculptures, musical instruments and cookware [27]. Various estimates of existing Cu reserves available for mining vary from 25 years to 60 years. In 2005, Chile was the top mine producer of Cu with at least one-third world share followed by the USA, Indonesia and Peru. The long history and widespread use of Cu has resulted in significant anthropogenic emissions, which have caused increased environmental Cu concentrations [36]. Local Cu concentrations can be far above natural background values because of agricultural practices (e.g., sludge application, Cu fungicides) and industrial activities (e.g., mining).

Copper is an essential trace element that is vital to the health of all living organisms (humans, plants, animals, and micro-organisms). It is found in a variety of enzymes and proteins, including the cytochrome C oxidase and certain superoxide dismutases. Soils with low bioavailable Cu can result in losses in crop yield and deficiency symptoms in livestock, especially in intensive farming systems.The recommended daily intake of Cu for humans is 1–2 mg Cu day^{-1} [96]. It has been assumed that most diets satisfy this requirement because of the ubiquitous presence of Cu in most foodstuffs and therefore Cu deficiency in humans is rare.

Elevated soil Cu concentrations can cause toxic effects on soil organisms (plants, invertebrates, micro-organisms) and can affect soil ecosystem functioning. Copper toxicity to terrestrial organisms strongly depends on its bioavailability in soil and the sensitivity of the organisms. Secondary poisoning of Cu though the food chain to vertebrates and humans is considered of low risk due to the strong regulation of internal concentrations of this essential element in plants and soil-dwelling invertebrates.

13.2 Geochemical Occurrence of Copper

The average natural abundance of Cu in the earth's crust is 60 mg kg^{-1} (Table 13.1). The Cu abundance in rock material is highly variable. Basaltic igneous rocks have a larger average Cu concentration (90 mg Cu kg^{-1}) than granitic rocks (15 mg Cu kg^{-1}). Sedimentary rocks, formed by weathering of igneous rocks, mainly reflect the Cu concentrations of the igneous rocks. Clays and shales have typical Cu concentrations ranging between 20 and 200 mg Cu kg^{-1}, whereas sand- or limestone generally contain between 1 and 20 mg Cu kg^{-1} g (see also Sect. 2.3.1).

Copper is one of the few metals to occur naturally as an un-compounded mineral (i.e., native copper). Minerals such as sulphides (chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), covelite (CuS), chalcocite (Cu_2S)), carbonates (azurite ($Cu_3(CO_3)_2(OH)_2$) and malachite ($Cu_2CO_3(OH)_2$)) and the oxide cuprite (Cu_2O) are other sources of Cu. Most Cu ore is mined or extracted as Cu sulphides from large open pit mines in porphyry Cu deposits that contain 0.4–1.0% Cu. Large Cu ore deposits are found in the U.S., Chile, Zambia, Zaire, Peru, and Canada.

Typical background Cu concentrations in soils vary between 2 and 50 mg Cu kg^{-1} dry weight, but natural Cu concentrations above 100 mg Cu kg^{-1}can also be found in some soils (Table 13.1). The Cu content in soil shows a positive correlation with Fe content, reflecting the relative concentration in intermediate to mafic igneous rocks compared to felsic rocks (granite). The amount of Cu measured in a soil

Table 13.1 Copper background concentrations in parent materials and soils

	Cu (mg kg^{-1})			Reference
	Range	Average	Median	
Earths crust		60		[42]
Igneous rocks				[56]
Basic igneous rocks (e.g. basalt, gabbro)	30–160			
Acid igneous rocks (e.g. granite, rhyolite)	4–30			
Sedimentary rocks				[56]
Shales and clays	18–120			
Black shales	20–200			
Soils				
USA, agricultural soils	<0.6–495	29.6	18.5	[35]
China			23	[14]
Europe, natural topsoil (XRF)	0.8–256	17.3	13.0	[77]
Europe, natural topsoil (AR)	1.0–239	16.4	12.0	[77]
Europe, natural subsoil (XRF)	0.9–125	17.2	13.9	[77]
Europe, natural subsoil (AR)	<1.0–118	16.5	13.0	[77]

strongly depends on the extraction procedure. Soil Cu concentrations reported in this chapter are expressed as mg Cu kg^{-1} dry soil and are generally "near-total" concentrations based on *aqua regia* or comparable concentrated acid destructions, followed by Cu analysis by inductively coupled plasma spectrometry (ICP) or atomic absorption spectrometry (AAS). Total concentrations determined by HF extraction or X-ray fluorescence (XRF) additionally include a Cu fraction built into the crystal structure of the soil minerals. Differences in soil Cu concentrations between aqua regia destructions and real total concentrations are however generally limited ($<$10%, Table 13.1) and most data from national or international monitoring programs report Cu-concentrations obtained after destruction with *aqua regia* (See also Sect. 4.5.2).

13.3 Origin of Copper in Soils

Because of historical and current anthropogenic inputs from diffuse sources, the direct measurement of real natural background concentrations for Cu (i.e. the natural Cu concentration in the environment that reflects the situation before any human activity disturbed the natural equilibrium) is not feasible in most parts of the world [23, 73]. For most soils, the Cu concentration measured is the sum of the natural Cu background concentration and diffuse anthropogenic inputs in the past or present and therefore the term ambient background is used. These anthropogenic inputs differ with land-use and the vicinity of point sources (e.g., smelters).

Average ambient background Cu concentrations in European soils away from point sources vary from 11.4 mg Cu kg^{-1} for forest soils (low anthropogenic pressure) to 15.4 and 17.0 mg Cu kg^{-1} for agricultural and grassland soils, respectively [26]. These differences in soil Cu concentrations between land uses can be attributed to both differences in soil properties and differences in Cu inputs. In the past, loamy and clayey soils were preferred over sandy soils for agricultural purposes due to their mineral composition. Consequently, many (forest) soils that were not brought into cultivation have a rather sandy texture, connected with lower Cu levels than clayey or loamy soils (see Sect. 13.3.1). Secondly, the Cu input and output also depends on the soil use. The increased Cu concentration in agricultural soils compared to forest soils may be caused by increased Cu input through the use of fertilisers and sewage sludge as well as the use of biocides and pesticides (see Sect. 13.3.3). A part of the Cu present will be removed from the soil through uptake by crops and harvest. This is less of the case for grassland soils where there is an input related to cattle manure but only a limited output (grazing), which may explain the higher Cu concentration compared to the other soil uses.

13.3.1 Soil Parent Material

The most important natural source of Cu is the geological parent material. The spatial distribution of Cu in soil is mainly related to regional and local geology.

Table 13.2 Copper concentrations in soils from different texture classes

	Cu (mg kg^{-1})	
Texture class	England and Wales (median) [99]	USA (geometric mean) [35]
Sandy	7.4	6.0
Coarse loamy	15	10.3–10.8
Coarse silty	19	18.1
Fine silty	19	28.7
Fine loamy	19	18.6–22.7
Clayey	23	33.6–37.6
Peaty	15	75.8–97.9

Table 13.3 Geometric mean total Cu concentrations in various soil orders in USA and China

	Cu (mg kg^{-1})	
Soil order	USA [35]	China [14]
Ultisol	6.2	17.8
Alfisol	10.9	15.1
Spodosol	48.3	No data
Mollisol	19.1	10.0
Vertisol	48.5	19.6
Aridisol	25.0	21.7
Inceptisol	28.4	21.8
Entisol	21.1	22.2
Histosol	183.2	No data
Oxisol	No data	10.9

The background Cu concentration in soil is correlated with texture and organic matter content. Soils containing high amounts of clay minerals and organic matter generally have higher natural Cu background concentrations (Table 13.2). Geometric mean Cu concentrations in mineral U.S. surface soils vary between 6.0 and 37.6 mg Cu kg^{-1}, while organic horizons have mean Cu concentrations up to 97.9 mg Cu kg^{-1} [35]. The effect of soil parent material and texture also reflects in different Cu concentrations across major soil types (Table 13.3). Soil types characterised by high clay content (e.g. Vertisols) or high organic matter contents (e.g. Histosols and Spodosols) have generally the highest Cu concentrations.

13.3.2 Atmospheric Deposition

Except for agricultural land, atmospheric deposition is responsible for the main input of Cu in soil. Country-specific Cu deposition rates vary from 5 to 100 g Cu ha^{-1} year^{-1} for European countries, with a European average of 34 g Cu ha^{-1} year^{-1} [57]. Copper generally exists within the atmosphere as a component of particulate matter. Copper emissions to air and subsequent atmospheric deposition on land are the results of both natural and anthropogenic processes. Copper can be released into the environment from natural sources through a variety of processes including

Table 13.4 Global natural and anthropogenic emissions (reference year 1983) of Cu to the atmosphere (10^3 t Cu year^{-1})

	Median	Range
Natural sources [59]		
Wind-blown dust	8	0.9–15
Volcanoes	9.4	0.9–18
Sea salt	3.6	0.23–6.9
Wild forest fires	3.8	0.1–7.5
Continental vegetation	0.32	0.01–0.62
Marine vegetation	0.39	0.02–0.75
Pollen & Spores	2.6	0.1–5
Total natural sources	**27.7**	**2.3–54**
Anthropogenic sources [61]		
Coal combustion	5.2	2.3–8.1
Oil combustion	2.0	0.5–3.4
Non-ferrous metal production		
Primary production	23.7	15.1–32.4
Secondary production	0.11	0.06–0.17
Pig iron and steel production	1.49	0.14–2.84
Municipal waste incineration	1.47	0.98–1.96
Sewage sludge incineration	0.11	0.03–0.18
Wood combustion	0.9	0.6–1.2
P-fertilisers	0.41	0.14–0.69
Total anthropogenic sources	**35.4**	**19.9–50.9**

volcanic eruption, forest and bush fires and wind-blown suspension of dust and sea salt spray. An evaluation of the global atmospheric natural emissions of metals, including Cu, identified volcanoes and wind-blown soil particles as the major natural sources of Cu emissions [59] (Table 13.4). Estimated anthropogenic Cu emissions to the atmosphere for 1983 are within the same order as the total natural emissions (Table 13.4). The major anthropogenic emissions of Cu to the atmosphere are from non-ferrous metal production and fuel combustion (industrial and domestic heating, power production). During the last decades, Cu emissions due to metal production significantly decreased, resulting in smaller global Cu emission to the atmosphere [26, 60] (See also Sect. 2.3.2.1.1).

13.3.3 Agricultural Materials and Sewage Sludge

Agricultural materials are responsible for the majority of Cu inputs in agricultural soils. Both the Cu content and application rate vary largely across different agricultural materials. The main sources of Cu input to agricultural soils are manure, sewage sludge, mineral fertilisers, and pesticides (Table 13.5). Copper occurs in manure through the animals' feed, like roughage, concentrate and especially Cu-containing additives [26]. Copper is especially added to growing pig diets, explaining the large contribution of pig manure to overall Cu input from manure. Across the inorganic fertilisers, phosphate fertilisers generally show the highest Cu concentrations and

Table 13.5 Copper inputs to agricultural soils in England and Wales in 2000 (data from [57])

Source	Quantity applied 10^3 t DM year^{-1})	Cu concentration (mg Cu kg^{-1})	Cu addition rate (g ha^{-1} year^{-1})	Total annual Cu input in 2000 (t)
Atmospheric deposition	NA	NA	57	631
Livestock manures	13.48	16–470[a]	168–1679	643
Cattle	10.19	16–45	168–321	215
Pigs	1.64	168–470	1488–1679	360
Poultry	1.65	32–90	175–422	70
Sewage sludge	0.44	565[a]	3210	271
Inorganic fertilisers	4.91	2–94	0.4–12	53
Agrochemicals	ND	ND	ND	8
Irrigation water	ND	ND	16	2
Composts	0.06	25	ND	<1

NA not applicable
ND no data
[a] based on application rate equivalent to 250 kg N ha^{-1} year^{-1}

they are another important source of Cu in soils. Copper is an essential element for plants and in cases of deficiency, Cu may also be applied directly to crops and soils, e.g., with a foliar spray.

Copper-based fungicides (such as the Bordeaux mixture, $CuSO_4$ + $Ca(OH)_2$, $Cu(OH)_2$, Cu_2O, etc.) have been intensively used since the end of the 19th century to control vine fungal diseases, such as downy mildew caused by *Plasmopara viticola*. Besides vineyards, Cu-based fungicides have also been extensively used in hop fields, coffee, apple and avocado orchards [24] and during the cultivation of several vegetables (e.g., tomatoes, potatoes). Copper-based fungicides are even indispensible for organic vine and fruit cultivation. Typical application rates vary from 2 to 4 kg Cu ha^{-1} year^{-1} and their long-term application and subsequent wash-off from the treated plants have resulted in elevated Cu concentrations in some vineyard soils [38, 55, 91].

Sewage sludge is often used as a soil conditioner because of its nutrient and organic matter content. However, it may be also an important source of metals and other contaminants. The quality of sewage sludge is largely determined by the composition of the wastewater (industrial or domestic) and the removal efficiency in the wastewater treatment plant. The removal of Cu from raw sewage in sewage treatment plants is usually very effective, with removal rates varying between 80 and >95% [26]. Total Cu concentrations in sewage sludge of various European countries vary between 190 and 641 mg Cu kg^{-1} dry matter [26].

13.3.4 Traffic and Other Sources

Traffic is responsible for some important local Cu inputs in soil. This is both due to rail transport (corrosion of overhead wires) and road transport (brake and tyre wear) [26].

Road transport can result in elevated Cu concentrations in the immediate vicinity of roads [20, 29, 49]. These elevated Cu concentrations can be up to $>$100 mg Cu kg^{-1}, but Cu concentrations decrease rapidly with both distance and depth and fall back to ambient background levels within 30–50 m distance from the roads. Copper is also used in wood preservation products (e.g. $CuSO_4$, chromated copper arsenate CCA), resulting in additional local elevated soil Cu concentrations [31, 52]. Run-off from external building applications (e.g., Cu roofs) is another, minor, potential local source of Cu inputs into soil.

13.4 Chemical Behaviour of Copper in Soils

13.4.1 General Soil Chemical Reactions of Copper

Copper is a transition metal and thus has more than one oxidation state. The principal forms are cuprous (Cu^{1+}) and cupric (Cu^{2+}). The trivalent form (Cu^{3+}) occurs, but is relatively unimportant in physical and biological systems. Cuprous Cu is unstable in aqueous media and soluble Cu^{1+} compounds form Cu^{2+} ions or compounds and/or Cu(s) as a precipitate. However, monovalent Cu cations are only susceptible to such transformation when they are not chemically bound in insoluble compounds or stabilised in complexed forms.

When Cu^{2+} is introduced into the soil, the cupric ion typically binds to inorganic and organic ligands. In the soil pore water Cu^{2+} binds to dissolved organic matter (e.g. humic or fulvic acids). The Cu^{2+} ion forms stable complexes with $–NH_2$, –SH, and, to a lesser extent, –OH groups in these organic acids. Cupric ions will also bind with varying affinities to inorganic and organic components in soils. The general order of Cu adsorption maxima for soil constituents is: Mn oxides $>$ organic matter $>$ Fe oxides $>$ clay minerals. However, in general, soil organic matter dominates specific Cu adsorption in soil and is mainly responsible for retaining adsorbed Cu [51]. The binding affinity of Cu^{2+} with inorganic and organic matter is dependent on pH, the oxidation-reduction potential in the local environment, and the presence of competing ions. Most of the dissolved Cu in soils is complexed with dissolved organic matter [1]. The proportion of free Cu^{2+} in solution generally decreases with increasing soil pH (Fig. 13.1). Between 73% and 99.96% of the total dissolved Cu in pore water of 11 European soils (pH 3.4–6.8) spiked with $CuCl_2$ up to 3,700 mg Cu kg^{-1} was complexed [70]. In a study of Cu speciation in soil extracts (0.01 M $CaCl_2$) from 66 field soils with varying levels of contamination, Sauvé et al. observed that for most soils more than 98% of the soluble Cu was bound to organic ligands [78]. Both the quantity and quality (aromaticity) of dissolved organic matter control the mobility of Cu in soil [1].

Under most soil conditions, precipitation of Cu will be limited and sorption processes will control Cu concentrations in soil solution [13]. However, in the absence of ligands other than OH^- and depending on the Cu concentration, the solubility of Cu above pH 7–8 can be very low, due to the precipitation of

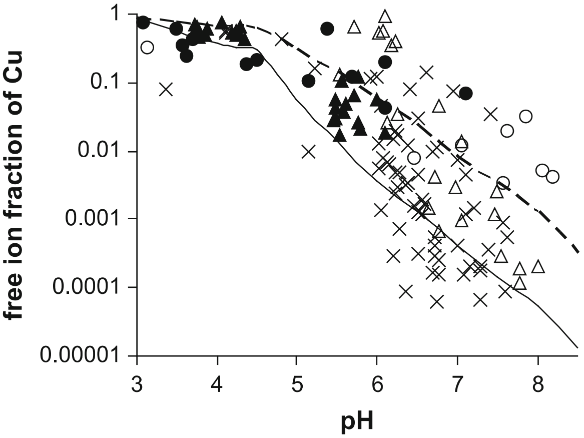

Fig. 13.1 Free-ion fractions of metals in soil solution or in a 10 mM $Ca(NO_3)_2$ extract measured with Donnan dialysis or ion selective electrode. The lines show the free-ion fractions predicted with WHAM6 for a generic composition of solution (50 mg L^{-1} dissolved organic matter, 2 mM $Ca(NO_3)_2$), for either 'low' (5×10^{-7} M Cu, *solid line*) or 'high' (5×10^{-6} M Cu, *dotted line*) Cu concentration (From Degryse et al. [19])

amorphous $Cu(OH)_2$ or tenorite (CuO). Moreover, in the presence of abundant carbonate, relatively insoluble Cu^{2+} carbonate minerals, such as malachite ($Cu_2(CO_3)(OH)_2$) and azurite ($Cu_3(CO_3)_2(OH)_2$) can precipitate. Copper is highly insoluble in reduced environments, where it precipitates as metal or as very stable sulphides. Sulphide formation indeed appeared dominant in determining the mobility of Cu in flooded soils [21, 94].

13.4.2 Solid-Liquid Partitioning

The solid-liquid partitioning of metals is a critical parameter for assessing their mobility and availability in soils. Transport of metals to deeper soil horizons and leaching to groundwater is related to the dissolved metal concentrations and the amount of metal on the solid phase buffering the metal in solution. The free metal ion is often considered to be the major determinant of bioavailability and its concentration largely depends on the total metal pool in soil, the solid-liquid partitioning and the speciation in solution. The partitioning of metals in soil is usually quantified by a distribution coefficient (K_d), i.e., the ratio of metal concentration on the solid phase (mg kg^{-1}) and in the solution phase (mg L^{-1}). There is plenty of information in the literature on the solid-liquid partitioning of Cu in soils. A sound comparison of K_d data from literature is however often complicated by methodological differences among studies. The methods used to characterise the solid and liquid phases both determine the metal pools (total, labile, free ion concentration, etc.) analysed and affect the solid-liquid distribution by their effect on the composition of the liquid phase (pH, ionic strength, concentration dissolved organic matter), which can influence competition for sorption sites and potential for complexation [19, 79]. K_d values further depend on total metal concentrations as sorption sites become saturated and K_d progressively decreases with increasing total metal loading.

In a review of over 70 studies on partitioning coefficients, Sauvé et al. [79] identified 452 K_d values for Cu in soil, ranging from 6.8 to 82850 L kg^{-1}, with a median of 2120 L kg^{-1}. All Kd values are based on aqua regia soluble soil metal content and total dissolved Cu concentrations in the actual soil solution or soil extracts. K_d values were significantly correlated with pH and organic carbon content of the soil and an empirical regression was derived to predict K_d for Cu in soil:

$$\begin{aligned}\text{Log } K_d = {} & 1.75 + 0.21^{*}\text{pH(soil solution)} \\ & + 0.51^{*}\log(\%\text{ Organic Carbon})\left(R^2 = 0.42,\ n = 353\right)\end{aligned}$$

Similar equations for K_d values based on aqua regia soluble total Cu concentrations and either total dissolved or free ion Cu concentration in pore-water were obtained in an excellent review on metal partitioning in soils by Degryse et al. [19]:

$$\text{Log } K_d = 0.45 + 0.34^{*}\text{pH} + 0.65^{*}\log(\%\text{ Organic Carbon})\left(R^2 = 0.44,\ n = 128\right)$$

$$\begin{aligned}\text{Log } K_{d\,\text{free}} = {} & -1.88 + 1.05^{*}\text{pH} \\ & + 0.65^{*}\log(\%\text{ Organic Carbon})\left(R^2 = 0.97,\ n = 32\right)\end{aligned}$$

Compared to other metals (Cd, Ni, Pb and Zn), pH has a relatively limited effect on the solid-liquid distribution of total dissolved Cu in soils. This can be explained by the very high affinity of Cu for organic matter. If pH increases, the sorption of the free Cu^{2+} ion on solid organic matter increases, but the complexation of Cu with dissolved organic matter also increases, resulting in a small (or zero) net effect on the total solution concentration [19]. If Cu binds only on organic matter and there is no inorganic complexation in solution, the Kd of Cu is expected to reflect the solid-liquid distribution of organic matter in soils. Figure 13.2 indeed shows a good correlation between K_d values for Cu and the partitioning of organic matter between the solid and liquid phase in soils with moderate to high pH, where free-ion fractions of Cu are small [19]. Land management practices that affect soil pH and organic matter dynamics will obviously also have a directly impact on Cu mobility in soil. The application of biosolids can, e.g., increase Cu mobility through enhanced dissolved organic matter [2, 33].

13.4.3 *Ageing Processes: Effect of Time on Fate of Copper in Soils*

Initial partitioning of metals, taking place within hours after addition of soluble metals to a moist soil, are often followed by much slower reactions, termed fixation

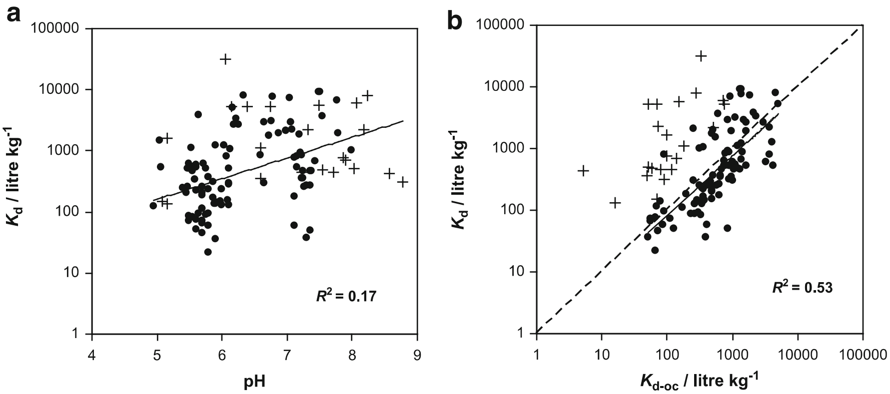

Fig. 13.2 The Kd of Cu for soils with pH > 5 (**a**) as a function of pH, or (**b**) as a function of the solid-liquid distribution of organic C, Kd-OC (*dotted line* is the 1:1 line). Solid lines are regressions relating logKd of Cu to pH or to logKd-OC (From Degryse et al. [19])

or ageing, that further decrease the bioavailability of added metal with time. Examples of such ageing reactions for Cu are diffusion of Cu into micro-pores, precipitation of insoluble Cu phases, occlusion of Cu into organic matter and inclusion of Cu in the crystal structure of soil minerals. There is substantial evidence for the decreased extractability with time after addition of soluble Cu to soils [34, 95] or soil constituents, such as peat [12], oxides [66] and clay [97]. It was also shown that the extractability of Cu fertilisers in field soils decreased over a period of 6 years after application [15]. Results from sequential fractionation schemes to partition soil Cu into various operationally-defined pools confirm that soluble Cu migrates with time from easily extracted pools to more strongly bound forms, mostly associated with organic matter and mineral oxides [30, 67].

Next to this chemical evidence for ageing reactions, there also are some biological indications for decreased availability of Cu with time. In a series of pot trials with Cu-deficient soils (<3.5 mg Cu kg^{-1}), the plant uptake of Cu was significantly reduced with increasing contact time between soil and Cu. The Cu fixation rate increased with increasing temperature, increasing pH and addition of straw [5–8]. There is however no direct evidence for reduced residual effect of Cu in non-deficient soils, which may be related to the strong regulation of plant root uptake of Cu when abundant Cu is available. At higher soil Cu concentrations, it has been shown that ageing significantly reduces Cu toxicity to plants, invertebrates and micro-organisms [64, 68, 69, 80, 81]. It must however be noticed that at these high concentration ranges, the elevated ionic strength and decreased pH in soil solution of Cu-salt spiked and unleached soil samples also may affect Cu behaviour in soil (see Sect. 13.6.1).

Ageing of Cu in soil removes Cu from available pools into a pool that is more strongly retained, from which its desorption is much slower. Consequently, two Cu pools can be defined in soil, the labile fraction and the fraction of Cu that is

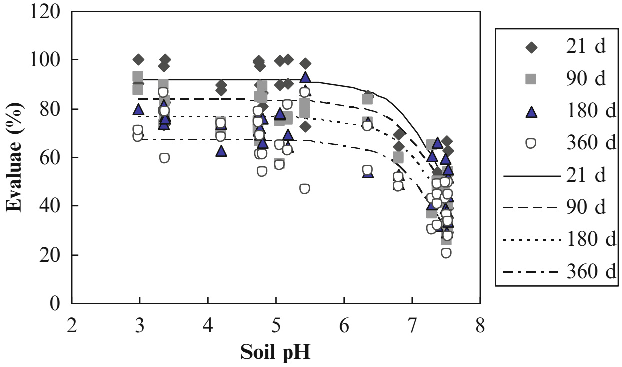

Fig. 13.3 The effect of time and pH on lability (E-values, % of total added Cu) of added Cu in soils incubated for different times. The curves are predicted by a semi-mechanistic model based on time and pH (Based on Ma et al. [47])

fixed. The labile fraction of Cu contributes to the solid-liquid distribution whereas the fixed fraction of Cu does not. Isotopic dilution is a convenient method of measuring the labile pool of Cu in soils. The radiolabile Cu in soil (or the E-value) is, by definition, that amount of Cu in soil that has the same fate as a soluble Cu salt after 24 h equilibration in the soil. The fraction labile Cu varies strongly across soils and is generally lower in uncontaminated soils (between 2% and 35%) compared to field contaminated soils (27–57%) [47, 58].

Ma et al. [46, 47] assessed ageing of freshly added $CuCl_2$ in 19 soils at two total Cu concentrations, after leaching of the excess salt and 2 years of incubation outdoors. The lability of Cu added to soils rapidly decreased after addition, especially in soils with pH >6.0, followed by a slow decrease in Cu lability. The short-term (30 days) attenuation of Cu lability depended on soil pH, organic matter content, temperature and Cu addition rate [46]. The long-term changes in Cu lability were well described based on soil pH and time alone, with a semi-mechanistic model taking into account a slow diffusion process and precipitation/nucleation of Cu in alkaline soils (Fig. 13.3). There was little difference between the two Cu concentrations, suggesting that within the relevant range, total Cu concentration does not greatly affect the rate and extent of fixation [47].

Buekers et al. [10, 11] also studied the fixation of added Cu salt in 28 soils with varying pH (3.4–7.7), organic carbon (0.2–23.5%), clay content (5–81%) and Fe oxides (0.1–7.3 g kg^{-1} oxalate extractable Fe). After 850 days incubation, on average 43% of the added Cu was fixed. A significant positive effect of pH on the amount of fixed Cu was observed, but compared to Ni, Zn and Cd, fixation of Cu in soils was generally poorly related to soil properties. The relatively large fixation of Cu (approx. 50%) in two organic soils did however suggest that Cu can be fixed in organic matter [10]. In contrast to Ni, Zn and Cd, fixation on Fe oxyhydroxides does not well explain ageing of Cu and modelling fixation of Cu requires more information on fixation on organic matter [11].

13.5 Soil-Plant Relationships of Copper

Copper is an essential micronutrient for plants and is involved in several metabolic processes. It plays an important role in photosynthesis, respiration, oxidative stress responses, cell wall metabolism and hormone signalling [50]. Copper also acts as a cofactor in many enzymes such as plastocyanin, cytochrome c-oxidase and amino oxidase. Copper deficiency mainly affects young leaves and reproductive organs and typical symptoms are twisted or malformed leaves, chlorosis or even necrosis [50]. Crops known to be highly susceptible to Cu deficiency include wheat, alfalfa and lettuce. Copper deficiency is mainly related to sandy, light textured soils with low ambient background Cu concentrations or strong Cu-binding peat soils with low plant available Cu. High nitrogen levels delay the translocation of Cu from older leaves to the growing points and may enhance Cu deficiency in intensive farming systems. In Europe, it is estimated that up to 19% of the arable land is deficient in bio-available Cu [83]. Despite its essentiality, excess Cu in soil has a phytotoxic effect, resulting in plant growth retardation and leaf chlorosis. The first effect of Cu toxicity in plants is rhizotoxicity, resulting in reduction of root elongation and stunting, abnormal root branching and thickening and dark coloration of the roots [39, 50, 82]. Translocation of Cu towards shoots is efficiently restricted by the large accumulation of Cu in roots and deleterious physiological effects (e.g., altered root growth and nutrient uptake) are expected to occur before shoot Cu concentration reaches abnormal values [69].

Typical Cu concentrations in plants growing in uncontaminated soils vary between 4 and 15 mg Cu kg^{-1} dry matter [17, 56] and rarely exceed 20 mg Cu kg^{-1} dry matter [37]. The Cu concentration in plants depends on the plant species, growth stage and lime or fertiliser applications. In non-deficient soils, plant tissue Cu concentrations are rather constant over a wide range of soil Cu levels, reflecting the homeostatic control of Cu content in plants.

The onset of Cu toxicity and reduction in yield is found at shoot and leaf concentrations between 5 and 40 mg Cu kg^{-1} dry matter (Table 13.6). The small difference in Cu concentrations in shoots from healthy plants and plants affected by Cu toxicity again reflects the strong translocation barrier for excess Cu between root and shoot. Root Cu concentrations are more affected by soil Cu concentrations than shoot Cu concentrations (Fig. 13.4) and critical Cu concentrations in plant roots are in the range of 100–400 mg Cu kg^{-1} dry matter [18, 69, 82].

The efficient homeostatic mechanisms in plants, whereby Cu levels in edible crops are relatively insensitive to soil Cu, and the translocation barrier of excess Cu from roots to shoots limit Cu residues in plant shoots to levels chronically tolerated by livestock and humans [26, 76]. In contrast, Cu deficiency symptoms in livestock occur and can be caused by either low Cu concentration in herbage (<5 mg Cu kg^{-1} dry matter) or by reduced Cu absorption in ruminants due to elevated dietary Mo or S uptake [87].

Plant growth affects Cu solubility and bioavailability in soil, especially in the rhizosphere, due to their effect on pH and dissolved organic matter. Depending on the pH of the bulk soil, this may result in either increased or decreased

Table 13.6 Critical toxic Cu concentrations in plant shoots and leaves (data from [17, 48])

Plant species	Critical level (mg Cu kg^{-1} dry matter)
Ryegrass	21–40
Barley	14–25
Wheat	11–18
Maize	5–21
Lettuce	8–23
Rape	15–22
Beans	15–30
Cabbage	25
Sugar beat	17
Spinach	25–35

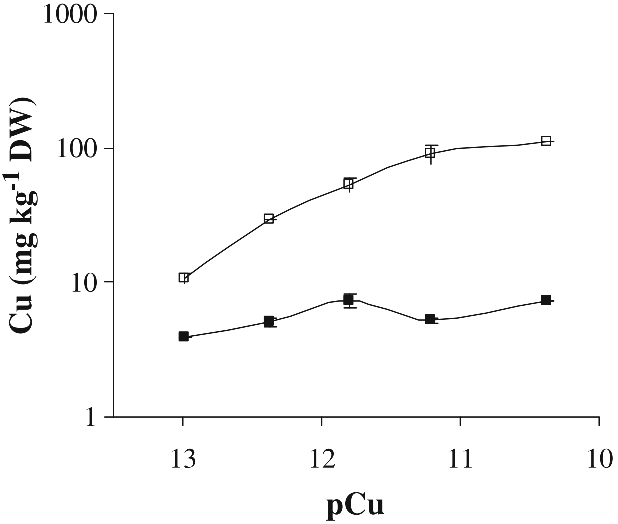

Fig. 13.4 Copper concentrations in shoots (*closes symbols*) and roots (*open symbols*) of tomato plants grown in nutrient solutions as function of the free metal activity (From Degryse et al. [18])

total dissolved Cu concentrations. The free Cu^{2+} activity in soil solution however generally decreases with plant growth due to enhanced complexation with dissolved organic carbon [4, 18, 74].

13.6 Toxicity of Copper in Soils

13.6.1 Copper Toxicity to Plants, Invertebrates and Micro-Organisms

Toxicity of Cu to terrestrial organisms (plants, invertebrates and micro-organisms) is typically studied by exposing these organisms to an uncontaminated soil recently

Table 13.7 Chronic soil Cu toxicity threshold concentrations (NOEC, No Observed Effect Concentrations, or EC10, concentrations yielding 10% inhibition in response) for plants, invertebrates and microbial processes [26]

	Range (mg Cu kg^{-1} soil)	Number of data
Monocotyledon plants	18–537	32; 5 species from 3 families
Dicotyledon plants	36–698	35; 4 species from 2 families
Arthropods	31–1460	57; 5 species from 3 families
Annelida and Nematoda	8.4–728	51; 5 species from 3 families
Microbial C transformation	30–2402	49; 4 processes
Microbial N transformation	31–1270	26; 4 processes
Microbial biomass	150–500	2

amended with increasing doses of a soluble Cu salt (e.g. $CuCl_2$ or $CuSO_4$). From the resulting dose–response relationship, toxicity thresholds (NOEC, No Observed Effect Concentrations, i.e. highest dose at which no significant inhibitory effect is observed, or EC10 values, i.e. effective concentration yielding 10% inhibition in response) can be calculated for the effect of Cu on the endpoint studied (e.g., plant growth or invertebrate reproduction). In total 252 reliable NOEC or EC10 values for the effect of Cu on terrestrial organisms were identified in the framework of a European risk assessment of Cu (Table 13.7). These data cover a wide range in terrestrial organisms and are derived from tests focusing on sensitive life stages (e.g., plant root elongation, invertebrate reproduction) or from chronic exposure (e.g., growth, mortality). Data were obtained in a variety of soils with a wide range in pH (3.0–7.7), organic carbon (0.3–38%), clay (5–60%) and ambient Cu background concentration (2–158 mg Cu kg^{-1}). Copper toxicity thresholds varied almost 3 orders of magnitude (3–2,400 mg Cu kg^{-1}) across endpoints and soils and overlap with the range in ambient background Cu concentrations in soil.

The ecological relevance of standardised laboratory tests immediately or shortly after freshly spiking with soluble metal salt is however limited (Fig. 13.5). Standardised toxicity tests result in a sudden disturbance of the soil, while in field conditions Cu generally accumulates slowly with time due to e.g., industrial emissions, sludge application or the use of Cu fungicides. Spiking soils with soluble Cu salts not only increases the Cu content of a soil but also increases the ionic strength of the soil solution and decreases the soil pH by replacement of protons from the exchange complex with the metal cations (Fig. 13.6). The higher ionic strength and lower soil solution pH in freshly amended (spiked) soils compared to leached or field-contaminated soils (that are naturally leached) may affect the response of the organisms both directly and indirectly by increasing metal bioavailability. Testing soils immediately after adding Cu also ignores the ageing reactions that further decrease bioavailability of added Cu beyond the duration of these tests (Sect. 13.4.3). Standard toxicity experiments in soil result therefore in a potentially higher bioavailability compared to field conditions and soil metal concentrations needed to produce toxic effects generally are lower for laboratory contaminated than for field contaminated soils. Additionally, lower toxicity to microbial processes in field-contaminated or aged soils can also be caused by microbial

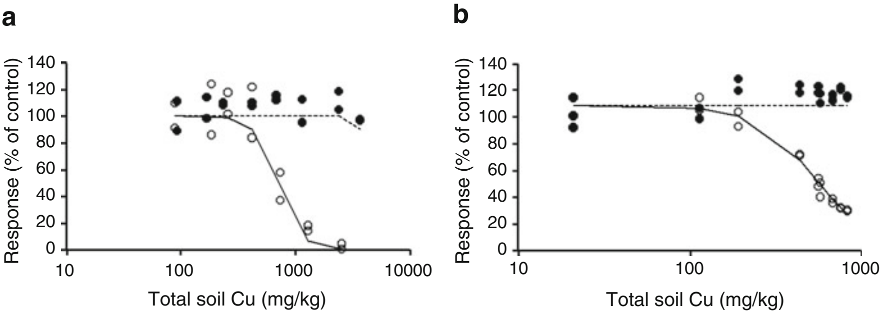

Fig. 13.5 Discrepancy of the microbial response to elevated Cu between standard toxicity tests (*open symbols, full line*) and long-term contaminated soils (*closed symbols, dashed line*). (**a**) Toxicity of Cu on nitrification measured 7 days after amending the soil with $CuCl_2$ or after spiking with $CuCl_2$ and18 months equilibration and leaching. (**b**) Effect of Cu on respiration of glucose in a field transect of a contaminated soil (70-year-old $CuSO_4$ spill) and the corresponding control soil amended with $CuCl_2$ to identical concentrations (Based on Oorts et al. [64])

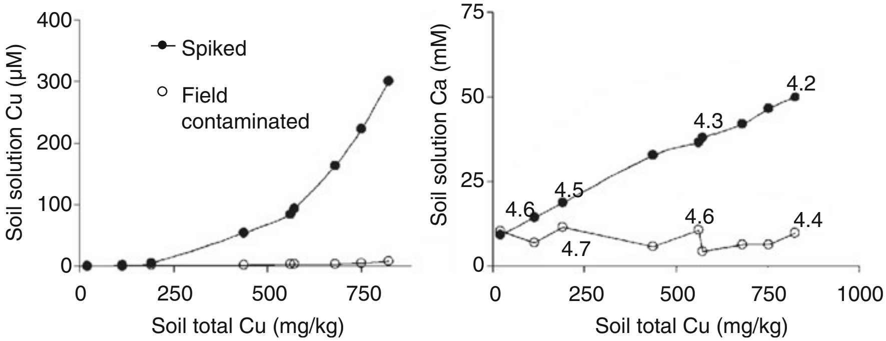

Fig. 13.6 Difference in soil solution properties of a field-contaminated soil (field gradient with a 70-year-old $CuSO_4$ spill) and the corresponding freshly spiked reference soil (amended with $CuCl_2$ to identical Cu concentrations). Soil pH (indicated in *right panel*) gradually decreases with Cu dose in spiked soils (From Smolders et al. [85], data based on Oorts et al. [64])

acclimatization or adaptation of the microbial biomass in the soil to gradually increased Cu concentrations [3, 28, 54] (see also Sect. 5.6).

Several studies have confirmed the larger Cu toxicity in soils freshly spiked with Cu salts compared to corresponding laboratory leached and aged soils or field contaminated soil [64, 68, 69, 80, 81]. The factor for the decrease in toxicity is expressed as the ratio of EC10 value after ageing to the corresponding value in freshly amended soil, both based on measured added concentrations. This factor is termed the leaching–ageing factor (L/A factor) and is the net result of effects of both leaching and ageing. Most of the L/A factors based on EC10 values were larger than 1 (i.e. decreased toxicity after leaching and ageing), with a median of 3.4 (Fig. 13.7).

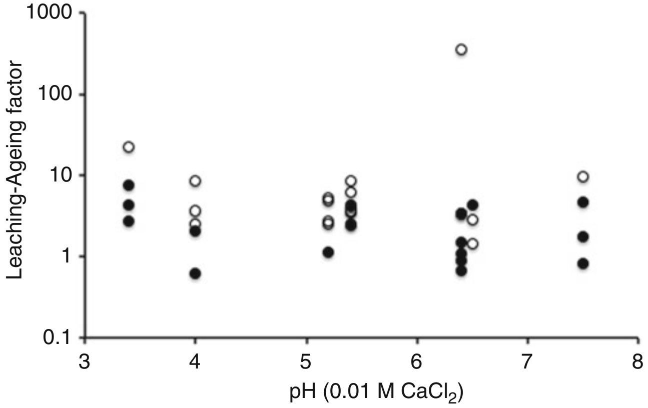

Fig. 13.7 The leaching–ageing factors that quantify the difference in Cu toxicity between aged soils (experimental or field-contaminated) and corresponding freshly amended soils. The factors are the ratios of the doses resulting in 10% inhibition (EC10 values) in aged to that in freshly amended soils. Closed symbols are bounded values; open symbols refer to unbounded values (no toxicity found in a field-contaminated or aged soil and a (*lower*) estimate for the L/A factor was selected, based on the ratio of the largest concentration in the aged soil to the ED10 of a freshly amended soil) (Based on EU [26]

The L/A factors for Cu vary largely among the species or process studied and no effect of soil pH or other soil properties was observed on the effect of leaching and ageing on Cu toxicity in soils.

13.6.2 Effect of Soil Properties on Copper Toxicity in Soils

Toxicity thresholds for the effect of Cu on the same endpoint can vary up to two orders of magnitude among different freshly spiked soils [9, 16, 40, 41, 65, 75]. It is generally accepted that the total metal concentration in soil is a poor predictor for toxicity to the environment. However, there is as yet no generally accepted method for measurement of the bioavailable fraction of Cu or other metals in soil [53, 98]. The free metal ion concentration in soil solution is generally regarded as the most active Cu species and the determinant of bioavailability. It is however often observed that toxicity thresholds based on total soluble Cu or free metal ion activity of Cu are more variable than other indices of Cu doses in Cu spiked soils (Fig. 13.8) [9, 65, 98]. This observation that free metal ion activities do not explain variability in toxicity does not necessarily violate the concept that the free metal ion in solution is the directly available and toxic metal species. This is readily explained by the concept of the biotic ligand model (BLM), which is an extension of the free metal ion model. According to the BLM, toxicity depends on the metal bound to a target location at or in the organism (the biotic ligand), which, in turn, depends

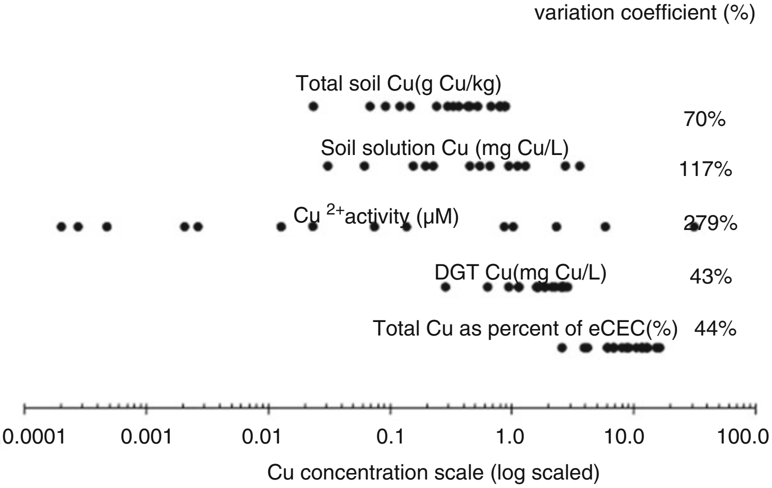

Fig. 13.8 Five different expressions of the toxic Cu concentrations at the 50% effective concentration (EC50) in 17 freshly amended soils, with shoot growth of tomato seedling as the measured endpoint. The coefficients of variation (standard deviation divided by mean of untransformed EC50 values) of the EC50 values for the 17 soils are given. DGT = diffusive gradients in thin film technique; eCEC = effective cation exchange capacity (i.e. CEC at pH of the soil) (From Smolders et al. [85], data based on Zhao et al. [98]

on the metal ion activity in solution and the concentrations of competing ions (e.g. protons, Ca^{2+}, and Mg^{2+}). A BLM has been successfully calibrated with the data from soils freshly amended with Cu salts and this revealed protective effects of protons for all endpoints and additionally of Mg for the nitrification assay [88, 89]. A meta-analysis of metal toxicity data also suggested that protons strongly mitigate the toxicity of the free metal ion on the biotic ligand [43].

Soil properties can explain a significant part of the variation in Cu toxicity thresholds for plants, invertebrates and micro-organisms based on total soil Cu concentrations and empirical regression models are derived for a wide range of European, Chinese and Australian soils (Table 13.8). Copper toxicity is generally best related to the effective CEC (‘eCEC’ i.e. CEC at pH of the soil), compared to pH, organic matter or clay content. The importance of the eCEC may refer to the role of cation exchange processes in short-term sorption of Cu in soils [92]. Although soil pH generally is acknowledged as a key factor in determining Cu solubility and speciation in soils, no consistent effects of soil pH on total soil Cu toxicity thresholds were found. This is explained by the counteracting effect of soil pH on free Cu ion toxicity at the biotic ligand (increasing toxicity of free Cu ion with increasing pH because of decreasing competition of protons) and on Cu solubility and speciation in soil (decreasing free Cu ion concentration with increasing pH due to increasing sorption) [43, 65]. The similar pH effect on metal toxicity and metal adsorption suggests that metal binding on the biotic membrane and on soil components are controlled by the same reactions.

Table 13.8 Soil properties best predicting Cu toxicity (EC50 values) in freshly-spiked soils

Endpoint	Soil properties	Reference
Eisenia fetida (earthworm) reproduction	eCEC[a]	[16]
Folsomia candida (springtail) reproduction	eCEC	[16]
Potential nitrification rate	eCEC	[65]
Substrate induced respiration	Organic carbon and clay content	[65]
Maize residue mineralisation	pH and eCEC	[65]
Barley root elongation	eCEC	[75]
Tomato shoot yield	eCEC	[75]
Substrate induced nitrification	pH	[9]
Substrate induced respiration	clay	[9]
Wheat shoot yield	CEC	[93]
Substrate induced nitrification	Total calcium concentration	[41]
Barley root elongation	pH and organic carbon	[40]

[a] eCEC = effective cation exchange capacity, i.e. CEC at pH of the soil

13.6.3 Toxicity of Copper in Soils Amended with Sewage Sludge and Manure

Application of sewage sludge and manure to agricultural land is an important source of Cu in agricultural land (Sect. 13.3.3). The bioavailability of Cu in these soil amendments is however generally lower compared to Cu salts. The ecotoxicological assessment of Cu added with sludge or manure to soils is different from Cu added as salt because the application of these products also changes a range of other soil properties apart from the total Cu content. Application of sewage sludge or manure to a soil may increase metal binding capacity of the soil as these products contain organic matter and Fe or Al oxyhydroxides, which all have Cu binding properties. Additionally, metals present in these materials have a different speciation, and typically lower availability, than metal salts [32, 33, 62]. Both mechanisms may decrease the risk of increasing total trace metal concentrations. On the other hand, long-term mineralisation of organic matter from biosolids may again decrease the Cu binding capacity of the soil and increase bioavailability of Cu.

Results on the difference of Cu bioavailability between biosolids- and $CuSO_4$-amended soils in 12 Australian field trials were inconclusive due to the strong regulation of Cu concentration in plant shoots and the confounding effect of dissolved organic matter on Cu extractions [33]. A comparison of toxicity of added Cu-salt in 22 paired sets of soils amended with sewage sludge, manure or compost and corresponding control soils from field trials in Europe, Asia and Australia, showed that the protective effect of additional metal binding capacity in biosolids-amended soil was limited (average factor 1.4 difference in EC50 for barley root elongation) [84]. A larger difference was observed in the lability (E-values) of Cu added via these biosolids compared to soluble metal salts, even after correcting for ageing. Therefore, it seems that application of biosolids indeed results in a protection of Cu availability, and that this protection is mainly related to the

Table 13.9 Copper limit concentrations in soil according to various legislations

Legislation	Limit (mg Cu kg^{-1} DM)	Comment	Reference
Europe (Regulation (EEC) 793/93)	10–200	Predicted No Effect Concentration (PNEC, 95% protection level) for plants, invertebrates and micro-organisms; depending on eCEC, pH, clay and organic matter content	[26]
US EPA	70 (plants) 80 (invertebrates) 28 (birds) 49 (mammals)	Ecological soil screening level (ECO SSL); no correction for soil properties	[90]
Australia	8–970	Added contaminant level for soils with varying pH (4–8) and organic carbon content (1–6%). Based on protection of 95% of plant species	[32]
Australia	11–2078	Added contaminant level for biosolids amended soils with varying pH (4–8) and organic carbon content (1–6%) Based on protection of 95% of plant species	[32]
Europe (EU Directive 86/278/EEC)	50–140 1000–1750	Limit values for Cu in soil Limit values for Cu in sludge for use in agriculture.	[25]

speciation and low availability of Cu originally present in the sewage sludge and manures and less to the additional Cu binding capacity of a biosolids-amended soil [84]. The marginal effect of increased binding capacity also explains the lack of significant release or mobilisation of Cu in biosolid-amended soils due to organic matter decomposition within the time frame of the field trials studied [63, 84].

13.6.4 Critical Soil Copper Concentrations

Based on the toxicity data available, critical soil Cu concentrations can be derived for risk assessment purposes. These critical Cu concentrations vary between legislations as they depend e.g., on the protection goal (organisms covered), the toxicity data included, the application of normalisation models for the effect of soil properties on Cu bioavailability, the protection level and the margin of safety included to correct for remaining uncertainty (Table 13.9).

The incorporation of bioavailability models into the derivation of ecological soil standards (Predicted No Effect Concentrations, PNEC) in the European risk assessments of Cu and other metals is described by Smolders et al. [85]. In summary, this European risk assessment for Cu [26] was based on reliable chronic toxicity data (NOEC and EC10) from standard tests in soils freshly amended with Cu salts and sufficient information on the soil properties (Table 13.7). In order

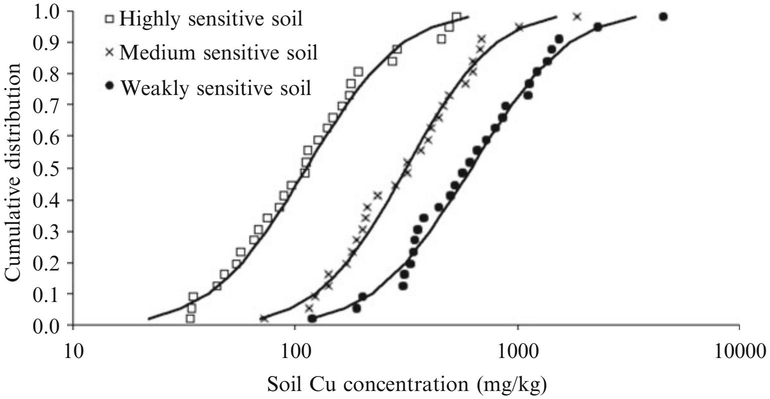

Fig. 13.9 Species sensitivity distribution (SSD) of species-mean NOEC or EC10 values for plants, soil invertebrates and micro-organisms, corrected for ageing processes and normalised for soil properties of a highly sensitive, medium sensitive and weakly sensitive soil according to the models selected for the European risk assessment of Cu [26]. Properties for these three soils are, respectively, eCEC, 4, 15, and 35 $\mathrm{cmol_c\ kg^{-1}}$; pH, 4.5, 5.5, 7.0; % organic carbon, 1.0, 2.9, and 12% and % clay, 5, 15, and 30%. Corresponding PNEC values, based on a 95% protection level, are 30, 93 and 162 mg Cu $\mathrm{kg^{-1}}$ soil, respectively

to correct for differences in bioavailability and toxicity of Cu between such freshly amended soils and realistic field conditions due to leaching and ageing processes (Sect. 13.6.1), all toxicity data based on added Cu concentrations were multiplied with a generic leaching-ageing factor of 2. This L/A factor is obviously only applied on the added dose as the bioavailability of the background Cu concentration in soil is not expected to further change with time. After adding the background concentration, the total 'aged' NOEC and EC10 values were normalised for differences in metal availability between the tested soil and the soil to which the PNEC is calculated, using the slope of the regressions between toxicity and selected soil properties (eCEC, pH, organic carbon and clay content). Based on these normalised values, a species mean threshold was calculated for each plant, invertebrate and microbial process covered. A critical concentration protecting 95% of all species or processes was derived as the 5th percentile of the cumulative distribution of species mean thresholds (species sensitivity distribution, Fig. 13.9). This results in soil specific PNEC values for direct ecotoxicological effects of Cu to terrestrial organisms, between 10 and 200 mg Cu $\mathrm{kg^{-1}}$ for the relevant range of soil properties in European soils. Because plants and invertebrates are good Cu regulators and they maintain internal Cu levels over a large range in environmental Cu concentration, the direct toxicological effects on terrestrial organisms are most critical and risks for secondary poisoning to birds, mammals and humans are absent at PNECs for direct effects to terrestrial organisms [26, 76].

Clean-up standards for Cu in soils are generally higher than these ecological standards for risk assessment purposes and clean-up limits for Cu in residential and industrial land vary between 63–3,100 and 91–41,000 mg Cu $\mathrm{kg^{-1}}$, respectively among individual legislations [71].

13.7 Contaminated Soils

High Cu concentrations, potentially requiring remediation, can be found in topsoils affected by e.g., mining and smelting activities (up to >2000 mg Cu kg^{-1}) (e.g. [22, 45, 86]), wood treatment facilities (up to >1000 mg Cu kg^{-1}) [52], or-long-term application of high doses of Cu pesticides (200–500 mg Cu kg^{-1}) [38]. When Cu levels affect soil functions or exceed soil clean-up values, Cu contaminated land can be remediated by either excavation of contaminated soil and off-site treatment or landfilling, or the on-site stabilisation by limiting the mobility and bioavailability of Cu in soil. The first option is very invasive and hence only suitable for small highly contaminated areas. Decreasing the mobility and bioavailability in soil can be done by raising the pH by liming or by adding soil amendments, such as organic matter or oxides, to increase the Cu binding capacity of the soil [44, 86]. It seems however that the major effect of most soil amendments on Cu bioavailability can still be attributed to the associated increase of the pH [44]. Because the effect of increased pH on Cu bioavailability is reversible, a continuous land management is required in order to prevent re-acidification and corresponding increase in Cu bioavailability. Phytostabilisation has also some potential in case of large areas of relatively low contamination levels [72]. A vegetation cover will prevent spreading of the contamination by e.g. air or wind erosion. The low transfer of Cu to aboveground plant parts further limits Cu dispersion by litter fall or increased exposure to herbivores.

13.8 Concluding Remarks

Copper is probably among the best-studied heavy metals in soil. Although the long history of global use of Cu resulted in significant diffuse anthropogenic emissions of Cu to soil, natural processes (e.g., geology) drive the regional and continental distribution patterns of soil Cu concentrations. At a local scale, the main anthropogenic input comes from point sources (e.g. mining or smelting activities) and agricultural practices (use of sewage sludge, Cu-pesticides etc.). Soil organic matter and pH are the main soil factors controlling solid-liquid partitioning of Cu in soil, with higher solubility at low pH and low organic matter content. Copper is an essential element and internal Cu concentrations are well regulated in plants and soil-dwelling invertebrates. Elevated soil Cu concentrations first affect plant root growth and translocation of excess Cu to shoots is efficiently restricted over a wide concentration range. Toxicity of Cu to terrestrial organisms varies largely depending on the species sensitivity and the bioavailability of Cu in soils. Chronic soil Cu toxicity thresholds even overlap with the range in ambient background Cu concentrations. However, both background Cu concentration and Cu toxicity are partly controlled by the same soil factors (organic matter and clay content). When bioavailability of Cu in soil is taken into account and toxicity data are normalised for soil properties, there is a factor 2–10 difference between the ambient background concentrations and predicted no effect concentration of Cu in soil.

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Chapter 14
Lead

Eiliv Steinnes

Abstract Lead (Pb) is among the elements that have been most extensively used by man over time. This has led to extensive pollution of surface soils on the local scale, mainly associated with mining and smelting of the metal and addition of organic Pb compounds to petrol. Other sources of soil Pb pollution are shooting ranges and sewage sludges. Release of Pb to the atmosphere from various high-temperature processes has led to surface contamination on the regional and even global scale. Lead is particularly strongly bound to humic matter in organic-rich soil and to iron oxides in mineral soil, and is rather immobile in the soil unless present at very high concentrations. Transfer of Pb from the soil to green parts of plants is generally small, except in cases with extensive surface soil concentration. Concerns about health effects due to Pb pollution particularly in urban areas and to Pb uptake in agricultural crops have led to development of a variety of soil remediation techniques.

Keywords Lead • Air pollution • Atmospheric deposition • Smelters • Leaded petrol • Shooting ranges • Sewage sludge • Sorption • Leaching • Plant uptake • Surface contamination • Soil remediation

14.1 Introduction

Lead (Pb) is believed to be the first metal extracted by man from its ores, and was extensively used throughout antiquity for a great variety of objects and purposes [76, 77]. It is estimated that during the Roman Empire about 140,000 workers were occupationally exposed to Pb each year. Since Pb and its compounds are very toxic to

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man and there is no evidence that deliberate attempts were made to prevent Pb exposure during the production and use of Pb-based items, it seems evident that a great number of people may have suffered from acute or chronic Pb poisoning. In modern times, the primary use of Pb has been in the production of alkyl Pb compounds for anti-knock agents in gasoline, as pigments in paints and in automobile batteries.

As far as is known, Pb is neither essential nor beneficial for any living organisms (see also Chap. 7). The various uses of Pb and its compounds have lead to considerable exposure of large population groups also during recent times, and there are fears that human body burdens below those at which clinical symptoms of Pb toxicity appear may cause mental impairment in young children [25]. Concerns about the toxicity of the metal have led to a significant decrease in the application of the metal in recent years.

In the environment, Pb and its compounds tend to accumulate in soils and sediments, where they may remain bioavailable for a long period of time.

14.2 Geochemical Occurrence

The abundance of Pb in the continental crust is 14.8 mg kg^{-1} [115]. The Pb^{2+} cation replaces K^{+} in silicate lattices or Ca^{2+} in carbonates by isomorphic substitution. In silicate rocks Pb has a tendency to increase with increasing Si content. Lead also has a strong affinity for S, and therefore concentrates in S phases in rocks. Among common sedimentary rocks [1] shales have higher Pb abundance (22 mg kg^{-1}) than sandstones (10 mg kg^{-1}). Black shales are rich in organic matter and sulphide and tend to have higher Pb contents [70]. The major Pb ore mineral is galena (PbS).

14.3 Origin of Lead in Soils

14.3.1 Soil Parent Materials

The mean content of Pb in uncontaminated soils worldwide has been estimated to be 17 mg kg^{-1} [76]. This general level has been confirmed by other extensive studies [51, 61, 83, 90]. Other large-scale soil surveys have reported higher values [19, 23], but there is evidence that much of the observed soil Pb in many areas has originated from anthropogenic emissions [26, 94, 99].

14.3.2 Atmospheric Deposition

Several compounds of Pb are relatively volatile, and Pb is therefore readily emitted from high-temperature processes such as Pb ore smelting, coal burning, and the use of leaded petrol in automobiles. Since the outset of the industrial period, Pb has therefore accumulated in terrestrial surface materials, frequently resulting in considerable contamination of surface soils. Lead has a tendency to be concentrated on the smaller particle fractions in emissions from high-temperature sources [35] and may thus become available for long-range atmospheric transport. Analyses of ice and snow from Greenland and the Antarctica [10, 73] showed that the contamination of land surfaces from airborne Pb has a global distribution. In the 1970s large-scale contamination of natural surface soils far from major emission sources became evident in southern Scandinavia [108] as well as in New England [85]. In Norway the Pb content of organic-rich surface soils decreased regularly from $>120\ \mathrm{mg\ kg^{-1}}$ in the south of the country to $<10\ \mathrm{mg\ kg^{-1}}$ in the north, and the main reason for this difference was stated to be long-range atmospheric transport from more heavily industrialized and densely populated areas elsewhere in Europe [96, 100]. Studies from other countries have confirmed substantially higher Pb levels in the surface soil compared to lower soil horizons e.g., [9, 40, 83, 102]. The extent of Pb contamination of surface soils has been demonstrated in several countries by different ratios of stable Pb isotopes in the indigenous and the supplied Pb [7, 9, 31, 101]. Steinnes and Friedland [98] reviewed the character and extent of Pb pollution in boreal forest soils.

Although the main source of airborne Pb in soils has been generally assumed to be the use of Pb alkyls in petrol (cf. Sect. 14.5.1), studies of the temporal trends in Pb deposition using dated peat cores from ombrogenous bogs [92] have shown that a substantial part of the deposited Pb could be derived from emissions that occurred prior to the introduction of leaded petrol. Some peat studies even showed evidence of Pb contamination in peat layers corresponding to the Roman period and medieval Pb production [11, 59, 93]. Similar information on historical Pb deposition in Europe was obtained from the Pb isotopic record of a sediment monolith from an Icelandic salt marsh [66].

Another way of illustrating the Pb contamination of surface soils is the application of multivariate statistics on multi-element sets of data [26, 29, 100], where Pb invariably shows a preference for some factor characteristic of air pollution.

More than for any other metal, human industrial activities have strongly influenced the extent and fate of Pb in soils, including impacts on human beings e.g., from soil ingestion or contamination of food crops from surface contamination or root uptake. A further discussion of different anthropogenic sources and their influence related to soils is presented in Sect. 14.5.

14.4 Chemical Behaviour of Lead in Soil

Lead in soils exists predominantly in the +2 oxidation state. In reduced soils it occurs primarily as insoluble PbS precipitated by sulfide generated from sulfate reduction. Under oxidizing conditions it exists as the Pb^{2+} ion, but becomes less soluble with increasing pH in the soil solution due to complexation with organic matter, sorption on oxide and silicate clay minerals, or precipitation as the carbonate, sulfate, or phosphate. In alkaline soils, solubility may increase due to formation of soluble Pb-organic and Pb-hydroxy complexes [68].

The chemical behaviour of Pb in soil depends very much on the organic matter content. Lead is strongly adsorbed on humic matter at pH 4 and above [13, 54]. According to Christl et al. [21] the binding of Pb to soil humic fractions is predominately as a monodentate complex. Only small differences were observed between different size fractions, and it was generally suggested that Pb binding to humic substances is almost unaffected by differences in their chemical composition. With the exception of Hg and Cu, the binding of Pb to soil humic matter is stronger than for the other heavy metals and metalloids discussed in this volume. The high affinity to humic matter plays a key role in the behaviour of Pb derived from air pollution, in particular in boreal forest soils and other soils with a high organic matter content, and the release of Pb to deeper soil horizons depends mainly on transport of dissolved Pb-organic complexes [8, 108].

In the absence of appreciable humic matter, Pb is strongly adsorbed on clay minerals [42] and Fe oxides [43, 55]. Lead is generally more strongly sorbed than other heavy metals, such as Cu, Zn, Cd, and Ni [30, 110]. Lead sorption occurs primarily on the clay size fraction of the soil [65]. Hooda and Alloway [44] found that Pb sorption in agricultural soils correlated with pH, CEC, organic matter content, clay content, and $CaCO_3$. Sipos et al. [95] reported that organic matter in soils absorbs more Pb than clay minerals. Appel and Ma [4] observed that the Pb sorption in oxisols was greater than the amount of negative surface charge, indicating participation of Pb in inner-sphere surface reactions. This was confirmed by X-ray absorption studies on interactions of Pb^{2+} with ferrihydrite [106]. At pH > 5 bidentate complexes on the oxide surface dominated, whereas at pH 4.5 a mixture of monodentate and bidentate complexes was indicated.

Alternating aerobic and anaerobic conditions, as observed e.g. by soil flooding, lead to changes in pH and redox potential and are likely to affect most of the processes regulating the speciation of metals in soil [14]. In the case of Pb the reduction of Mn and Fe oxides and induced pH changes may lead to release of Pb from solid phases to the soil solution but prolonged flooding can lead to fixation again [18].

14.4.1 Chemical Speciation of Lead in Soil

Different approaches have been applied in order to fractionate different binding forms of Pb in soils. Reaves and Berrow [83] found that the acetic acid-extractable fraction of Pb in an extensive series of Scottish soils was positively correlated with total Pb. The mean value was 1.7% of the total, and the variation was small. There was little variation with depth and no appreciable difference between organic-rich soils and mineral soils. More recently applications of sequential extractions schemes have confirmed that easily releasable forms of Pb in soils constitute a very small fraction of total Pb, although results vary among different studies [5, 8, 33]) and with extraction time [64]. According to Sauvé et al. [86] however, investigations of the soil solution may seem to be more relevant in order to assess the mobility and bioavailability of Pb in soils. They showed that the free Pb^{2+} activity in the soil solution could be predicted simply by means of total soil Pb and pH with no significant contribution from soil organic matter content and phosphate in solution. Yet about 60–8% of the total dissolved Pb was present as organo-Pb complexes. In organic horizons of forest soils [88] the fraction of total Pb in the soil solution was on average about 2 orders of magnitude higher than normally observed in mineral soils, partly due to the low pH and partly because of the high organic matter content.

14.4.2 Leaching of Lead from Polluted Surface Soil

The extensive Pb pollution of surface soils in many parts of the world, including vast otherwise "clean" areas, has raised concern about the possible future contamination of drinking water sources. Tyler [109] first addressed this issue by performing a field lysimeter study where O-horizon profiles of an organic-rich soil were exposed to ambient acid precipitation and monitoring the leaching of metals. Leaching of Pb occurred predominantly under conditions favoring release of organic matter from the soil. In a lysimeter experiment Bergkvist [8] found that artificial soil acidification decreased the release of Pb due to lower leaching of dissolved organic matter. Dörr and Münnich [28], using atmospheric ^{210}Pb as a tracer, confirmed that the downward migration of Pb appeared to be associated with downward migration of organic matter. Brännvall et al. [12] reported that the largest inventories of anthropogenic Pb in Swedish forest soils were found in the Bs horizon in spite of higher Pb concentrations in the O horizon. Steinnes and Friedland [97] pointed out that a larger fraction of anthropogenic Pb is seen at greater depths in southern Scandinavia compared to the northeastern USA, which might be related to later onset of Pb pollution in USA.

Wang and coworkers [112, 113] studying mobility of Pb in spodosols (Podzols) found that a substantial part of Pb downward transport from the O horizon occurred in the colloidal form, but assumed that these colloids might be completely retained in lower horizons and not contribute appreciably to the Pb content of streams. Kaste et al. [52] using sequential extractions found that hydroxylamine hydrochloride in 0.02M HCl extracted 30–40% of Pb from organic horizons of contaminated spodosols, suggesting that inorganic phases play an important role in determining Pb mobility even in surface soils dominated by organic matter. Use of synchrotron-based X-ray techniques [53] showed the presence of amorphous Pb-enriched soil grains, and correlations with Fe indicated that Pb is bound to amorphous Fe oxides by inner-sphere complexes. Following a soil organic matter decomposition experiment, these authors confirmed redistribution of Pb from organic binding sites to pedogenic Fe oxide sites [89].

All in all the total residence time of anthropogenic Pb in soils on the catchment scale may be in the order of centuries to millennia, as indicated by dynamic modeling [104].

14.5 Sources and Consequences of Lead Pollution in Soils

14.5.1 Lead Derived from Automobile Exhausts

Lead alkyls (tetraethyl and tetramethyl Pb) were introduced as anti-knocking agents in petrol in the 1920s. During the 1960s several reports occurred in the literature on elevated Pb concentrations in soil and vegetation near roads, decreasing with distance from the road [25], and mostly in inorganic forms. Stable Pb isotope studies confirmed that automobile exhaust was the source of this Pb [20, 38]. Teutsch et al. [103], using the stable isotopic composition of Pb along with a sequential extraction procedure, showed that the Pb in roadside soils along a major highway in Israel had penetrated the soil down to 30 cm depth.

It was generally assumed that background levels were reached within 100 m or less from the roadside (*e.g.,* Wheeler and Rolfe [116]). From present knowledge however, it is evident that a substantial part of the emitted Pb is transported much farther away from the source on airborne ultra-fine particles (cf. Sect. 14.3.2).

14.5.2 Lead Mining and Smelting

Soil infertility problems due to pollution from Pb mining were recognized as a problem already a century ago [36]. Later on numerous investigations of soils severely polluted from Pb mining and smelting have been carried out in the UK [25]. As an example, Colbourn and Thornton [22] reported a mean soil level of 30,000 mg Pb kg^{-1} within 100 m of an old smelter. Recent studies of dated peat cores indicate that areas far away from the smelters were also appreciably affected by long-range atmospheric transport [32].

At the high levels apparent at such sites, the Pb mobility in the soil may be much higher than in uncontaminated soils. Maskall and Thornton [67] applied sequential extractions on soil cores from historical Pb smelting sites, and found that the proportion present in readily mobile forms increased significantly at pH values below 5, and in one case reached 37%. In a similar study, Kabala and Singh [50] found that the mobility of Pb in soil profiles from the vicinity of a Cu mine increased with increasing metal load. Jensen et al. [48] reported that a significant amount of Pb in severely contaminated soils was present in exchangeable forms.

Soils heavily polluted by Pb can exceed their Pb carrying capacity [80], which could have potential impacts on shallow groundwater systems and represent further exposure to humans and ecosystems.

14.5.3 Sewage Sludges

Soils amended with sewage sludge generally contain elevated contents of a wide range of heavy metals and are therefore of interest with regard to their potential impact on human health [2]. The global discharge of sewage sludge to land was estimated at 2×10^{13} kg year^{-1}, amounting to 0.6–0.9% of the total supply to terrestrial systems [78]. Typical high concentrations of Pb found in sewage sludge prior to 1990 were within the range 496–2,117 $\mu\text{g g}^{-1}$ [2].

Nicholson et al. [75], quantifying heavy metal inputs to agricultural soils in England and Wales, reported a weighted average of 221 mg Pb kg^{-1} in sludge, which constituted 77% of the total Pb added to agricultural land. The solubility of Pb in sewage-sludge-amended soils shows a strong positive correlation to the solubility of organic matter, particularly at high pH [6]. However, according to Chaney [17] Pb from sludge does not give rise to an increase in plant Pb unless the concentration is very high.

14.5.4 Shooting Ranges

Due to its softness and relatively high specific gravity, Pb is a very suitable material for shotgun ammunition. Hence soil pollution from corroding Pb bullets is a significant problem in the vicinity of shooting ranges. Although the range of Pb released from individual bullets may be short [111], the total effect on the surrounding ecosystem may be significant, and remediation efforts may be needed. Turpeinen et al. [107] found that in a boreal soil in Finland pine seedlings had a major role in immobilization of Pb in the contaminated soil, whereas liming did not reduce the solubility, mobility or bioavailability in the soil. The concentration of bioavailable Pb, as assessed directly by a luminescent bacterial sensor, was only 4–6% of total water soluble Pb in humic surface soil and 13–43% in mineral soil. Cao et al. [15], assessing Pb contamination in soil of two shooting ranges in Florida, found a substantial migration of Pb to the subsoil in one case presumably related to the presence of organic material, whereas in the other case low organic matter content and presence of more phosphate retained the Pb in the surface layer, indicating that phosphate-induced immobilization might be an effective way of reducing Pb mobility in shooting range soils. Levonmäki and Hartikainen [62] pointed out that liming of shooting range soils may increase the leaching of metalloids contained in Pb bullets such as As and Sb. Apparently the most effective measures to reduce Pb mobility from shooting range soils differ considerably depending on the soil properties, and no universal procedure for preventing leaching of bullet Pb has yet been found.

14.5.5 Urban Soils

High levels of Pb in urban soils have been confirmed in numerous studies [25]. Soil is an important pathway of human lead exposure, in particular to children engaged in hand-to mouth and pica behavior [71]. Many potential sources of Pb contamination may contribute to high Pb levels in urban soils such as abandoned tyre material, coal burning, plastics and rubber production, insecticides, and car batteries [34]. Two products in particular have added massive amounts of Pb to the urban environment in modern times, notably Pb-based paint and leaded gasoline (see also Chap. 2, Sect. 2.3.2.2). In the United States about equal amounts of Pb have been used in white-Pb based pigment and in leaded gasoline over time. Epidemiological studies however show that child population blood levels of Pb are strongly associated with leaded gasoline and Pb in food, but not with Pb-based paint [71]. Reasons for this difference may be that gasoline Pb is more uniformly distributed in the urban home environment and is associated with smaller particle sizes than Pb in paint dust, leading to higher bioavailability.

14.6 Soil-Plant Relationships

Most of the lead in soils appears to be generally unavailable to the plant tops. Plant-absorbed Pb^{2+} concentrates in the roots, and very little is translocated from roots to tops as the plant is growing [49, 63]. Koeppe [58] reviewed the uptake and translocation in plants, and concluded that translocation is dependent on physiological status. Under conditions of optimal growth Pb precipitates on root cell walls in an insoluble, amorphous form, which in maize was identified as Pb phosphate.

According to Davies [24, 25], there appears to be a positive relationship between the concentration of Pb in the soil and that in the plant in broad terms. More recent work however [86, 87] indicates that the phytoavailability of trace metals may be more strongly correlated to the free metal ion activity in the soil solution than to total metal contents of the soil, although Murray and Hendershot [74] found that neither total Pb, total dissolved Pb, or free Pb in solution were satisfactory predictors of plant uptake.

A large number of studies have been carried out in order to find chemical extractants (salt solutions, dilute acids, complexing agents, etc.) separating the plant-available fraction of heavy metals from soil samples. Menzies et al. [69] critically reviewed the available literature on extractants for Cd, Zn, Ni, Cu, and Pb and concluded that there is generally no correlation between the total metal content and the phytoavailable fraction. Similarly, trace metal concentrations determined by extraction using complexing agents or dilute acids were generally poorly correlated to plant uptake, and generally neutral salt extractants provided the most useful indication of metal phytoavailability. In the case of Pb however Qian et al. [82], studying correlations between extractable Pb in soil and concentrations in alfalfa and winter wheat, found the highest correlation with DTPA-extracted Pb. The number of selective extraction studies dealing with Pb is still limited, and more research is needed.

The extensive atmospheric deposition of Pb observed in many countries over the last century (cf. Sect. 14.3.2) may complicate studies of Pb translocation to the green parts of plants, as first pointed out by Chamberlain [16]. The use of radioactive ^{210}Pb or stable Pb isotope ratios as tracers may help to distinguish airborne Pb deposited on plant surfaces from that supplied from the soil by internal transport in the plant. Klaminder et al. [56, 57] studied the turnover of Pb in a coniferous forest in northern Sweden where the ^{206}Pb/^{207}Pb ratio in the soil C-horizon differed substantially from that supplied to the vegetation and soil surface by atmospheric deposition. They found that roots and basal stemwood of trees had higher the ^{206}Pb/^{207}Pb ratio than needles and apical stemwood, and concluded that the latter are more dominated by Pb from atmospheric deposition. In a similar woodland study in rural south central Ontario [114] between 65% and 100% of the Pb in vegetation was estimated to be from anthropogenic sources. Tjell et al. [105] made a pot experiment in a rural area of Denmark with Italian ryegrass, where they equilibrated the soil with radioactive ^{210}Pb and measured the specific activity (^{210}Pb activity divided by stable Pb concentration) in the crop and the soil. From this comparison it was evident that 10% or less of the Pb in the crop was derived from the soil and the rest from atmospheric deposition. Recently Hovmand et al. [45] made a corresponding pot experiment with Norway spruce, and found that less than 2% of the Pb in the needles was due to root uptake.

The substantial influence of airborne Pb to the total Pb content of vegetation was hardly realized during the early studies of Pb uptake in plants, and in some cases the conclusions drawn may have been influenced. For instance the finding of Guha and Mitchell [37] that Pb in leaves of deciduous trees fell over the growth season but increased again at senescence together with Na might partly be explained by airborne Pb. Generally the Pb translocation from soil to shoots was probably overestimated.

According to Antonovics et al. [3] the uptake of lead by a plant is generally constant with increasing soil lead levels until a certain point is reached when uptake becomes unrestricted and rises abruptly. Excess above a critical level will impair the health of the plant or will kill it [39]. In the vicinity of Pb ore deposits where the surface soil may reach very high levels the frequency and distribution of plant species is strongly modified. As an example the heather species *Vaccinium myrtillus* and *Calluna vulgaris* are being replaced by the grass species *Deschampsia flexuosa* [60, 79]. Reeves and Brooks [84] described some plant species growing on mine tailings showing Pb levels up to 8,200 mg kg^{-1}.

14.7 Remediation of Lead Polluted Soils

Over the last 20 years considerable efforts have been exercised in order to reduce the hazard associated with strongly contaminated soils either by *in situ* stabilization or by removal of the major fraction of metal by chemical or biological means. Various soil remediation techniques described in the literature were reviewed by Mulligan et al. [72]. *In situ* stabilization of Pb-contaminated soil by amendment with phosphate in various forms has been suggested by many researchers [41] and seems to be favorable in the case of agricultural soils. Other approaches suggested depend on physical or chemical separation based on soil washing (reviewed by Dermont et al. [27]) or phytoextraction; growing plant species that can accumulate high amounts of Pb [46]. Addition of synthetic chelating agents may increase the plant uptake (*e.g.,* Huang et al. [47], Shen et al. [91]).

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Chapter 15
Mercury

Eiliv Steinnes

Abstract In spite of its low abundance in the Earth's crust, mercury (Hg) has aroused substantial attention, first because of its numerous applications and more recently because of its toxicity. The extensive use of Hg has resulted in significant contamination of soils locally and regionally and sometimes to human and animal exposure at toxic levels. Human use of Hg started already in antiquity and reached a maximum around 1975. Since then the major applications have been strongly reduced in many countries. All chemical forms of Hg are toxic to humans and animals, methyl Hg in particular. In soils Hg may originate from Hg minerals, diffuse air pollution, and local pollution sources such as chlor-alkali factories and the use of sewage sludge and organic Hg compounds in agriculture. Elemental Hg from the atmosphere mainly due to previous human emissions is a dominant source of soil pollution worldwide. In soils, Hg occurs as various forms of Hg(II), generally strongly bound to organic matter and sulphides. The Hg content is generally higher in organic-rich soils than in mineral soils. Root uptake of Hg in plants is generally low, and Hg in above-ground plant material is mostly derived from atmospheric deposition. Under reducing conditions in soils methyl Hg may be formed and subsequently transported to lakes and rivers and accumulated in aquatic food chains.

Keywords Mercury • Contamination • Chlor-alkali plants • Coal burning • Methyl mercury • Agricultural chemicals • Sewage sludge • Soil organic matter • Volatilisation • Toxicity

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15.1 Introduction

There is archaeological evidence that mercury (Hg) has been known and used by humans for at least 3,500 years [68]. The ancient Egyptians apparently knew how to make amalgamations with tin (Sn) and copper (Cu) as early as the sixth century BC, and uses of Hg metal and cinnabar (HgS) in medicine existed in China and India at the same time. The Greeks were also familiar with techniques for the extraction of Hg from ores and with medical applications of the element. The Romans inherited most of this knowledge and greatly extended the commercial applications of the metal, mainly by production of the red pigment vermillion. After the fall of the Roman Empire, Hg consumption was chiefly restricted to medicinal and pharmaceutical uses until the sixteenth century when silver (Ag) mining started in Spanish America [34]. Somewhat later the invention of scientific instruments such as the barometer and thermometer involved the introduction of metallic Hg into scientific research. More recently Hg and its compounds have found a great number of new applications. The extensive use of Hg has led to large-scale dispersion of the element in the environment and in some cases to significant human health problems.

World production of Hg remained at a high level for several centuries [34]. Already around the year 1600 annual production was about 400 t, increasing gradually to about 1,000 t around 1800, 2,000 t in 1850, 4,000 t in 1900 and 8,000 t during the period 1961–1980. During the 1990s the annual world production declined from about 6,000 t to less than 2,000 t, following the increasing concern about the toxicity of Hg compounds to man and the environment. The total amount of globally mined Hg over all years may approach 1,000,000 t. The main Hg mines in Europe were located in Spain, Italy, and Slovenia. In the year 2000, predominant contributions to Hg mining were from Algeria, Australia, China, Kyrgyzstan, Spain, Tajikistan, and Tunisia.

15.1.1 Previous and Current Uses of Mercury

The principal uses of Hg have undergone great changes over the last century. At the turn of the nineteenth century the main uses of the metal were in the recovery of Au and Ag and the manufacture of fulminate and vermilion [68]. While these uses have essentially disappeared, a number of new applications of Hg and its compounds appeared during the first half of the twentieth century; in pharmaceuticals, agricultural chemicals, paints, measuring instruments, and electrical components. One significant industrial application is the Hg-cathode electrolysis cell used in the production of chlorine (gas) and sodium hydroxide (chlor-alkali process), which is still leading to significant local pollution problems in some places [74]. The trends in Hg use are illustrated in Table 15.1, which shows the developments in annual consumption among major areas of use in the U.S.A. for selected years

Table 15.1 Main areas of Hg consumption in USA (metric tons) during the period 1941–1990 (Jasinski [37])

Areas of use	1941	1950	1960	1970	1980	1990
Chloralkali industry	5	45	214	517	326	247
Paint	23	106	146	357	297	22
Pharmaceutical uses	92	207	60	24	na	na
Agriculture	68	155	223	70	na	0
Electrical uses:						
Batteries	na	na	na	na	959	106
Total	162	415	319	550	1,106	209
Measuring and control instruments	125	186	225	167	105	106
Dental uses	21	50	61	79	61	44
Other uses	1,041	506	471	294	125	58
Total	1,544	1,697	1,764	2,120	2,033	720

na Not available

during the period 1941–1990 [37]. Applications of Hg and its compounds have been strongly restricted in many countries over the last two to three decades, but some uses continue, such as small-scale Au mining from river sediments in several developing countries [71].

15.1.2 Release of Mercury to the Environment

The most significant anthropogenic activities giving rise to past and present emissions of Hg to land, water, and air appear to be the following:

(i) Mining and smelting of ores, in particular Cu and Zn smelting.
(ii) Combustion of fossil fuels, mainly coal.
(iii) Industrial production processes, in particular the Hg cell chlor-alkali process and cement production.
(iv) Consumption-related discharges, including waste incineration.
(v) Gold production using Hg technology

Primary Hg emissions are to the atmosphere, followed by subsequent transfer to land and water. The period of highest global anthropogenic emissions was the late 1970s and the early 1980s [69] when the annual release amounted to around 3,600 t. Over the next two decades there was a decrease to about 2,200 t worldwide. In Europe emissions in the year 2000 were less than 30% of those in 1980. The global atmospheric Hg emission in 2000 was estimated to be ca. 2,190 t, about 65% of which was from fossil fuel combustion. Other appreciable sources were Au production (11%), non-ferrous metal smelting (7%), cement production (6%), caustic soda (NaOH) production (3%) and waste disposal (3%). More than 50% of the emissions occurred in Asia, with China as the main contributor. Other countries with high emissions included South Africa, India, Japan, Australia, and USA.

15.1.3 Harmful Effects of Mercury

No essential biological function of Hg is known. On the contrary, Hg is among the most toxic elements to man and many higher animals. All chemical forms of Hg are toxic to humans [18]. Inorganic forms of Hg show high acute toxicity, with a variety of symptoms and damage to organs. Some organomercurials, in particular low-molecular-weight alkyl compounds, are considered even more toxic to humans because of their high chronic toxicity with respect to various, largely irreversible, defects of the nervous system. Methyl Hg (CH_3Hg^+) is particularly significant in this respect because it is produced in nature by microorganisms where reducing conditions prevail. Methyl Hg shows strong teratogenic effects, and carcinogenic and mutagenic activity has also been implied.

Occupational Hg poisoning, e.g. in miners, has been known over the last few centuries. Environmental Hg poisoning however is probably of more recent date. The first known case was in Japan during the late 1950s where inhabitants of the small town of Minamata were poisoned by the consumption of fish containing high levels of methyl Hg. Several cases of wildlife poisoning from seeds treated with methyl Hg were documented in Sweden during the period 1948–1965 [52]. Investigations initiated because of these events and carried out during subsequent years showed that elevated methyl Hg levels in fish were widespread globally. Thus methyl Hg is the dominant toxic Hg species in the environment, consumption of fish and crustacea being the main hazard to humans and higher animals.

On the other hand Hg does not seem to represent a major problem with respect to phytotoxicity [2]. The levels at which toxicity symptoms are apparent in plants are far above those encountered under normal conditions. In general the availability of soil Hg to plants is low, and the roots serve as a barrier to Hg uptake.

Hg^{2+} is one of the metal ions that are the most toxic to soil biota. Experiments carried out in forest soil in Sweden showed that adding Hg^{2+} to a level of 5 $\mu g\ g^{-1}$ reduced microbial respiration by 30–40% after a period of 60 days [11].

15.2 Geochemical Occurrence

Although more than 20 principal Hg minerals are known in nature, commercial production of Hg is made almost entirely from cinnabar, HgS [68]. Mercury also occurs in the Earth's crust as complex sulphides with Zn, Fe, and other metals, but only to a small extent as the native metal. The major Hg deposits may have formed from hydrothermal solutions, which transported Hg as sulphide or chloride complexes. The crustal average content of Hg is of the order of 50 $\mu g\ kg^{-1}$ [2] or perhaps even lower. A further discussion of Hg abundances in different rocks is given in Sect. 15.3.

Cinnabar is resistant to the normal processes of oxidation and weathering and is extremely insoluble in water, and therefore enters the geochemical cycle mainly in the form of mechanically degraded particulate material. A far more important source for the release of Hg from crustal rocks is degassing of elemental Hg. Some gaseous Hg is also contributed by volcanic emissions, from vegetation, and from the ocean. The most significant chemical species of Hg participating in the geochemical cycling of this element may be classified as follows [52]:

Volatile compounds: Hg^0; $(CH_3)_2Hg$.

Reactive species: Hg^{2+}, HgX_2, HgX_3^-, and HgX_4^{2-} with $X = OH^-$, Cl^- or Br^- ; HgO on aerosols, Hg^{2+} complexes with organic ligands.

Non-reactive species: Methyl mercury (CH_3Hg^+, CH_3HgCl, CH_3HgOH) and other organomercurial compounds; $Hg(CN)_2$; HgS; Hg^{2+} bound to S in humic matter.

Typical background concentrations in air [52] are about 3 nM m^{-3} over land and slightly lower over sea, mostly in the form of Hg^0. In aquatic systems representative concentration ranges of dissolved Hg may be considered to be 0.5–3 ng L^{-1} in the ocean and 1–3 ng L^{-1} in lakes and rivers, most of which as inorganic Hg(II) species.

15.3 Origin of Mercury in Soils

The original Hg sources common to all soils are the minerals constituting the rocks forming the soil parent material. In the case of surface soils atmospheric deposition is also a significant source, which has become exceedingly important with the increasing contributions from anthropogenic activities to atmospheric Hg. In the case of agricultural soils the use of fertilisers (commercial fertiliser, manure, sewage sludge), lime, and Hg-containing fungicides may sometimes increase substantially the Hg load.

15.3.1 Soil Parent Materials

Data for Hg in rocks have been produced for more than 50 years, and more data are available than for most other trace elements present in rocks at similar concentration levels. Some of the older data reported in the literature however, may be erroneously high. Nevertheless, there is reasonable consistency in at least one respect, notably that the Hg content of rocks containing no organic matter is very low, frequently below 30 μg kg^{-1} [86]. Organic-rich shales can contain concentrations of >1,500 μg kg^{-1} [16]. Wedepohl [93] estimated the mean crustal Hg concentration to 40 μg kg^{-1}, assuming 56 μg kg^{-1} in the upper and 21 μg kg^{-1} in the lower crust.

15.3.2 Atmospheric Deposition

Some of the Hg present in soil and natural waters may be transformed to volatile species that are emitted to the atmosphere [52], mainly as Hg^0 and dimethyl mercury ($(CH_3)_2Hg$), which can both be released by biogenic processes. Around 97% of gaseous Hg in the atmosphere is Hg^0. The residence time of Hg^0 in the atmosphere is long, probably as much as 1 year [52].

It is suggested that Hg^0 is eventually subjected to atmospheric oxidation processes that yield water-soluble forms subsequently scavenged by wet or dry deposition [12]. In industrial areas, air pollutants such as ozone may significantly influence the formation rate of oxidized Hg species [36]. The extent of Hg removal from the atmosphere by dry deposition is not well known [52]. As far as wet deposition is concerned typical concentrations in precipitation at remote sites appear to be of the order 2–10 ng L^{-1}, whereas levels in more polluted areas may typically be of the order of 5 times higher, excluding areas in the vicinity of specific Hg-emitting industries. With an annual precipitation of 1,000 mm and a Hg content of 20 ng L^{-1} the wet deposition is 20 mg/m^2/year, which corresponds to the values reported by Lindqvist et al. [53] for southern Scandinavia. More recent wet deposition values in this region are significantly lower, consistent with reduced Hg emissions in Europe over the same period, whereas the deposition of total gaseous Hg shows no similar decrease [94].

It has generally been assumed that most of the Hg emitted to the atmosphere even from anthropogenic sources is in the elemental vapour form [57]. For high-temperature combustion processes at least, this seems questionable. Brosset [13] found that a fraction of the order of 50% of the emission from a coal combustion plant was present as forms of Hg[II]. If this is representative the deposition of Hg from coal-fired power plants or waste incinerators may be more significant than generally assumed in the past.

Investigations in Scandinavia [32, 87] and USA [66] indicate that long-range transport from anthropogenic sources is a much more significant source of Hg to surface soils than previously anticipated, at least for humus-rich natural soils. In Sweden more than 50% of Hg in the soil humus layer was supposed to be of pollution origin [32], partly from a small number of domestic point sources, partly from source regions elsewhere in Europe. Recent studies on dated peat cores from ombrotrophic bogs indicate that deposition of Hg during recent decades may have been several times higher than in medieval times [10, 89]. There is evidence that Hg^0 may be retained by soils as an organo-complex [47]. A review on sequestration of atmospheric Hg in forests and peatlands was published by Grigal [31].

The high content of methyl Hg in fish in several regions of Europe and North America focused great attention on the widespread atmospheric deposition of Hg even very far from the source regions. Perhaps the most extensive study on the pathways of Hg from air via soil to fresh waters was carried out in Sweden [53, 61]. At the deposition rates observed, about 80% of the supplied Hg was accumulated in the soil humus layer [1]. The transport of Hg into surface waters was found to occur mainly with humic matter, and was not appreciably affected by factors such as acidification [42].

Recently a new natural source of Hg deposition was discovered in the Arctic [78]. During the 3 months following polar sunrise frequent episodic depletion of gaseous Hg concentrations in air occurred. Presumably this effect is a result of photochemical activity involving reactive halogen species [51]. An important consequence of this depletion is increased deposition of oxidised Hg species during the same episodes, presumably leading to increased Hg loads to surface soils and to biota. Mercury depletion episodes at the arctic site of Ny-Ålesund were traced some days later at the north coast of Norway [9], indicating that the increased Hg deposition may also affect greater parts of the Northern hemisphere.

15.3.3 Agricultural Materials

Considerable amounts of Hg may be added to agricultural land along with fertilisers, lime, and manures, as evident from the literature figures summarized by Andersson [5]. Most commercial fertilisers have Hg concentrations less than 50 μg kg^{-1}, but considerably higher values occur in P fertilisers. The Hg may be derived partly from the phosphate rocks and partly from the H_2SO_4 used for their dissolution. Samples of lime tend to show values less than 20 μg kg^{-1}, whereas manure typically exhibits Hg levels on the order of 100 μg kg^{-1}.

Since the beginning of the twentieth century and several decades afterwards, Hg compounds were used in agriculture as fungicides and seed disinfectants. During most of the time organic Hg compounds were used, in particular during the period 1945–1970. The supply of Hg to the soil by seed dressing could in some cases be as high as 1 mg m^{-2}. A reasonable average from this supply seems to be 100–200 mg m^{-2} year^{-1} for cereal-producing soils, which is of the same order as the Hg already present in the upper 20 cm of the soil, and considerably more than what may be normally supplied by atmospheric deposition. Mercury fungicides however are no longer used in most countries.

15.3.4 Sewage Sludge

Sludge from wastewater treatment plants is frequently applied as fertiliser on arable land. Often restrictions are imposed on the use of sludge because of the high content of some heavy metals found in this material, including Hg. It appears from the examples of literature values selected by Andersson [5] that 5–10 mg kg^{-1} is a typical level in sludge, and more recent literature values [55, 66] confirm Hg levels of this order. Assuming that 50 t ha^{-1} of sludge containing 5 mg kg^{-1} of Hg are applied to the soil, the added amount of Hg is 25 mg m^{-2}, which is a considerable increment with respect to a normal background level. Fortunately, general efforts to reduce water pollution have led to a significant reduction of the Hg level in sludges in some countries [39, 67]. Cappon [14] studied the chemical form of Hg in sludge and found on average 6.0% methylmercury.

15.4 Chemical Behaviour of Mercury in Soil

15.4.1 Occurrence and Stability of Inorganic Mercury Species in Soil

Depending on the redox conditions, Hg may occur in three different oxidation states, namely as Hg(0), Hg(I), and Hg(II), of which Hg(0) and Hg(II) are the states normally encountered in soil. In addition to the redox potential, pH and Cl^- concentration are key parameters in the determining the speciation of Hg in the soil solution and the chemical transformations occurring. In addition to chemical reactions, transformations may also be mediated by microbial activity. Knowledge of the speciation and transformation reactions of Hg is important in order to explain its retention and mobility in the soil, equilibria between solid phases and soil solution, and availability for plant uptake.

Due to its strong ability to form complexes, Hg(II) rarely occurs as the free Hg^{2+} cation under natural conditions. In acid solution Hg(II) is stable at a redox potential above 0.4 V, and normally occurs as the $HgCl_2^0$ complex. Above pH 7 the complex $Hg(OH)_2^0$ complex is the corresponding stable form. Hg^{2+} also forms strong complexes with humic matter where bonding to reduced organic sulphur groups plays a major role [73, 84].

Another important property of Hg is its ability to bind strongly to the sulphide anion. Under strongly reducing conditions Hg^0 is stable in the presence of H_2S or HS^-, but at increasing redox potential HgS will precipitate, or in the case of strongly alkaline soils the soluble HgS_2^{2-} anion will be formed. Further increase will bring about oxidation of sulphide to sulphate, but at this point the potential may still not be high enough to prevent reduction to Hg^0. An increase in redox potential to the level normally found in surface soil may finally oxidise Hg^0 to the Hg(II) state. A more detailed treatment of the physical chemistry of Hg in aqueous solution is found in Andersson [5]. Schuster [79] reviewed the literature on behaviour of mercury in soil with emphasis on complexation and adsorption processes.

Only a very minute fraction of Hg^{2+} occurs in the soil solution, the major fraction being either bound in soil minerals or adsorbed to inorganic or organic solid surfaces. Since $HgCl_2^0$ is only weakly retained by mineral matter it can be assumed that Hg^{2+} is mainly attached to organic matter in acid soils, whereas in neutral or slightly alkaline soil mineral components are also active. According to Varshal et al. [92] Hg solubility in peat is mainly associated with fulvic acid complexes, whereas high-molecular-mass complexes with humic acids tend to immobilize the Hg.

15.4.2 Volatilisation of Mercury from Soil

Some investigators have observed loss of Hg added to soils in the form of inorganic salts [23, 76, 77] and found that organic matter tended to enhance the loss. The volatilisation seemed to be mediated by microorganisms [77], but significant losses were also reported from sterilised soils [23]. These studies were mostly carried out with Hg concentrations far above naturally occurring ones, and it is hard to evaluate the significance of the demonstrated reactions and processes for the Hg turnover under natural conditions [5].

Some of the experimental evidence seems conflicting with regard to the influence of pH and organic matter on the volatilisation of Hg from soil [97]. For soils low in clay and humus, more was evaporated from a neutral than from an acidic soil, whereas for two soils with 4–5% humus content and 15–17% clay the opposite was observed. In acid soil the higher humus content inhibited the vaporisation of Hg at the 1 mg kg^{-1} level in the surface layer, whereas at 50 mg kg^{-1} the loss was greater with the higher humus content. According to Andersson [5] a probable explanation might be that at low Hg content the humus exhibits sufficient complexing capacity to allow only a very small fraction to be present in the soil solution. At higher Hg contents, a significant fraction may be present in the solution and eventually be lost after reduction to Hg^0.

Under natural conditions the release of Hg^0 and possibly also other volatile Hg compounds from soil is probably very significant in the global cycling of Hg. Anomalously high concentrations of Hg^0 in air are frequently observed in the vicinity of Hg-bearing ores.

15.4.3 Leaching of Mercury from Soil

The strong ability of soil to fix Hg^{2+} species means that the removal of Hg from soils by leaching is in most cases insignificant [24, 33, 54, 96]. In an experiment where radioactively labelled Hg compounds were applied to soil columns, which were then leached with sewage effluent [33] neither $HgCl_2$, methyl mercuric chloride, nor phenyl mercuric acetate was found in measurable amounts below 20 cm depth in the soils. Lodenius et al. [54] studied the leaching of Hg in peat lysimeters and found that addition of chloride, fertiliser, or steriliser did not affect the leaching. The only treatment that had an effect was drying of the column, which resulted in cracks presumably allowing Hg bound to humus colloids to penetrate the column. Similar transport might occur laterally in surface soil layers during periods with surface runoff. The annual transport of Hg on humus colloids from forest soils to lakes in Sweden however is estimated to be less than 1% of the amount stored in the humus layer of the soil [41].

15.4.4 Retention of Mercury in Soil Material

Adsorption is apparently dominant in providing the retention of Hg species in soil. Adsorption of Hg depends on a number of factors, including the chemical form of Hg introduced, the grain size distribution of the soil, the nature and amount of inorganic and organic soil colloid, the soil pH, and the redox potential. In addition Hg^{2+} may be fixed in the form of low-solubility precipitates, in particular the sulphide and the selenide.

The retention of Hg^{2+} may occur as a result of ion exchange, but stronger bonds are probably involved to a large extent, such as hydroxyligands in the case of sesquioxides and various ligands in the case of humic substances. Andersson [5] found the following retention of inorganic Hg under neutral conditions: $Al(OH)_3 < \text{kaolinite} < \text{montmorillonite} < \text{illitic clay soil} < \text{lateritic soil} < \text{organic soils} < Fe_2O_3.nH_2O$. Below pH 5.5 where $HgCl_2^0$ is the dominant species in solution, organic matter will be mainly responsible for the retention of $Hg^{2+\cdot}$ The maximum adsorption occurs at around pH 7, where $HgOHCl^0$ is the dominant species [5]. Also organomercury compounds such as methylmercuric chloride and phenylmercuric acetate are strongly adsorbed in soil in the pH range around neutrality [33].

15.4.5 Methylation of Mercury in Soil

Since the observation that microorganisms in natural lake sediments could methylate Hg [40] numerous studies confirming the production of methyl-Hg in the aquatic and terrestrial environment have been carried out. It appears that methyl-Hg may be formed in soils under a variety of conditions, including purely abiotic methylation [76] possibly associated with the fulvic acid fraction of the soil. Matilainen et al. [58], in a lysimeter experiment in pine forest, supplied precipitation containing mercuric chloride labelled with radioactive ^{203}Hg. After a treatment period of 97 days they measured extractable ^{203}Hg and found significant formation of methyl ^{203}Hg in the surface soil and particularly in the moss covering the soil surface. Significant methyl-Hg runoff was observed from forested catchments subject to logging operations using heavy machinery strongly disturbing the surface soil [65, 72]. Some of this methyl-Hg, however, may have been derived from litterfall [80]. Skyllberg et al. [85] studied methyl-Hg in streams draining spruce forest stands subjected to clear-cut, and found that 4 years after the clear-cut, less than 20% could be ascribed to enhanced mobilisation from the soil whereas the rest was due to new methylation of Hg(II) during the intermediate period.

Methylation is generally most likely to occur in water-saturated soils where anaerobic conditions prevail, and Hg(II) in the soil solution appears to be more available for methylation than soil bound Hg(II) [83]. The amounts of methyl-Hg reported for forest surface soils are of the order of one to a few percent of the total Hg content.

Table 15.2 Selected literature data for Hg contents of surface soils

Country	Soil type	Number of samples	Hg (ng g^{-1}) Range	Average	References
Austria	Cultivated and non-cultivated (0–20 cm)	40	5–340	95	[90]
Belgium	Cultivated and non-cultivated (0–20 cm)	316	30–4,190	100[a]	[35]
Canada	Virgin soils, A-horizon	65	<5–660	64	[48]
	Cultivated and virgin, A-horizon	170	13–741	102	[77]
	Cultivated (0–15 cm)	290	10–1,140	110	[66]
Norway	Forest soil, A0-horizon	700	20–550	188	[54]
	Ombrogenous peat (0–5 cm)	21	35–255	115	[17]
	Ombrogenous peat (0–5 cm)	11	56–341	188	[27]
	Ombrogenous peat (30–100 cm)	42	3.3–34	13.3	
Spain	Predominantly cultivated	618	1–216	34	[20]
Sweden	Cultivated and non-cultivated (0–20 cm)	273	4–920	60	[74]
UK	Cultivated and non-cultivated (0–15 cm)	51	10–1,780	32	[94]
	Cultivated (0–15 cm)	305	20–400	90[a]	[18]
USA	Surface soils (entire country)	912	<10–4,600	112	[70]
	Surface soils (Western states)	492	<10–4,600	83	
	Surface soils (Eastern states)	420	10–3,400	147	
	Surface soils (Florida)	600	10–670	162	[36]
	Surface horizon (Missouri)	1,140	<10–800	39	[53]
	Surface horizon (Colorado)	168	<10–420	35	
	B horizon (Eastern states)	420	10–3,400	96	
	B horizon (Western states)	492	<10–4,600	55	
	Urban and agricultural (0–5 cm)	264		110	[24]
	Cultivated (0–15 cm)	200		30	[44]
	Cultivated (0–7.5 cm)	96	50–360	120	[1]

[a] Median value

15.4.6 *Concentration and Distribution of Mercury in Soils*

In most soils the Hg content changes with depth, which means that the sampling depth is important. In cultivated soils the plough layer (0–20 cm) is homogenised due to soil management. Comparison of data from cultivated and non-cultivated soils is therefore difficult. In the case of comparisons between different virgin soils, similar sampling depths or the same horizons should be used [5].

In Table 15.2 some selected literature data showing typical Hg levels in presumably uncontaminated soils are listed. Most of the data are from North America, Scandinavia, and the UK. Few comprehensive data sets seem to exist for southern and eastern Europe, Asia, Africa, Latin America, and Australia. Some of the early investigations listed in Table 15.2 may have included agricultural soils treated with organomercurials. By and large, however, the data are thought to be representative for areas with no appreciable influence from local anthropogenic sources giving rise to elevated levels in the surface soil.

Organic soils commonly have higher average Hg contents than mineral soils [22, 43]. This is also demonstrated by the examples shown in Table 15.2, where soils rich in organic matter generally show Hg values of 0.1–0.2 mg kg^{-1} whereas mineral soils and surface soils from areas poor in organic matter are typically 0.05 mg kg^{-1} or less. Låg and Steinnes [48] found a highly significant correlation between Hg and organic matter content in the surface layer of forest soils. Andersson [4] in a study of Hg profiles of virgin soils demonstrated a very close correlation between Hg and organic matter content in acidic soils, whereas in neutral soils ($pH > 6$), where the dominated species are HgOHCl and $Hg(OH)_2$ rather than $HgCl_2$, the co-variation between Hg and Fe was stronger than that of Hg and organic matter. The distinctly higher Hg content observed in soils in the eastern compared to the western USA [82] could possibly in part be explained by differences in soil organic matter.

In some cases, such as the Chernozem and Luvisol soils in Alberta studied by Dudas and Pawluk [19], Hg appeared to be depleted in the surface layer relative to lower horizons. In soils with low organic matter content and $pH > 6$ this trend might be expected. However, McKeague and Kloosterman [59], in an extensive survey of soils from all the provinces of Canada, observed that in more than half of the samples, particularly podzolic and gleysolic soils the highest Hg concentrations were present in the surface layer.

In cultivated soils the Hg level is normally quite constant within the plough layer. Below this layer there is a gradual decrease downwards to the background level in the parent material [5, 95]. In some cases however the content in the surface horizon is similar to that of the subsoil [63].

Ombrotrophic bogs offer a unique opportunity to study the transfer of Hg between the atmosphere and organic soil virtually independently of the underlying mineral material [25, 38]. In a study of ^{14}C-dated peat profiles from six bogs at different latitudes (58–69°N) in Norway [89] the Hg concentration in the surface peat layer was of the order of 10–20 times higher than at 50 cm depth, representing an age of 2200–3600 BP. This indicates that the recent atmospheric supply of Hg in this area may have been an order of magnitude higher than the pre-industrial level, provided that no re-distribution of Hg in the peat has occurred.

In the survey presented by Ure and Berrow [91], data for the Hg content of 3049 soils averaging 0.098 mg kg^{-1} were reported. No similar calculation is presented for the data listed in Table 15.2, because the format of reporting is not uniform. Some investigators include all data obtained on a given material, while others exclude anomalous values before calculating the average. What seems to be evident, however, is that the Hg content of surface soils frequently exceeds to a substantial degree that of the mineral material from which it was derived. Much of this excess Hg may be present in some form that permits its participation in exchange processes in the soil and between soil and atmosphere. It also appears that the surface content is distinctly higher in soils with high organic matter contents.

15.5 Mercury in the Soil-Plant System

The uptake of Hg in terrestrial plants has been the subject of numerous investigations [2]. Most of the work has been performed on agricultural crops under experimental conditions, and almost exclusively with Hg loads far above those encountered under normal conditions. In general the availability of Hg in soil to plants is low, and there is a general tendency to Hg accumulation in the roots, indicating that roots serve as a barrier to Hg uptake [50]. Experiments on the uptake of Hg^{2+} in higher plants from a solution culture [8] showed a certain transport to the shoots at levels exceeding 0.1 mg kg^{-1} of Hg in the external medium. The fraction of Hg retained in the roots was about 20 times that observed in the shoots. Lindberg et al. [50] studying the plant uptake of Hg from agricultural soils near a Hg mine found that the relative Hg content in roots was closely related to the NH_4OAc-extractable Hg in the soils. The Hg content in above-ground parts of plants, on the other hand, appeared to be largely dependent on foliar uptake of Hg^0 from the atmosphere. More recent research [26, 29, 30, 62] supports the view that translocation of Hg from plant roots to the foliage is very limited. Ericksen et al. [20] found that almost all Hg in aspen foliar tissue originated from the atmosphere.

The Hg content in plants grown on soils low in Hg was reported to be in the same range as for the soils [28]. In the case of cereals the content in grain was about 3–10 times lower than that of the straw. Other work indicated still lower Hg levels (1–2 μg kg^{-1}) in grains of barley and wheat [49]. Even at these low levels it may be assumed that foliar uptake of Hg^0 from the air plays a significant role.

15.6 Soils Heavily Polluted with Mercury

Anthropogenic activities giving rise to Hg emissions to the atmosphere may significantly contaminate soils in the neighbourhood of the emission sources. These activities include smelting of non-ferrous metals, burning of fossil fuels, industrial activity such as the chlor-alkali process, and waste incineration. Soil contents of the order of 1–10 mg kg^{-1} Hg were found at distances <0.5 km from a chlor-alkali plant [64]. The highest concentration value ever reported for Hg in soil appears to be 17,100 mg kg^{-1} (1.71% Hg) at a chlor-alkali plant in Kazakhstan [74].

In the vicinity of mercury mines, values of the order of 100 mg kg^{-1} have been observed in agricultural soils [50, 64]. In the Idrija Hg-mine region the total Hg concentrations in contaminated soils varied between 8.4 and 415 mg kg^{-1} [46], and fractionation experiments indicated cinnabar to be the predominant Hg fraction, followed by Hg^0. Ferera et al. [21] reported values within the range 90–212 mg kg^{-1} in soils at Monte Amiata, a mining area in Italy. Sometimes elevated Hg levels are observed in soils from volcanic areas [44].

For a long time the most significant problem of Hg pollution of agricultural soils was that of organic mercury compounds added in the form of seed dressing and of foliar spray against plant diseases [5]. These practices have now been discontinued in most countries, but seed dressing applications have been reported until recently [70].

15.7 Global Distribution of Mercury

The release of volatile Hg compounds from the land surface and the atmospheric deposition of Hg acting in the opposite direction are important processes not only for the Hg chemistry in soils but also for the global circulation of Hg. According to Mason et al. [56], 70–80% of the current Hg emissions to the atmosphere are of anthropogenic origin. As most of the Hg deposited to the oceans is recycled to the atmosphere, the terrestrial environment becomes the principal atmospheric Hg sink. Mason et al. estimated the annual global Hg deposition on land to be about 1.8×10^9 g, and a similar deposition to the oceans. Andren and Nriagu [6] estimated the global Hg store in soils to be 2×10^{13} g, which may seem slightly high. Assuming a mean Hg concentration in surface soils (upper 0.5 m) of 0.05 μg g^{-1} worldwide (cf. Table 15.2) and a mean soil density of 1 g cm^{-3} the total amount of Hg in the Earth's surface soils is around 3×10^{12} g.

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Chapter 16
Selenium

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Abstract Selenium (Se) is both an essential micronutrient for animals and humans and potentially toxic at relatively low intakes. Total soil Se is usually low (0.01–2 mg/kg), but parts of China, India and the USA have toxic soil Se levels. Available soil Se is poorly correlated with total soil Se and is highly variable, both locally and globally. The plant availability of Se in soil depends on the major Se species present and on soil characteristics, including the quantity of sorption components (aluminium and iron oxide/hydroxides), pH and redox status. Also, the presence of anions competing for the same sorption surfaces (including sulphate, phosphate and organic anions) affects root uptake and retention of Se in soil, and microbial activity is important for Se interactions with organic matter. Depletion of Se and S is common in soils of Sub-Saharan Africa, due to soil erosion, leaching and volatilisation through burning. The only viable long-term solution, especially for farmers who cannot afford commercial fertilisers, is to re-establish agricultural ecosystems that are closer to the natural ecosystems they replaced. Selenium is not considered to be essential for higher plants; however, it has numerous health roles

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in humans and animals, mostly mediated by Se-dependent enzymes. Although diseases associated with profound Se deficiency (Keshan disease, Kaschin-Beck disease and myxoedema) are rare, suboptimal intake is widespread and may increase risk of heavy metal toxicity, certain cancers, cardiovascular diseases and HIV disease. It is possible to biofortify food crops using selenate, but a high proportion is retained in the soil, and more targeted supplementation may be preferable to conserve this scarce micronutrient.

Keywords Selenium • Micronutrient • Selenate • Selenite • Redox • pH • Availability • Se deficiency • Seleniferous • Adsorption • Selenide

16.1 Introduction

Selenium (Se) is a non-metal (or metalloid) capable of strong antagonistic biological interactions with a number of potentially toxic metals (depending on dosage range and time of accumulation), like cadmium (Cd), mercury (Hg) and silver (Ag); it can thus protect against various toxic effects of these metals [47, 153, 161], although it is less effective against the toxic effects of lead (Pb) [47], perhaps because PbSe is much more easily oxidized compared to CdSe, HgSe and Ag_2Se (with Pb^{++} being easily oxidized to Pb^{+++}, while Cd^{++} and Hg^{++} are resistant to oxidation). The biological interaction with some of the metals concerned, as seen in animal experiments [47, 153, 161], is so strong that it may almost be compared to a chemical titration process. Selenium belongs to the same group in the periodic system as sulphur (S) and is similar to S in its general chemical properties, but somewhat different from the latter in its oxidation-reduction (redox) behaviour at ambient temperature (with the oxidation number +4 being much more stable for Se than for S). It is highly chalcophile (in Goldschmidt's classification system [54]), almost more than S itself, with selenide ions substituting for S in sulphide minerals, and heavy metal selenides are less soluble than the corresponding sulphides [20, 25]. Like S, Se is also highly siderophile [120].

16.2 Geochemistry of Selenium

The name *selenium* refers to the Greek Moon goddess Selene. While the Moon is more depleted than the Earth in several moderately volatile elements including alkali metals and gold (Au), S and Se are found at similar concentrations in lunar rocks as on the Earth [120]. This (and also the high FeO concentration of the lunar mantle) can only be explained if the Moon was formed from matter that had been in a moderately oxidizing environment, where the H_2/H_2S and H_2/H_2O ratios were two orders of magnitude less than in solar gas. Both S and Se are much less volatile under these conditions than in a more reducing environment, corresponding to the composition of the Sun [120]. The Earth must also have been formed from matter that had been in a similar, moderately oxidizing environment in order to explain the high total abundance of ferrous iron (Fe) in the Earth's mantle while also being depleted in alkali metals [120], although not as much as the Moon. The low average abundance of S and Se in mantle and crustal rocks on the Earth can therefore not be explained by evaporation from planetisimal matter before the Earth was formed (even though the temperature was high enough that Na and K partially evaporated). Instead it must be explained as a consequence of the strongly siderophile properties of these elements; *i.e.* they must have sunk down as part of an Fe-rich, but also sulphide-rich melt phase when the Earth's core was formed. It is therefore likely that S must be the principal so-called 'light element' in the Earth's core, which is important for estimation of the temperature regime during core formation.

The average Se/S concentration ratio in igneous rocks like basalts and granites on the Earth is similar to the Se/S concentration ratio found in the solar system as a whole with Se being four orders of magnitude less abundant than S, when considering atomic proportions [81, 143]. Thus there seems to have been little fractionation of Se relative to S both when the Earth itself and when its core were formed. Selenium must apparently have been highly abundant in the seawater or in the atmosphere at the time when life originated on our planet and the universal genetic code appeared, judging from the presence of selenoproteins in all three major subdivisions, or kingdoms, of living organisms, *viz.* the archaea, the bacteria and the eukaryotes, with the amino acid selenocysteine being incorporated during translation and using the same codon (UGA, or TGA in the DNA molecule) in all three. The use of selenocysteine as a building block in proteins seems thus to go back to the time when the universal genetic code originated. It may be speculated that this could have happened as a result of the different redox behaviour of Se and S at low temperatures, with both elements released abundantly during volcanic degassing (possibly at the same time as the Earth's core was formed). Sulphur was removed from seawater much more rapidly than Se both in the form of sulphate (or sulphate/silicate, such as scapolite) and sulphide minerals, but Se would stay in solution together with phosphate in the form of selenite ions (at a time when the Ca^{++} concentration was several orders of magnitude less than in seawater today because of the combination of high CO_2 fugacity and simultaneous equilibrium of the seawater with dolomite and hydrous Mg carbonate minerals). It is likely that Se, because of its redox, catalytic and metal-binding properties, may have played an important role during the prebiotic evolutionary emergence of the first living systems.

16.3 Selenium Concentration, Behaviour and Plant Bioavailability in Soils

16.3.1 Origin of Soil Selenium and Variable Levels in the Earth's Crust

Total Se concentrations are low in most soils, usually in the range 0.01–2.0 mg kg^{-1}, although levels as high as 1,200 mg kg^{-1} can occur in seleniferous soils [45].

The average concentration of Se is much higher in some of the common sedimentary rocks, especially shale and coal, compared to igneous rocks such as basalt, andesite and granite [4, 81]. The surplus Se found in sedimentary rocks comes partly from volcanic gases, but perhaps also from hydrothermal exchange processes between seawater and lava along the mid-oceanic ridges. Topsoil Se concentrations are often, but not always, much higher than in the local bedrock, which can partly be explained by Se vertical transport through the plants, but sometimes also by long-term accumulation of Se deposited from the atmosphere. However, available (soluble or not too strongly adsorbed) soil Se is poorly correlated with total soil Se and is also highly variable both locally and globally [30, 114]. An example of local variability in soil available Se is provided from a South Australian field trial, where four replications of a single wheat (*Triticum aestivum*) cultivar were grown in one field, and the grain Se concentration varied sixfold (0.110–0.690 mg kg^{-1}) [95]. The mobility and plant-availability of Se in soil is controlled by numerous chemical and biochemical processes: sorption, desorption, microbial activity, formation of organic and inorganic complexes, precipitation, dissolution and methylation to volatile compounds [13, 17, 59, 109].

Sewage sludge is widely used as a fertiliser, being valued for its content of organic matter, N and P. However, it can also contain high levels of undesirable elements such as Pb and Cd [109, 119]. Most Se is removed from municipal wastewater at the first stage and thus concentrated in the sludge, but is generally found at lower levels than Cd, Pb, Ni and Zn [109]. It is not easy to evaluate the net biological effect when intakes of Se and Se-antagonistic toxic metals are simultaneously enhanced (as from sewage sludge) because one must take into consideration important differences between Se and the metals both as regards the extent of intestinal absorption and rates of excretion, with Cd and Pb both having extremely long biological half-lives in humans [153]. Selenium concentrations in the range 1.7–8.7 mg/kg were found in a study of sewage sludges from 16 metropolitan areas in the USA [109], but Se in sewage sludge has been found to be of low bioavailability to plants [76]. In a study in Japan, selenite was found to be the predominant Se form [144]. Conversely, in a study of Se and As in soil solutions of fly ash-, poultry litter- and sewage sludge-amended soils, selenate was found to be the main soluble Se form in all treatments [71].

16.3.2 Role of Atmospheric Deposition as a Source of Selenium in Soils

The atmosphere constitutes a significant source of Se to surface soils, with atmospheric Se coming from both anthropogenic and natural sources. The major anthropogenic source of Se to the atmosphere is combustion of fossil fuels, responsible for 62% of the worldwide emissions in 1983 [113]. The average Se concentration in coal is high (because of the combined effects of atmospheric Se deposition from natural sources and active Se uptake in the plant roots), and coal combustion is therefore one of the major anthropogenic sources of Se emission to the atmosphere. However, coal combustion is also a major source of the Se-antagonistic elements As and S, as well as of various toxic metals. Another 22% is estimated to come from pyrometallurgical processes (metal production from sulphide ores), and the total emission is estimated at 5,780 t. Selenium is emitted in volatile form (as SeO_2) from high-temperature sources, including forest fires and garbage combustion, and is likely to condense preferentially on small particles [52]. This makes it available for long range atmospheric transport, which may affect land areas far from the source [139].

Emissions from natural sources must be considered an equally, if not even more important source of atmospheric Se, especially since they sometimes can lead to Se accumulation in the soils over very long periods of time (thousands or ten thousands of years), while much of the anthropogenic emissions (*e.g.* from large-scale coal combustion) only go back to the start of the industrial revolution. While Se deposition from anthropogenic sources can locally be more important compared to natural deposition (near areas with much industrial activity), the natural sources are nevertheless equally or more important when considering the planet as a whole. Natural soils in Norway were shown to exhibit substantially higher Se concentrations near the Atlantic coast than further inland. In some areas, topsoil Se concentrations are so high as a result of high deposition rates from the atmosphere, both naturally from the sea and from acid rain, that they approach levels found in seleniferous areas in the USA [97, 98, 138]. The observations from Norway indicated that the ocean is a major source of Se to the terrestrial environment, but this remained unexplained until the discovery of biological methylation of Se in the aquatic environment [33]. Mosher and Duce [107] estimated a mean global annual emission of Se to the atmosphere of 6,000–13,000 t, with 60–80% of marine biogenic origin. Marine biogenic emission in this order of magnitude has more recently been confirmed by other authors [3].

16.3.3 Speciation of Selenium in Soils: Inorganic Compounds

The oxidation states of Se in soils range from −2 to +6, depending on pH and redox potential. The dependence of Se speciation on pH and redox potential is illustrated in Fig. 16.1. At pH levels above 6, which includes most agricultural soils, the element exists predominantly in oxidation states +4 and +6. However, it can be reduced to negative oxidation numbers, even in well-oxygenated environments, as a result of biological processes (*e.g.* in the form of dimethylselenide). The actual distribution of different Se species in soil does not correspond strictly to what should be expected in a situation of thermodynamic equilibrium either in well-aerated or waterlogged soils. Selenide ions can be formed by living organisms even under conditions where they are not at all thermodynamically stable.

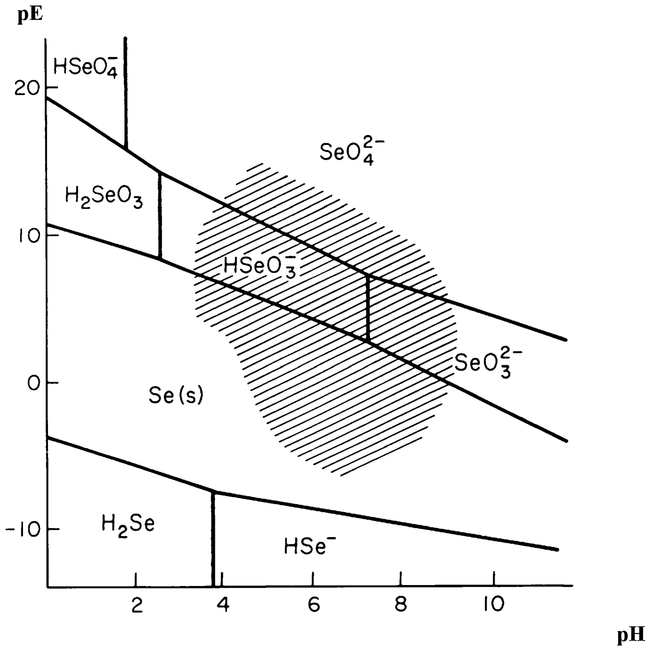

Fig. 16.1 pE-pH diagram for the system Se-H_2O under the condition $Se_T = 78.96$ μg l^{-1} (1 mmol m^{-3}) (Reproduced from Neal [109], Copyright (1995) with permission from Springer)

The speciation of Se in the soil is very important for its bioavailability for uptake into the plant roots. Selenate is the major form in soil solution under high redox conditions (p*e* + pH > 15, where p*e* is a negative measure of electron activity, derived from the redox potential, Eh, similarly as pH is a negative measure of proton activity), while selenite is the main form at medium redox potential (p*e* + pH 7.5–15) [42]. Se^{4+}, which may exist either as selenite (SeO_3^{2-}) or biselenite ($HSeO_3^-$) depending on pH, and Se^{6+} as selenate (SeO_4^{2-}) are the forms of selenium primarily responsible for the reactivity of this element in soils. The position of Se redox couples relative to the reactions normally governing the redox potential in soils is shown in Table 16.1. According to this table SeO_4^{2-} should be reduced before MnO_2, but after NO_3^- on decreasing redox level. This sequence has been verified in experimental studies on soil [135] and sediment [103]. Similarly, presence of nitrate in the soil should be expected to retard selenate reduction chemically [160] or biochemically [115].

Factors such as dry climate, low organic matter concentration, high temperature, high pH and absence of waterlogging (well-oxidised soils) tend to favour selenate over selenite. However, irrigation of such soils may leach the Se below the root zone [42, 109]. Selenate is less strongly adsorbed to minerals in the soil and more readily taken up by plants than selenite, while selenite binds tightly to Fe and aluminium (Al) oxides and hydroxides, to allophane (formed by chemical weathering of volcanic glass, *e.g.* in New Zealand) and to a lesser extent also

Table 16.1 Redox sequence of some reactions relevant to this chapter [109]

Reaction	pe
O_2/H_2O	0.82
NO_3^-/NO_2^-	0.54
SeO_4^{2-}/SeO_3^{2-}	0.44
MnO_2/Mn^{2+}	0.40
$SeO_3^{2-}/Se(0)$	0.27
$FeOOH/Fe^{2+}$	0.17
SO_4^{2-}/HS^-	−0.16
CO_2/CH_4	−0.24

to clay minerals [13, 109], especially to the positively charged edges of the latter. Previously it was considered that plants take up mostly selenate from aerobic soils; however, recent studies of Se species in arable soils in the UK found selenite to be the main form available for plants [86], which may partly be explained as a consequence of bioreduction of selenate. In a more recent study, using a very sensitive method for determining the speciation of Se in soil, no selenate was detected at all in some British soil samples [172]. At lower pH values, as frequently found in organic-rich soils, the element may also occur in the more reduced oxidation states 0 and −2, particularly under conditions of water saturation, more than happens under conditions of better oxygenation, less soil organic matter and higher pH. Physicochemical factors other than pH and oxygen partial pressure that may affect Se speciation include the chemical and mineralogical composition of the soil, organic matter content, the nature of adsorbing surfaces, and microbial intervention, frequently leading to the production of organo-selenium compounds. Selenide and elemental Se mainly occur in reducing environments ($pe + pH < 7.5$) and are generally unavailable [42, 109].

In some cases, and particularly at high Se levels, concentrations of Se oxyanions in the soil solution may be controlled by the solubility of Se minerals in the soil. Elrashidi et al. [42], discussing equilibrium reactions and constants for a wide range of Se minerals and inorganic species in solution, indicated that metal selenate and selenite minerals are generally too soluble to be stable in most soils. Under reducing conditions, according to these authors, the formation of metal selenides, e.g., Cu_2Se, PbSe, and SnSe, is likely to prevent the precipitation of elemental Se. However, in a similar study of Se speciation in anoxic soil solutions, also based on equilibrium calculations, elemental Se and the formation of FeSe and $FeSe_2$ were determined to control Se solubility [104]. The quotient between the solubility products of FeSe (10^{-26}) and CuSe ($7.9 \cdot 10^{-49}$) [20] is much larger than the ratio between average concentrations of Fe (54,000 mg kg^{-1}) and copper (Cu) (50 mg kg^{-1}) in the Earth's continental crust [81]. In a situation with thermodynamic equilibrium and Cu^{++} as the stable form of copper, all selenide ions will thus precipitate as cupric selenide before ferrous selenide can form. In the natural system in the soil, it is possible, however, that precipitation of these two minerals will be governed by kinetic factors rather than thermodynamic equilibria, so that most of the selenide ions actually might be bound to ferrous Fe rather than Cu^{++}, and Cu_2Se with a solubility product of $1.6 \cdot 10^{-61}$ [20] is also more soluble than CuSe.

The main reason why Se will not easily form minerals of its own in the soil is the low total concentration of Se in most soils, combined with the high capacity for inorganic Se species to bind to the surfaces of non-Se minerals by adsorption, and to enter the lattices of non-Se minerals either by equilibrium or non-equilibrium solid solution. As for Se complexes in the soil solution under oxic conditions, calculations have shown that only such complexes as $MnSeO_4^0$, $NiSeO_4^0$, $NaHSeO_3^0$, $KHSe^0$, and NH_4HSe^0 appear to make appreciable contributions to soluble Se in normal cultivated soils [109].

16.3.4 Speciation of Selenium in Soils: Organic Compounds

Selenite is the dominant form of inorganic Se in soils with high concentrations of organic matter, such as are found in the Nordic countries (because of low soil temperatures causing slower microbial degradation of soil organic matter than in tropical countries), and also in water-logged soils, for example those under wetland rice cultivation [62].

Inorganic forms of Se may be reduced by soil organisms, such as fungi and bacteria including actinomycetes, to a variety of volatile and non-volatile forms. Reamer and Zoller [118], adding selenite to soil and incubating for 30 days in the presence of air, demonstrated the formation of dimethylselenide [$(CH_3)_2Se$], dimethyldiselenide [$(CH_3)_2Se_2$], and dimethylselenone [$(CH_3)_2SeO_2$]. These and other organoselenium compounds are formed by fungi [46, 148], but may be rapidly demethylated by anaerobic bacteria [115] forming hydrogen selenide (H_2Se). The biological reduction processes may also involve the formation of many other organoselenium compounds analogous to those bearing sulphur, such as selenoaminoacids and selenoproteins. For instance Van Dorst and Peterson [156] identified selenoglutathione after adding selenite to soil extracts. Abrams et al. [1], extracting organic substances from Californian soils with alkaline pyrophosphate and fractionating the humic substances, identified selenomethionine (Se-Met) among the products.

Several studies have shown that a major fraction of Se in soils may be associated with the organic component. Gustafsson and Johnsson [58], adding selenite to forest soils and subsequently employing sequential extraction procedures and chromatographic separations, found that most of the added selenite was fixed to the organic matter, and preferentially to low-molecular weight fractions of the humic substances. Kang et al. [78], employing a similar fractionation procedure, found that in soils with organic matter contents exceeding 1.6%, more than 60% of the total amount of Se was bound to organic matter. Séby et al. [124] recovered 50% Se from a seleniferous soil by a single 2M NaOH extraction and separated the extract into a humic and a fulvic fraction. In both fractions about 50% of the Se was inorganic, mostly Se^{4+}, whereas the rest consisted of unidentified forms assumed to be Se organic compounds. Yamada et al. [165], studying soils with less than 1% organic carbon, found that 40% of the Se remained bound to organic matter, and the Se species did not change appreciably with variations in soil conditions. Coppin et al. [35], assessing the effect of soil ageing on Se behaviour on a series of soils initially contaminated with Se^{4+}, found that both the quality and quantity of soil organic matter played a significant role in Se retention. In each case about 60% of Se was extracted with the humic fraction.

So far, little is known about the chemical speciation of the Se associated with soil organic matter as well as about the pathways leading to the observed distributions. Most reported studies dealing with the interaction of different Se forms with humic matter are concerned with microbial action. Bruggeman et al. [18] conducted experiments where selenite and selenate were added to reaction vessels containing a solution of humic substances and stored in the absence of O_2 and microorganisms. In the case of selenate no speciation change occurred, whereas in the selenite solution most of the Se was transformed chemically to a colloidal species associated with the humic substances. Coppin et al. [34] performed experiments with selenite sorption to organic matter separated from a grassland soil by size-density fractionation. The samples were assayed by scanning electron microscopy combined with X-ray analysis. It appeared that the distribution of Se corresponded strongly to that of Fe in the sample, suggesting that the association might be with mineral impurities in the separated organic matter rather than with the humic matter itself. It might be speculated that selenite ions are attached to a ferric Fe complex-bound to soil polyphenolic macromolecules, and also to other organic matter complexes with highly charged metal ions, such as Al or trivalent manganese (Mn). Studies have shown either decreased Se availability with higher organic matter content in soils [130, 166] or the opposite [36], and organoselenium compounds can be readily taken up by plants [163]. Apparently more research is needed to elucidate the association of Se with soil organic matter.

16.3.5 Selenium Adsorption in Soils

The difference in behaviour between the selenite and selenate anions in soils may be largely explained by differences in their adsorptive properties, selenite being adsorbed to soil constituents to a higher degree than selenate. This is very important, especially in areas with humid climate, for the kinetics of Se loss from the topsoil as a result of leaching processes. Long-term accumulation of Se from atmospheric deposition will thus be favoured when the organic matter concentration and the selenite/selenate ratio in the topsoil are very high, as in Scandinavia, but probably not so much in areas with a humid tropical climate and low organic matter concentrations in the soil, as in some of the Se-deficient parts of Africa. Selenite is largely adsorbed on solid surfaces by ligand exchange, usually involving a hydroxyl group residing on the surface of clay minerals or metal hydrous oxides [13, 66, 116]. This mechanism of specific adsorption, which is supposed to be similar to those of other oxyanions such as phosphate and arsenate, is highly dependent on pH, since the presence of hydrogen ions will affect the ability of the surface to attract anions. As a result, the amount of selenite adsorbed to a surface will decrease with increasing pH. However, the effect of pH is less in cases of specific adsorption than would be expected in a case of simple electrostatic interactions between ions in solution and a surface with charge density that depends on pH in the solution.

Selenate on the other hand behaves in a manner similar to non-specifically adsorbed anions such as sulphate and nitrate. This mechanism is believed to involve the formation of an outer-sphere complex involving a water molecule between the surface and the adsorbing species [134]. This difference between selenite and selenate sorption behaviour was supported by an X-ray absorption fine structure (EXAFS) study of the two anions at a goethite-water surface [63]. A number of studies have examined the adsorption behaviour of Se oxyanions on specific minerals such as goethite [66], clay minerals [11, 51], and Fe oxides [13, 37]. These studies largely confirm that the selenate adsorption is a non-specific process, and, unlike selenite adsorption, is sensitive to changes in ionic strength [63].

Adsorption characteristics of soils depend on the extent of pedochemical weathering that will in large measure determine the mineral composition of the soil [134]. John et al. [75], in a study of 66 New Zealand soils, concluded that selenite adsorption increased as a function of soil weathering. In addition to the physical and chemical properties of the adsorbent, the solution composition may be of considerable importance with respect to differentiating adsorption mechanisms [109]. Experimental studies indicate that variation of ionic strength has little effect on the extent of selenite sorption, whereas selenate adsorption varies significantly with the anion composition of the solution [63, 66, 110]. Sulphate in particular appears as a strong competitor to selenate adsorption, whereas chloride, being more weakly adsorbed, is a weaker competitor. However, the competition of chloride with selenate adsorption on soil surfaces should not be ignored [123].

16.3.6 Selenium Soil-Plant Relationships

The subject of the Se soil-plant relationships has been reviewed extensively [17, 59, 83, 106, 109, 119].

Selenate is readily transported from roots to shoots, where it is likely to be transported to the plastids and assimilated via the S pathway [132, 147]. Selenite undergoes rapid conversion to selenate and organoselenium compounds in the roots, where the latter also tend to accumulate [86, 132, 170]. Interaction between these forms is evident, with selenite inhibiting selenate uptake and xylem transport [86]. Within the plant Se and S compete with each other in the biochemical pathways leading to synthesis of Se-Met and methionine in plant cells. The Se-Met/methionine ratio and the concentration of Se-Met in plant seeds must therefore be expected to depend on the ratio of Se uptake to S uptake in the roots [62].

Selenium is generally not considered to be essential for flowering plants [17, 83], although it can be beneficial, when supplied at low levels, in terms of reduction of oxidative stress, increased biomass [59] and increased seed production [93]. The biochemical explanation for such protective effects of Se in plants is unknown, but it might be speculated that it may at least in part be explained as a consequence of selenide ions substituting for sulphide ions in Fe-S proteins such as ferredoxin, leading to reduction of the rate of superoxide anion production because of ferredoxin autoxidation during photosynthesis (with O_2 reacting with Fe^{++} in ferredoxin, causing formation of $O_2^{-\cdot}$ and Fe^{+++}). This is because of the greater stability of the ferrous iron-selenide bond, compared to the ferrous iron-sulphide bond (as reflected by the lower solubility product of FeSe compared to FeS [20, 25]), which may be expected to lead to stabilization of Fe^{++}, compared with Fe^{+++}, or enhancement of the standard redox potential for the Fe^{++}/Fe^{+++} couple.

Field trials with wheat in South Australia [94] provide an example of the importance of soil characteristics, including texture and pH, in determining Se availability to plants. Grain Se concentration was used as a biomarker of available soil Se. Wheat grown on a clay loam (Typic Natrixeralf) of pH (H_2O) 6.6 had a grain Se concentration of 0.063 mg kg^{-1}, compared to 0.720 mg kg^{-1} in grain from a calcareous sandy loam (Calcareous Xerochrepts) of pH 8.6. Yet both soils had a total Se concentration of around 0.08 mg kg^{-1} (determined by ICPMS after digestion with nitric/perchloric acid) [94]. It has been considered that a total soil Se concentration of 0.1–0.6 mg kg^{-1} is deficient; however, this may need revision in view of the above finding, as a soil able to grow wheat grain with over 700 μg kg^{-1} Se could not be considered Se deficient, its low total soil Se level of 80 μg kg^{-1} notwithstanding [94]. Other studies have found higher Se concentrations in crops grown on soils of higher, compared with lower pH [24, 77], and increased Se concentration in plants grown on lime-amended soils [57].

The presence of anions such as phosphate and sulphate influences, as earlier mentioned, the extent to which Se is adsorbed by a soil and, depending on their relative concentrations, its availability to plants [109]. One hypothesis that may explain why low Se is sometimes associated with fertiliser application may be co-precipitation of selenite ions with phosphate. This renders much of the Se unavailable for uptake by plants [39, 68, 89]. When phosphate fertilisers are added to the soil and precipitation of phosphate minerals occurs, Se remains fixed in the precipitate and is unavailable for uptake. Conversely, phosphate may also cause desorption of selenite ions bound to minerals in the soil, as phosphate is bound more strongly to trivalent Fe and Al than selenite [39, 108]. Selenite uptake, in a study of wheat plants, was increased in P-starved plants, and (contrary to earlier assertions) this was found to be an active process, which probably involves phosphate transporters [86]. In USA and Canada there are large areas of prairie land where the soil is sufficiently fertile to preclude the need for high rates of phosphate fertiliser application. The high concentrations of Se found in cereals grown on these lands can therefore be explained by a combination of high natural Se concentration in the soil and excellent bioavailability of soil Se for uptake by the plant roots, due partly to lack of commercial P fertiliser application [62].

On the other hand, single superphosphate can contain up to 25 mg kg^{-1} Se [163], but it has generally been replaced by triple superphosphate, which typically contains less than 4 mg kg^{-1} Se [17]. Selenium concentrations in commercial fertilisers depend both on the source of S (with evaporite minerals and elemental S associated with salt diapirs being very poor in Se, compared with most sulphide ores), and on the source of phosphate, with sedimentary phosphate ores [105] containing much more Se than igneous phosphate rocks, but also much more Cd. But even though marine phosphorites (sedimentary phosphate rock) contain much more Se than igneous phosphate ores (*e.g.* from the Kola Peninsula), their Se/P concentration ratio [105] is not as high as often can be found in the topsoils of natural terrestrial ecosystems. It must therefore be expected that the application of commercial fertilisers in most cases (though not always) will lead to a reduction of the total Se/P concentration ratio in the soil (unless Se has been specifically added to the fertiliser), which sooner or later must also lead to reduction of the Se/P ratio of food and forage plants. It is possible that this may be the most important reason for the very poor plant uptake of Se found on most cultivated lands both in north, central and southern Europe (with the exception of Finland), and that it may explain why the average Se intake from most European diets (as can be inferred from human blood Se concentrations presently observed in several different parts of Europe) is significantly less than was common in the United States and Canada 40–50 years ago [25].

The uptake by plant roots of Se from fertilisers during the first weeks or months following fertiliser application must be expected to depend on Se speciation in the fertiliser, as well as on the competitive interactions between fertiliser selenate or selenite and those major elements also in the fertiliser that use the same membrane transport mechanisms as selenate or selenite for uptake in the plant roots.

As noted above, increasing concentrations of sulphate in soil solution often result in decreased Se uptake by plants, due to competition between sulphate and selenate for transporters in plant roots [146, 163]. This effect is less marked for selenite [50, 106]. In the more humid parts of Sub-Saharan Africa, there are large areas where the human diet is deficient in S amino acids [6], which is in part explained by a low total intake of dietary protein [5], but also may be due to S deficiency in the soil [43, 129], which is probably very widespread in the more humid parts of Sub-Saharan Africa, especially on the savanna as a consequence of frequent anthropogenic fires [43], but also in such tropical forest areas where the rainwater is very S-depleted because of long distance from sea. If one tries to correct the problem of S amino acid deficiency in the human diet by fertilisation with Se-poor S (in the form of gypsum or elemental S), it would be expected to reduce the rate of synthesis of Se-Met in the plants compared to methionine [62]. If the problem of nutrient element deficiency in the topsoil has arisen as a consequence of excessive disruption of natural systems of local biogeochemical recycling and retention through soil erosion and leaching, or volatilisation of S and Se by fires (especially on the savanna), the only viable long-term solution, especially for farmers who cannot afford to buy commercial fertilisers, is to try to re-establish agricultural ecosystems that are closer to the natural ecosystems they replaced. This can be achieved using methods such as terracing, agroforestry, and minimising anthropogenic fires [62].

In addition to soil traits, plant genotype is important for Se uptake and accumulation. Selenium biotransformation pathways play an important role in Se accumulation in plant tissues, and plants vary in their ability to transform inorganic Se to organic forms [88, 132]. Numerous selenocompounds have been identified in plants. Se-Met is the major selenocompound in cereal grains, grassland legumes and soya beans (*Glycine max*), while Se-methylselenocysteine (SeMCYS) is the major selenocompound in Se enriched plants such as garlic (*Allium sativum*), onions (*A. cepa*) and broccoli (*Brassica oleracea)* [162].

Plant species vary widely in Se uptake and accumulation [147, 162, 163]. Most plants (non-accumulators) accumulate Se in direct relationship to the amount available from the soil and rarely contain more than 100 mg kg^{-1} DM (whereas Se-indicators (*e.g. Morinda reticulata*) can contain up to 1,000 mg kg^{-1}) and accumulators like *Astragalus bisulcatus*, *A. racemosus* and *Stanleya pinnata* can contain up to 40,000 mg kg^{-1} [17, 119]. Non-accumulator plants have lower Se:S ratios in shoot tissue than Se-accumulators [17], and as much as 80% of the total Se in some accumulator plants is present as SeMCYS, which is less toxic to the plant (but not to animals) than other Se forms [83, 162]. Furthermore, differences exist in non-accumulators for both Se accumulation, for example a 15-fold variation among *Brassica* vegetables [121], and for tolerance to Se, with a threshold of toxicity generally in the range 2–350 mg kg^{-1} DW in leaf tissue. The threshold for toxic effects in plants is determined not only by plant species but also by soil factors, including Se form: selenite is more toxic than selenate [96, 106].

16.3.7 Phytoremediation of High Selenium Agricultural Soils?

Selenium accumulator plants can be used for phytoremediation of areas with toxic Se levels in the soil. This strategy has been used in the Westside region of the San Joachim Valley in California, where Se, B and salt levels are high in the soil. Banuelos and colleagues have screened crops for tolerance to salt and B and ability to accumulate Se. By using moderate Se accumulators in the *Brassica* family, for example broccoli (*B. oleracea*), canola (*B. napus*) and Indian mustard (*B. juncea*), Se-enriched feed or Se-enriched vegetables can be produced. Biofuel has also been produced from high-Se canola seed, and the seed residue can even be used as a biological herbicide [8].

The use of plants that naturally contain more Se than others, breeding crop varieties with enhanced Se-accumulation characteristics, or transferring Se-accumulation genes to crop species, may be plausible approaches to increase the Se concentration of the human diet, and constitute forms of *genetic biofortification* [17, 41, 60]. However, when the topsoil is too severely depleted with regard to a particular nutrient element (for example, as a consequence of accelerated soil erosion or frequent anthropogenic fires), it is not possible to compensate for this by plant breeding or bioengineering in order to improve uptake kinetics in the plant roots, except perhaps by increasing very much the overall length and depth of the root system. The alternatives are *agronomic biofortification* by Se fertilisation [17, 62], utilization of areas with Se toxicity problems (natural or because of pollution) for Se biomining/ phytoremediation using Se accumulator plants [9, 38], fortification of foods or feed mixtures with Se-Met, or intake of Se as dietary supplement pills.

16.4 Selenium in Animal and Human Health

16.4.1 Role of Synergistic Biochemical Interactions Between Se and S Amino Acids in Antioxidant Defense

Geomedical problems due, in part, to reliance on Se-deficient soils for growing of food crops, are common in much of Sub-Saharan Africa [137] and may be very harmful for HIV patients [12]. But inadequate intake of S amino acids can also have several adverse medical consequences, which can in part be explained by the close collaboration between Se-dependent enzymes and glutathione (GSH) in cellular systems of antioxidant defense, DNA synthesis and DNA repair. The Se-dependent glutathione peroxidases GPx-1 and GPx-4 have been reported to display tert-uni ping pong kinetics (see glossary) [49, 155], which means that the rate of oxidizing substrate, *e.g.* H_2O_2 reduction (for a given concentration of the oxidizing substrate) is proportional to the first power of the enzyme concentration (that depends on the Se intake) and the second power of the GSH concentration (that depends on the intake of S amino acids, as well as of certain B-group vitamins). The antioxidant protective function of these enzymes is therefore even more vulnerable to deficiency of S amino acids in the diet than to Se depletion, and one must expect a synergistic (multiplicative) interaction when Se and S amino acids are simultaneously deficient, or when Se deficiency is combined with thiamine, niacin or riboflavin deficiencies.

It is therefore important that both problems (*i.e.* Se deficiency and S amino acid deficiency in the diets of humans or domestic animals), and also the problem of B-group vitamin deficiencies (*e.g.* because of overconsumption of refined cereal products or sugar), should be addressed simultaneously, and with a good understanding both of the synergistic and antagonistic biochemical interactions between Se and S as nutrient elements, as well as of the geochemical cycling [54] behaviour of both elements. It should not be forgotten that global reserves of low cost S (especially in form of evaporite sediments) are vastly larger than those of low cost Se. There is therefore no reason, as seen from the point of view of global resource economics, not to use S as a fertiliser wherever indicated because of S deficiency in the soil (or in the human diet), while for Se, this is contraindicated because of much more limited global reserves [62].

16.4.2 Selenium Toxicity

Selenium toxicity in humans and animals is a much rarer problem than Se deficiency, but does occur in places where high soil Se concentration is combined with high bioavailability for uptake by plants. In animals, this can lead to the diseases called blind staggers and alkali disease, often following the ingestion of Se accumulator plants with much higher Se concentrations than normally found in grasses or cereal grains growing in the same soil [29, 84, 153]. Symptoms in humans that have been reported from China following chronic high intake (in the range 3.2–6.7 mg Se/day) resemble some of those symptoms that have been described from other species, with the most common sign of intoxication being hair and nail loss, but also dental, nervous and skin disorders [84, 166]. Three especially interesting examples of geological situations which in combination with human actions have led to Se toxicity problems have been described from China (in an area with very Se-rich coal) and California (partly as a consequence of using Se-contaminated irrigation water) [109, 166]. Livestock consuming fodder grown on seleniferous soils in Punjab, India suffer from poor condition, hair loss and hoof sloughing [38, 39]. The Californian case is described below.

The toxic effects of Se can, at least in part, be explained by formation of Se derivatives of glutathione that function as redox-cycling agents generating reactive oxygen species (ROS) [140]. The net effect of Se at excessive levels is therefore not as an antioxidant, but as a strong pro-oxidant. This effect will become progressively more important, when Se intake is enhanced beyond the intake needed for optimal Se-dependent antioxidant protection (*i.e.* tissue saturation with Se-dependent antioxidative enzymes, but perhaps also dependent on near-saturation of Fe-S proteins with selenide ions, similarly as has been suggested above for explaining beneficial effects of Se that have been observed in plants).

For adults, daily intakes up to 500 μg Se would normally appear safe with very little, if any risk of toxicity. There are, however, paradoxical observations suggesting that an acute enhancement of the intake of Se in some situations may cause temporary reduction of the level of Se-dependent enzymes [19]. The responsible mechanism(s) is poorly known, but it is possible that it may be explained by reaction between selenite ions and the selenol group of selenocysteine, leading to formation of Se-Se covalent bonds and inactivation of the enzyme. It is thus possible that the threshold for acute toxic effects of Se may be much lower in patients suffering from Se deficiency than in persons with normal Se status. The same might also be the case in patients suffering from Hg or Cd poisoning. It may be theoretically expected that biological antioxidants with suitable pharmacokinetic properties (with the possible exception of glutathione) might be useful in cases of acute Se intoxication, *e.g.* a combination of coenzyme Q_{10}, melatonin, taurine (cf. [27] for an explanation of the possible antioxidant mechanism) and some polyphenolic plant antioxidant, all at high dosage levels.

Epidemiological studies of associations between health parameters and apparent Se status, as measured by blood Se concentrations, should take into consideration the competitive interaction between methionine and Se-Met. Higher average blood Se concentration in one population compared to another does not necessarily mean that the first population has a higher Se intake; it could also be because it has a lower intake of methionine, while the Se intake is the same in both populations. This is especially important to bear in mind when studying populations in poor countries with low total protein intake and/or S-deficient soils. However, one cannot exclude the possibility that individual differences in the intake of methionine might affect the outcome of epidemiological studies even in Europe and lead to the erroneous conclusion that too much Se (even at very moderate levels) in certain respects might be harmful, while the real culprit is an inadequate intake of S amino acids. Another possible cause of enhanced blood plasma Se concentration is undersecretion of insulin and/or impaired insulin sensitivity because of diabetes type 2, since insulin is a negative regulator of selenoprotein P expression [133].

There are numerous reports from *in vitro* studies (*e.g.* [140, 172]), showing that cancer cells are vulnerable to the toxic effects of Se, which creates the possibility of using Se at subtoxic levels as a cytotoxic agent in cancer therapy. It has also been reported that malignant cells resistant to other cytotoxic drugs are especially vulnerable to Se as a cytotoxic agent [125]. However, safe use of Se for this kind of therapy will hardly be possible without very good understanding of Se pharmacokinetics (with much slower excretion than for most other commonly used drugs), as well as of the nature of attendant side effects.

High soil Se concentration is most commonly a consequence of high bedrock concentrations (as in parts of China and parts of the United States), but it can also be a consequence of prolonged deposition from rainwater as occurs along the Norwegian coast. In Norway there are no problems of Se toxicity, but this occurs in parts of Ireland, perhaps as a result of superposition both of Se from a local bedrock source and from rainwater deposition for tens of thousands, if not hundreds of thousands years. It may also occur because of human interference with the local hydrogeological systems in connection with artificial irrigation in arid zones.

It has been reported from the United States that nearly all seleniferous soils have weathered from sedimentary rocks of the Cretaceous period [152]. The Cretaceous was a period with unusually rapid ocean-floor spreading, which led to wide-scale marine transgressions over the continents, so that epicontinental seas (like the North Sea today) had a much larger total extension than now, with a corresponding reduction of the land area [136]. Topographic relief of the emerging land was also on average less than now. The average rate of deposition of terrigenous matter (such as clay and sand) on the sea-floor was therefore less than now, since there was more seafloor at the same time as there was less emerging land. But the total rate of addition of S and Se to the atmosphere and hydrosphere from volcanic processes must very likely have been considerably higher than now, perhaps both from submarine volcanism at the mid-oceanic ridges (which were also an important source of calcium to seawater, thus helping to explain the abundance of carbonate sediments of Cretaceous age) and from very large mantle plumes, coming up from the lower part of the Earth's lower mantle [146]. It means that the ratio between the total flux of Se coming from volcanoes and the average rate of erosion on the continents must have been especially high during the Cretaceous, compared with other geological periods, leading to a corresponding enhancement of the average Se concentration of all marine sediments from the period concerned (after calcium carbonate has been subtracted).

Irrigation in situations where the ratio of selenate to selenite is high can lead to mobilisation of soil selenate with net leaching taking place where net water transport is downwards from the soil surface, while Se accumulation occurs in places where Se-enriched groundwater reaches the surface in topographic depressions. A good example of this is found in the San Joaquin Valley of California [109]. A series of outcrops of seleniferous marine rocks of the Coastal Range to the west of the San Joachim Valley is the source of most of the Se, which has been leached out of the rocks into alluvial fans and down to the valley floor. The Se was concentrated in agricultural runoff water and then transported via the San Luis Canal to the Kesterson ponds/reservoir. Water entering the ponds contained as much as 3,600 μg/l Se, and in the early 1980s this was found to be responsible for embryo deaths and deformities in waterfowl on the ponds. There was no evidence of adverse effects on humans [109, 119].

16.4.3 Protective Health Effects of Selenium

16.4.3.1 Antidote Effects Against Toxic Metals

Animal experiments have shown that Se at high intake levels has a strong protective effect against the toxicity of several chalcophile toxic metals, such as Hg, Cd and Ag [47, 153, 161]. This can most likely be partly explained by *in vivo* precipitation of the corresponding selenide minerals (*e.g.* HgSe, solubility product $3.2 \cdot 10^{-65}$ [20]). Selenide ions are obligatory precursors for selenocysteyl-tRNA, since they are used for making selenophosphate (which is an energy-rich, or 'activated' Se compound formed by reaction between selenide ions and ATP [70]), which is in turn used for making selenocysteyl-tRNA [128]. The cells have various pathways for making selenide ions that are specific for Se (without simultaneous formation of sulphide ions). The intracellular abundance of selenide ions is therefore relatively high, compared to the total abundance of Se in the cell, at the same time as solubility products of heavy metal selenides are several orders of magnitude less than for the corresponding sulphides [20, 25].

Toxic metals can bind to selenol groups in Se-dependent enzymes (and more strongly than they bind to thiol groups), thus inhibiting the enzyme molecule. Thioredoxin reductase is a flavoprotein that also contains a selenocysteyl and a cysteyl group in neighbour positions [56]. Chelates can therefore be formed where a heavy metal atom is coordinated to S on one side and Se on the other. This enzyme is exceptionally vulnerable to toxic effects of heavy metals, being 3 orders of magnitude more sensitive to inhibition with auranofin (an organic gold complex used for treatment of rheumatoid arthritis), compared to glutathione peroxidase (with isolated selenol groups offering no opportunity for chelate formation) and glutathione reductase (which is an ordinary dithiol enzyme, where a heavy metal atom can be captured between two S atoms) [56].

16.4.3.2 DNA Synthesis and Repair

Thioredoxin reductase participates in the transport of electrons from NADPH to ribonucleotide reductase, since the latter enzyme can alternatively use either thioredoxin or glutaredoxin as reducing cofactors. Inhibition of thioredoxin reductase may thus be expected to lead to disturbance of DNA synthesis and DNA repair, especially when cellular concentrations of reduced glutathione (GSH) also are low, since GSH is used for regenerating reduced glutaredoxin after it has been oxidized in the ribonucleotide reductase reaction.

Rates of cell replication are especially high in the intestinal mucosal epithelium and in leukocytes (or their progenitor cells) following immunological activation. Inhibition of leukocyte DNA synthesis will therefore lead to immunosuppression (because of slower recruitment of several different types of leukocytes), which will in turn affect morbidity and lethality for several different infectious diseases. Inhibition of DNA synthesis in the intestine can contribute to intestinal dysfunction, such as villous atrophy, which may in turn lead to reduced absorption of several different nutrients. Inhibition of DNA repair must be theoretically expected to lead to enhancement of the risk for cancer (when it happens in the nucleus) and enhancement of the rate of mitochondrial DNA aging (by progressive accumulation of mitochondrial DNA lesions [100]), which may not only affect the average life expectancy [10], but also the prevalence of various age-related degenerative diseases for a given age group.

16.4.3.3 Antioxidant and Antiatherogenic Protection

Thioredoxin is also important as a reducing cofactor for antioxidant enzymes called 2-Cys peroxiredoxins [22, 101], for reduction of abnormal disulphide groups in proteins [91], and for repair of oxidised protein methionyl groups [80]. These enzymes are – together with other Se-dependent or GSH-dependent antioxidative enzymes – important for protection against the oxidative and nitrative stress associated with infectious disease episodes [27], as well as against functional impairment and degenerative changes associated with normal as well as pathological ageing, with cataract representing a well-studied and typical example [91]. Optimizing intakes of S amino acids and Se may therefore be important not only for reducing the mortality from infectious diseases in young children (which is important especially in poor countries), but also for maintenance of a good quality of life in the higher age groups (which is important all over the world).

Tissue concentrations of Se-dependent enzymes such as glutathione peroxidase (especially GPx-1) and selenoprotein P depend on Se intake [25, 84, 102, 153]. GPx-1 scavenges H_2O_2, water-soluble organic hydroperoxides and peroxynitrite [16, 49, 154], while GPx-4 scavenges membrane-bound hydroperoxides [154]. Selenoprotein P has a double function both as a Se transport protein [14] and as an antioxidant protective enzyme found in blood plasma, and is important for protection of low density lipoprotein against oxidation [150]. It is possible that this may in large measure explain the negative correlation that has been found between Se intake and coronary heart disease mortality in geographic epidemiologic studies from USA, comparing states with high and low Se intake [126, 127], since oxidatively modified LDL is much more atherogenic than non-modified LDL [67]. The human gene for selenoprotein P codes for 10 selenocysteyl groups [65], but premature termination of translation (leading to incorporation of less than 10 Se atoms per molecule) can occur when the dietary Se intake is suboptimal [21, 99]. It is not known if there is one active site per Se atom or only one active site per molecule in this enzyme. Nor is it known – for human populations – how much Se per day is needed for $>90\%$ saturation of selenoprotein P with Se.

16.4.3.4 Selenide Ions in Iron-Sulphur Proteins

Selenide ions can substitute for sulphide ions in the Fe-S groups of Fe-S proteins [144]. Since FeSe is much less soluble than FeS [20, 25], it must be expected that the Se^{--}/S^{--}ratio will be much higher in Fe-S proteins than in the aqueous phase, *i.e.* that Se^{--} will be strongly captured (in V. M. Goldschmidt's terminology [54]) in the Fe-S proteins. The actual Se^{--}/S^{-} ratio in these proteins, depending on the dietary intake of Se must be expected to influence the standard redox potential for oxidation of one Fe atom, and hence the functional properties of these proteins.

The Se^{--}/S^{-} ratio in Fe/S proteins may, however, depend not only on the Se intake, but also on the intake of S amino acids because of the role of the latter as biochemical precursors of sulphide ions. Sulphide ions are produced mainly by enzymes in the trans-sulphuration pathway which is used when the cells make cysteine at the expense of methionine [131], for which reason it is possible that methionine may exert a more pronounced Se-antagonistic effect, compared to dietary cysteine. Such antagonistic interactions between Se and S not only in plants, but most likely also in animals and humans, may be important to bear in mind for agronomists, farmers and health personnel working in areas *e.g.* in parts of Africa where Se and S simultaneously are deficient both in the soil and in the human diet.

A higher Se^{--}/S^{-} ratio would be expected to stabilize ferrous compared to ferric iron, *i.e.* lead to enhancement of the standard redox potential for the Fe^{++}/Fe^{+++} reaction. It is possible, for similar reasons as earlier explained for plants, that this might in turn lead to reduction of the rate of mitochondrial production of superoxide anion radical, especially through reaction between redox-labile groups in complex I and molecular oxygen [15]. A reduction of the rate of mitochondrial ROS production must in turn be expected to lead to reduction of the rate of mitochondrial DNA aging. It might be speculated that this mechanism could explain why a high intake of selenium has been reported to enhance the lifespan in banana fruitflies (*Zaprionus paravittiger*) [79] and mice [72], while a high intake of methionine very paradoxically shortens the lifespan of rats because it enhances the rate of ROS production in the mitochondria and therefore the rate of mitochondrial DNA aging [23, 55].

It is also possible that changes in the functional properties of complex I indirectly could affect the kinetics of O_2 reduction and ATP production by cytochrome *c* oxidase, which might be important especially in situations of severe hypoxia, and perhaps might help to explain some otherwise very puzzling observations concerning the protective effect of Se at high dosage levels in situations of ischemia/reperfusion or global anoxia (cf. [7, 82, 92]). It is an intriguing question how not only the Se intake, but also the intake of S amino acids (acting antagonistically?) may affect the Se^{--}/S^{--} ratio of mitochondrial Fe-S proteins and hence the functional properties of the mitochondrial respiratory chain.

16.4.3.5 Epidemiological Observations Suggesting that High Se Intakes Are Needed for Optimal Protection Against Cancer and Cardiovascular Diseases

Selenium supplementation has been reported to protect against various forms of cancer (prostate, colorectal, lung and liver) in prospective clinical trials from the United States [28] and China [168]. These data are consistent with earlier epidemiological studies, especially geographical ones from the United States, showing that mortality from several, but not all forms of cancer, and also from cardiovascular diseases (especially coronary heart disease, as statistically defined, and hypertension) was negatively correlated to the intake of Se [25]. The states in the USA with the lowest Se intake had the highest mortality, while the US states with the highest Se intake in 1960 had the lowest mortality both from cancer and cardiac diseases [48, 122, 126, 127]. The most Se-rich states had about three times higher average Se intake than the most Se-poor states, and also compared to Norway 30 years ago, if a linear correlation between human blood Se concentrations and Se intake can be assumed both for USA and the countries in northern Europe [25, 29, 127]. Norway, however, was then among the most Se-rich countries in Western Europe, in terms of average Se intake [25], apparently being similar to that of Finland today.

If taken at face value, these data suggest that the Se intake needed for optimal protection against cardiovascular diseases and cancer cannot be less than in the US states with the highest average Se intake in 1960, or somewhat more than 200 μg Se/day (as estimated from blood Se concentration data). The geographic patterns observed both for cancer (see also Jansson et al. [74] and Jansson [73]) and cardiovascular disease [126, 127] cannot easily be explained as resulting either from human activity (*e.g.* industrial pollution) or genetic factors in the human population. And Se is so distinct from all other elements in its geochemical behaviour that it is not easy to explain the strong negative correlations observed, especially for deaths caused by ischemic heart disease or hypertension [127], as being caused only by natural variations in the intake of some other nutrient or toxic element, if Se should be only a confounding factor (*i.e.* a statistical marker for something else). The geographical epidemiological observations from the United States are, moreover, consistent not only with a large number of observations from animal experiments and from veterinary medicine [25], but also with much of what is known today about the biochemical functions of this nutrient element. They are also consistent with a more recent meta-analysis of Se and coronary heart disease, which included 25 observational studies (14 cohort and 11 case control studies) and 6 randomized trials [44].

16.4.3.6 Survival in HIV Patients

The effects of Se and GSH/S amino acid status on life quality, rate of disease progression and annual lethality (or life expectancy) in HIV disease can partly be explained by the importance of these nutrients for immunological functions and antioxidant protection [27] in infectious diseases more generally, *i.e.* because of their roles in DNA synthesis as earlier explained. However, Se and GSH status also directly affect the rate of HIV viral replication, since oxidatively activated transcription factors, including nuclear factor-*kappa*B (NF-*kappa*B) [87], stimulate transcription of the HIV proviral gene [141], and NF-*kappa*B activation is enhanced both by poor Se status [40] and GSH depletion [53]. Enhanced oxidative stress (*e.g.* because of other infections) or impairment of the cellular capacity for antioxidant defence will therefore be a direct cause of enhancement of the rate of HIV replication, and this must be expected to happen both when intracellular GSH and Se are depleted. There are now numerous epidemiological observations confirming the importance both of GSH and Se status in HIV patients. In a cohort study in the US, it was found that the death risk over the observation period was higher almost by a factor of 20 in subjects defined as Se-deficient compared with those defined as being of normal Se status [12] – but the upper boundary that had been arbitrarily chosen to define ‘Se deficiency’ in this study was higher than average blood plasma Se concentrations found in the normal population in parts of Central Europe (and much higher than in the most Se-deficient parts of Africa or China). GSH has, moreover, been reported to inhibit the growth of mycobacteria [158], which means that GSH depletion can lead to growth enhancement for tubercle bacilli as well. And coinfection with HIV and tuberculosis (sometimes multidrug-resistant) is a substantial problem in Sub-Saharan Africa [61].

16.4.3.7 Keshan Disease, Kaschin-Beck Disease and Myxoedema

The discussion above concerns sub-optimal Se intakes in a subclinical range (where the deficiency is not severe enough to cause manifest Se deficiency disorders). In parts of China and eastern Siberia two overt Se-deficiency diseases occur, Keshan disease and Kaschin-Beck disease. Both have similar geographic patterns of distribution, extending in a long diagonal belt across China from the Heilongjiang Province in the far northeast to the Yunnan Province and Tibet in the south [164]. They are found mainly in areas with hills or mountain terrain inland and not at all along the coast, but are again absent in the more arid zones in the northwestern parts of China. This is a geographic pattern that can be explained as resulting from the combination of low local bedrock Se and I concentrations, low natural rates of atmospheric deposition for Se and I in the inland and high rates of Se and I removal by soil erosion in the hillsides, while high rates of sedimentation in local topographic depressions will lead to corresponding dilution of the scarce Se and I that has been deposited from the atmosphere. Similar situations can obviously be found also on other continents, as well as in other parts of Asia. There is therefore good reason to suspect that Keshan disease and Kaschin-Beck disease might be much more prevalent also in other parts of the world than is commonly recognised today, but that they might be underdiagnosed because of lack of research attention.

One of the reasons why the situation is better in the arid northwestern parts of China could be better bioavailability of soil Se for uptake in the plants because of higher soil selenate/selenite ratios. Another factor could be a high ratio of annual evaporation to annual precipitation, leading to corresponding up-concentration both of halide ions, S and Se from snow and rainwater, even though annual deposition rates are low. Rates of S and Se removal by leaching processes and fluvial erosion will, of course, be strongly reduced in semiarid or arid steppe and desert zones. Bedrock Se and I concentrations must be another major determinant of soil concentrations of these elements in inland districts with arid climate – which is something that must be expected to apply to inland parts of Asia equally as much as it applies to central parts of North America.

Keshan Disease

Keshan disease affects mainly children and women of childbearing age and involves impairment of cardiac function, cardiac enlargement and arrhythmia [84, 119]. The disease's aetiology involves Se and perhaps vitamin E deficiencies, which often (but far from always) can be combined with infection with a malignant, cardiotropic variety of Coxsackie B virus [85]. It has been shown in animal experiments that Se deficiency leads to positive selection for the cardiotropic and malignant viral strain [85].

The incidence of Keshan disease is reported to vary with the seasons, being higher during the winter in North China and during the summer in South China [169]. These seasonal fluctuations, especially in North China, may be taken as an indication that temperature stress leading to enhanced catecholamine secretion also may play a role as a causal factor that may interact with Se deficiency in a way triggering the acute development of severe cardiomyopathy. This hypothesis is supported by observations from veterinary medicine. An interaction between Se deficiency and stress (*e.g.* during transport, but also temperature stress both from cold and excessive heat) has been reported to be important in the aetiology of sudden cardiac death in swine [151]. It may presumably be explained partly as resulting from the effect of catecholamines on Ca^{++} levels in the cardiomyocytes [25], with more intramitochondrial Ca^{++} leading to enhanced stimulation of rate-limiting dehydrogenases in the tricarboxylic acid cycle [90] and hence more electron feeding from the tricarboxylic acid cycle into the respiratory chain, which will in turn lead to enhanced oxidative stress because of enhanced mitochondrial production of ROS. It is reported that salt fortified with sodium selenite (15 mg/kg) increased average daily Se intakes in a highly deficient Chinese population from 11 to 80 μg, with a resulting 90% decline in Keshan disease prevalence [2].

Kaschin-Beck Disease

Kaschin-Beck disease is an osteoarthropathy especially affecting children, which appears as enlarged joints, shortened fingers and toes and, in severe cases, dwarfism [164]. Selenium and I deficiencies, acting in combination, are probably the most important etiological factors [111, 119, 164, 173], but other contributory causes, including vitamin E deficiency [119], fulvic acids in drinking water [117], and mycotoxins in food [171], might also be involved. Among those causal factors that have been proposed, only Se and I deficiencies can explain the geographic pattern of distribution of Kaschin-Beck disease in China (and the importance of Se deficiency has also been proved by clinical intervention trials [164]), but the others might possibly play a role in determining which individuals are affected in a given geographic district.

There is much similarity, comparing the biogeochemical behaviour of Se and I, *e.g.* regarding the importance of atmospheric transport from seawater to the continents (see Goldschmidt [54], for a discussion of the importance of this transport mechanism in the case of I). Both elements are also highly biophile in plants [26], and both are found in much higher average concentrations in shales than in igneous rocks [81]. It is therefore very common that Se-depleted and I-depleted soils are associated geographically, especially in erosion-prone highland areas distant from the sea when also the bedrock concentrations of both elements are low. This geochemical similarity between I and Se may presumably be important for explaining the geographical distribution pattern for Kaschin-Beck disease in China. But it would be expected to be important also in other parts of the world, for which reason there might be good reason to suspect that Kaschin-Beck disease, at least in its milder forms, might be more common than hitherto recognised, with its true prevalence possibly being masked by other dietary deficiency conditions and infectious diseases also leading to growth disturbances in children.

Leg Weakness and Osteoarthritis

There are important similarities between Kaschin-Beck disease and two other diseases, *viz*. leg weakness (or “*Bewegungsstörungssyndrom*”) in pigs [82] and osteoarthritis in humans. Like Kaschin-Beck disease in humans, leg weakness in swine is typically a disease affecting young animals (while they are still growing), and it is associated not only with degeneration of articular cartilage, but also of epiphyseal cartilage [82]. It is also associated with much skeletal muscle pathology [82], most likely resulting from a combination of poor skeletal muscle vascularization because the muscle cells are abnormally thick [82] and abnormal static loads resulting from the abnormal anatomy (with the back being abnormally long [82]) of animal breeds especially susceptible to this disease.

Neither leg weakness nor osteoarthritis can be considered Se deficiency diseases, but it is possible that there may be considerable overlap between the biochemical pathogenetic mechanisms both in Kaschin-Beck disease, leg weakness and osteoarthritis, even though they affect different age groups or species and result from different combinations of causal factors. The incidence of osteoarthritis in humans enhances drastically as a function of age, and there is no doubt that this must be regarded as a degenerative disease developing as a consequence of normal or pathological aging. It is therefore a plausible hypothesis that enhancement of intramitochondrial ROS production happening as a consequence of mitochondrial DNA aging [10, 100] could be the most important causal factor here. But if this hypothesis is correct, there may be good reason for hope that selenide saturation of mitochondrial Fe-S proteins in the chondrocytes may have an effect opposite to that of aging itself on the rate of mitochondrial ROS production, and also that a better average Se status over several decades may help to reduce the rate of mitochondrial mutagenesis and DNA aging in the chondrocytes

It is possible that oxidative stress inside and outside chondrocytes (cf. [64, 69, 149]), leading *i.e.* to enhanced expression and secretion of enzymes degrading extracellular molecules that are necessary for the mechanical integrity of the cartilage, could be of key importance both in Kaschin-Beck disease, leg weakness and human osteoarthritis. Studies on one of these diseases may thus held considerable potential for a better understanding also of the two others, leading hopefully to better methods of prophylaxis or therapy. The well-documented prophylactic and therapeutic effects of Se supplementation in Kaschin-Beck disease, where Se when applied to early-stage patients was found not only to prevent the aggravation, but also to accelerate the repair of metaphyseal lesions [164], might perhaps be highly relevant also for prophylaxis and therapy of osteoarthritis in elderly human patients. It has, moreover, been reported from studies in pigs that high Se intake (at a level much higher than needed for prevention of the ordinary Se/vitamin E deficiency diseases commonly found in this species [84, 151, 153]) had a very good prophylactic and therapeutic effect against leg weakness [82].

This might perhaps be explained as resulting not only from protection against the degenerative processes affecting epiphyseal and articular cartilage, but also a combination of anti-inflammatory protection [25, 40, 82] and antiischemic protective effects (cf. [7, 92]) in skeletal muscle when the cartilage disease is already established. It would be of interest to see if Se, perhaps in combination with S amino acids or other antioxidant nutrients including taurine, also could be used for prophylaxis or treatment of osteoarthritis and other skeletomuscular disorders (including skeletal muscle pains resulting from abnormal static loads, as in tension headache and “mouse disease”) in humans.

Myxoedema

The combination of I and Se deficiency can also lead to a third human disease, *viz.* myxoedema [32], which has been described from parts of DR Congo [112]. Myxoedema is a form of fibrotic degeneration of the thyroid gland that is associated with high intra-thyroid levels of the fibrogenic cytokine TGF-*beta* [32]. High levels of thiocyanate (from cassava consumption) may play a role as an additional etiological factor, interacting with the two others [31]. The occurrence both of Se and I deficiency in eastern Congo can probably be explained by the combination of humid tropical climate with long distance from the sea. Much of the rainwater in those parts of Congo is probably "recycled" water coming from evaporation over the land, where rates of evaporation of volatile Se and I compounds may be much less than from the sea surface. Additionally, no sulphate is brought into the atmosphere by seaspray particle formation. The result will be rainwater that is markedly depleted in Se, I and S, compared to rainwater over the sea or in coastal areas. It is a great humanitarian and political challenge to solve the serious public health problems arising from simultaneous deficiency of Se, I and S amino acids in these parts of Africa.

16.5 Experience from Finland with Selenium Fertilisation

Finland embarked on a national Se biofortification program through its "food system", mandating Se addition (as selenate) to fertiliser from 1985 [157]. This proved to be a remarkably effective and safe way to increase the Se status of Finland's food crops, livestock and human population. During the first 5 years of the program, the Se level in spring wheat grain increased around 25-fold to a peak of around 300 µg/kg. Selenium levels in milk and meat increased around 10-fold and 13-fold, respectively, in the period 1985–1991, and human serum Se level increased from around 55 µg/l to around 103 µg/l over a similar period. The current Se concentration in NPK fertiliser in Finland is 10 mg/kg [59]. It is difficult to isolate the effects of a single factor, such as dietary change, from other factors that can be involved in the aetiology of conditions such as cancer and cardiovascular disease. There have been significant decreases in the rates of cardiovascular disease and certain cancers in Finland since 1985, but with no controls for comparison, this cannot be ascribed to Se alone [59, 157].

16.6 Concluding Comments

Among trace elements needed for the survival and normal health of humans and other vertebrates, Se is geochemically the scarcest, most likely as a consequence of the low Se/S solar system abundance ratio combined with the high solubilities of S and Se in molten metallic Fe when the Earth's core was formed. Both soil concentrations and the ease of uptake of Se in plant roots can vary geographically by more than a factor of 10, leading to geographic variations in the Se concentration of cereal grains by more than a factor of 1,000 [153]. Selenium deficiency in food and forage plants can occur both as a consequence of low Se concentration in the soil and low bioavailability for uptake of soil Se in plant roots and mycorrhiza, while a combination of high soil Se concentration and high bioavailability for Se uptake in the roots is needed for toxicity problems to occur.

This combination is geographically much rarer and affects a much smaller total number of people than either Se deficiency in the soil or poor bioavailability of soil Se for uptake in the plants, causing the Se intake of human populations to be less than physiologically optimal, *e.g.* for protection against HIV disease, coronary heart disease or colorectal cancer. Observations on other mammalian species as well as on humans have shown that there is a wide margin between the minimum Se requirement for prevention of manifest Se deficiency diseases and the threshold for appearance of clinically observable signs of Se toxicity. However, the intake needed for optimal protection against HIV disease, some forms of cancer and cardiovascular diseases appears to be much higher than the intake needed for prevention of manifest Se deficiency diseases (like Keshan disease in humans), and more subtle signs of toxicity can be seen in animal experiments well below the limit of manifest toxicity [25], and also in humans [159]. Thus the real biological optimum range is most likely fairly narrow.

This optimum, if one can rely on the clinical trials and epidemiological studies referred to above concerning HIV disease, cancer and cardiovascular diseases, as well as on observations from veterinary medicine (*e.g.* [82]) and numerous animal experiments (*e.g.* [7, 92, 153]), appears to be much higher than what most people in the world actually eat. It is possible that the difference between the biological optimum and actual intake could have been much less before than it is today in many parts of the world, due to a combination of several factors, such as more sedentary lifestyles leading to reduction of total food energy consumption, high intakes of edible fats and sugar (containing practically no Se at all) from many modern diets, deforestation and enhanced soil erosion leading to rapid removal of Se-enriched topsoil (especially in developing countries), and (especially in the industrial countries) high rates of application of Se-poor commercial fertilizers, which contain either P or S (or both) inhibiting the uptake of Se in plant roots, while also causing a dilution effect because of their own growth-stimulating effects on the plants. To this may also be added the problem of high burden of Se-antagonistic toxic heavy metals, such as Cd and Hg that may inhibit Se-dependent enzymes such as thioredoxin reductase and selenoprotein P.

World reserves of Se as a constituent of sulphide ores are limited [62]. It is therefore important to take such steps that might be necessary at an international political level to stop all forms of unnecessary wastage of this vital nutrient element, so that it may be available at an acceptable price also for future human generations. Selenium that can be obtained as a byproduct of pyrometallurgical processes or from purification of smoke gases from coal combustion should be extracted and stockpiled for the benefit of generations to come. Areas where Se toxicity can today be a problem for domestic animals (and sometimes, but much more rarely, for humans as well) should be regarded as an asset for a Se-hungry world, rather than as a local problem. They should not be used for livestock production (with risk of Se poisoning of the animals), but instead be used either for cultivation of Se-rich food crops (*e.g.* wheat) that can be used for Se fortification of similar crops from more Se-deficient areas, or for Se biomining by cultivation of Se accumulator plants [8, 38], from which the Se can be extracted or converted into Se-Met, using either chemical or biotechnological processing methods.

Further research is needed on Se speciation in soil, plants and humans and on kinetic interactions under varying soil conditions in order to optimize interventions to deal with Se toxicity, suboptimality and deficiency.

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Chapter 17
Zinc

Jelle Mertens and Erik Smolders

Abstract Zinc (Zn) is naturally present in all soils in typical background concentrations 10–100 mg Zn kg^{-1}. Human activities have enriched topsoils with Zn through atmospheric depositions, fertilization and sewage sludge application. Zinc contaminated soils with negative impact on the soil ecosystem are found around Zn smelters, near Zn mining sites and under galvanized structures. The solubility of Zn in soils is almost invariably controlled by sorption reactions. Pure Zn minerals (carbonates, silicates, hydroxides) have been detected at high total soil Zn concentrations ($>$1,000 mg Zn kg^{-1}) but are rarely controlling Zn solubility. Zinc is specifically sorbed as Zn^{2+} on pH-dependent binding sites of oxyhydroxides and organic matter and, at high concentrations, by ion exchange reactions on clay minerals. In general, soil solution Zn concentrations increase fivefold per unit pH decrease. Zinc deficiency for agricultural crops is found in about 1/3 of worldwide soils due to low total Zn concentrations and/or high pH. Soils containing less than 0.5 mg Zn kg^{-1} diethylenetriaminepentaacetic acid (DTPA) extractable Zn are potentially Zn deficient. Dietary Zn deficiency in humans is often associated with Zn deficient soils and crop Zn biofortification is now a global initiative through selection for Zn-efficient crops or judicious fertilisation. Zinc toxic soils are less widespread than deficient ones. Risk of Zn toxicity is manifested by effects on soil dwelling organisms, i.e. plants, invertebrates and soil microorganisms. Toxic effects are identified at total Zn concentrations 100 to $>$1,000 mg kg^{-1} and toxicity decreases with increasing soil CEC. Risk assessments of Zn have proposed maximal additions as low as 26 mg added Zn kg^{-1} in the EU to maintain soil ecosystem structure and function.

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17.1 Introduction

Zinc (Zn) is the 24th most abundant element in the earth, and is present in all soils in typical background concentrations 10–100 mg Zn kg^{-1}. These concentrations are higher than pristine concentrations due to historical enrichments (e.g. atmospheric deposition). Local concentrations can be far above this range due to high Zn in the soil parent material, large applications of sewage sludge, deposits in Zn mining areas or atmospheric deposits of Zn smelters. Zinc alloys (brass) were used by the Romans in 200 BC, and metallic Zn was first produced in Asia the twentieth century. In Europe, metallic Zn was imported from the east at the end of the Middle Ages, and was not industrially produced until the middle of the eighteenth century in Bristol, England. Production has increased tremendously over time and almost doubled in the last 20 years to a global production of 11.3×10^6 t in 2007 [40]. The historical production of Zn has released Zn to the environment via air and water. Smelter activities have contaminated large areas worldwide via atmospheric deposition of airborne Zn. Zinc is a micronutrient for all biota. Elevated Zn concentrations can cause toxic effects to plants, soil dwelling organisms and microorganisms and these ecotoxicological effects precede effects on humans. There is no known case of chronic poisoning of Zn to humans or wildlife via the foodchain because the phytotoxicity barrier effectively limits Zn transfer. Therefore, risk assessment on Zn mainly focuses on their effects to soil biota and soil functioning. At the lower scale of concentrations is the worldwide problem of Zn deficiency to plants and, accordingly, to humans. It is estimated that about one third of the global agricultural land and human population is Zn-deficient due to a low soil Zn content and/or low soil Zn bioavailability. The Zn contents of crops grown on Zn-deficient land are low, and humans residing in these areas usually rely on these crops for their daily caloric intake. Zinc deficiency causes a variety of adverse effects such as growth retardation, delayed sexual and skeletal maturation and behavioral effects. Zinc fertilization and the (genetic) selection of Zn efficient cultivars are nowadays used to address the Zn deficiency problems along with the provision of Zn additives.

17.2 Geochemical Occurrence of Zinc

Zinc is naturally present in the earth's crust as part of rocks or Zn-rich ores. Zinc ores were locally formed by natural geological process and are located all over the world. Economically important ores contain typically 5–15% Zn as zinc sulphides (sphalerite or wurzite) or, to a lesser extent, other Zn minerals such as zinc carbonates (smithsonite) or Zn silicates (hemimorphite). Important deposits are located in China, Australia, Peru, Canada, U.S.A. and Iran. Soils that form on these Zn-rich locations can be

Table 17.1 Range of Zn concentrations in igneous rocks, sedimentary rocks and soils

	Zn (mg kg^{-1})	References
Igneous rocks		Data taken from [53]
Basalt	48–240	
Granite	5–140	
Sedimentary rocks		Data taken from [53]
Shales and clays	18–180	
Black shales	34–1,500	
Sandstone	2–41	
Soils		
USA	<3–264 (median **53**)	[39]
Europe	<3–2,900 (median **52**)	[63]
China	Geometric mean **67**, mean 74	[22]

extremely high in Zn with concentrations far above the average background Zn concentration. The Zn concentration of rocks is highly variable. Basic igneous rocks such as basalt (typically 110 mg Zn kg^{-1}) are Zn-rich due to the isomorphous substitution of Zn for Fe^{2+} or Mg^{2+} in ferromagnesian minerals (e.g. augite, hornblende, biotite). In contrast, silica-rich igneous rocks (e.g. granite) or metamorphic rocks (gneiss) are rather low in Zn (typically 40 mg Zn kg^{-1}). Sedimentary rocks are formed from weathering products of igneous rocks, and the Zn concentrations will be largely determined by the Zn concentration of the igneous rocks. Sandstone or limestone, originating from low-Zn parent materials, contain typically about 20 mg Zn kg^{-1} whereas clays and shales contain 100 mg Zn kg^{-1} and with Zn-rich black shales even up to 1,500 mg Zn kg^{-1} (Table 17.1) (see also Chap. 2, Sect. 2.3.1.1)

Zinc is naturally present in all soils, and the natural background Zn concentration is dependent on the chemical composition of the parent material. Once formed, further physicochemical reactions (weathering, leaching and ageing) as well as human activities (agriculture, industry) affect the background Zn concentration. The global average background Zn concentration in soil is 55 mg Zn kg^{-1}, but concentrations vary widely between soils (Table 17.1). In general, soils with a high clay content will be associated with higher background Zn concentrations than sandy soils due to their higher native Zn concentration and their higher capacity to adsorb and retain Zn. In France, the median Zn concentration in sandy soils is 17 mg kg^{-1} whereas this concentration is 132 mg kg^{-1} for soils with more than 50% clay [6]. In the Netherlands, background Zn concentrations are 20–45 mg kg^{-1} for sandy soils, 55–140 mg kg^{-1} for peat soils and 70–150 mg kg^{-1} for clayey soils [24].

17.3 Zinc Input to Soils: Atmospheric Deposition, Animal Manure and Sewage Sludge

Zinc has been industrially produced since the late eighteenth century, and the production has continued to increase till today. Fifty percent is used for galvanizing purposes, and the remaining fraction is used for the production of brass and other Zn

Table 17.2 Zn emissions to agricultural soils in England and Wales in 2000, expressed as total Zn quantities and as fluxes for the land where the applications are use

Source	Quantity applied (Mt year^{-1})	Zn concentration (mg kg^{-1})	Zn addition rate (g ha^{-1} year^{-1})	Annual Zn input (t in 2000)	Time to reach soil limit (year)
Atmospheric deposition	NA	NA	221	2,457	1,733
Sewage sludge	0.44	802	4,557	385	80
Livestock manure				1,858	
Cattle slurry	1.74	170	1,063	–	358
Pig slurry	0.27	650	2,321	–	151
Layer manure	0.30	583	2,734	–	130
Inorganic fertilizer				266	1,234
Nitrogen	1.3	14	2.2	–	–
Phosphate	0.33	654	34	–	–
Lime	2.87	11	53	–	–

Data from Nicholson et al. [54]

A time was calculated to raise the Zn concentration at the given annual input from the mean background to the maximally permissible Zn concentration in soil at pH 6–7 for land where sewage sludge is applied (200 mg Zn kg^{-1})

NA not applicable

based alloys, motor vehicle tyres, rubber, cosmetics etc. In 2007, most of the Zn production in smelters and refineries was located in Asia (55%) with America and Europe accounting for 16% and 20%, respectively. Several efforts have been made to reduce industrial Zn emissions and to protect the environment from excessive Zn concentrations with worldwide Zn emission decreasing from 3.4×10^6 Mg Zn in the early 1980s to 2.7×10^6 t Zn in the early 1990s [56, 57]. Reduction of atmospheric emissions are illustrated by the 2.5 fold decrease of the Zn concentration in snow at Summit (Greenland) between 1967 and 1990 [11]. Along the same lines, reductions of Zn emissions to wastewaters are reflected in a twofold decrease in the Zn concentration of sewage sludge of the largest wastewater treatment plant in Paris (France) between 1980 and 2000 [36]. The reductions of Zn emissions to water and soil are largely explained by the worldwide reduction of atmospheric SO_2 concentrations decreasing Zn run-off from galvanized structures [45]. Tyre debris along roadsides is another important cause of local Zn contamination. Tyres typically contain 1–2% ZnO, and more than 4,000 t Zn year^{-1} is released via tyre debris in the EU (data taken from [8]). Part of the debris is released to roadside soils.

The total diffuse emissions of Zn to soil are only partly related to industrial use of Zn that emit Zn to soil via sewage sludge and atmospheric deposition (Table 17.2). Natural processes such as volcanic activities, forest fires or wind emit yearly about 50×10^3 t Zn to the atmosphere and accounted for about 40%

of the total annual Zn emissions in 1983 [55]. The remaining 60% originate from human activities (traffic, coal and fuel combustion; data taken from [34]). Zinc is mainly associated with aerosols with gaseous Zn accounting for less than 1% of total atmospheric Zn [34]. Background Zn levels in air are typically 0.01–0.2 μg m^{-3}. Concentrations are somewhat larger in the neighbourhood of industrial or urban areas, but are generally smaller than 1 μg m^{-3} [34]. Atmospheric Zn can be deposited back onto soil via dry (settling) or wet (rain) deposition. The European average Zn deposition is 230 g ha^{-1} $year^{-1}$ with the Scandinavian countries showing the lowest (20–120 g ha^{-1} $year^{-1}$) and Germany and Poland the highest (540 g ha^{-1} $year^{-1}$) rates (data taken from [54]). In England and Wales, about 2,500 t Zn was added to agricultural land via atmospheric deposition, corresponding to 220 g Zn ha^{-1} $year^{-1}$in 2000 (Table 17.2).

Agricultural practices locally add Zn to the soil through the application of manure or inorganic fertilizers. The addition of Zn supplements to livestock diets, or the presence of Zn in bedding material (e.g. straw) or drinking water (e.g. corrosion of galvanized drinking facilities) are the major Zn sources in manure. Zinc concentrations vary between fertilizers and the amount and type of fertilizers determines the rate at which Zn is introduced in agricultural soil (Table 17.2). In inorganic fertilizers (excluding Zn fertilizers themselves), Zn is only present as an impurity in very low doses; the median Zn concentration in 196 fertilizers on the European market was 115 mg Zn kg^{-1} [58]. The average addition of Zn to agricultural soils through the application of phosphate fertilizers is estimated about 43 g ha^{-1} $year^{-1}$ in Europe in 1999/2000 [58].

Sewage sludge can be used as a fertilizer and is a major source of Zn where it is applied: however, sewage sludge is not a major source of Zn at a large scale (Table 17.2). Zinc concentrations in sewage sludge depend on the wastewater discharge characteristics (e.g. industry or domestic) and can vary in time for a single sewage sludge treatment plant. Industry accounts for more than 50% of the Zn load in sewage sludge and the use of body care products is the main source of domestic Zn (www.iza.com). The awareness of metal effects on the environment resulted in decreased Zn concentrations in sewage sludge; concentrations decreased about twofold in Austria in the period 1980–2000 and in Germany in the period 1977–1993 (data taken from [3]). The average sludge Zn concentration in the EU ranges 142–2,000 mg Zn kg^{-1} dry matter (dm) (1993–1998) [3].

Removal of Zn with the harvested crop and Zn leaching are generally smaller than the annual additions. Moolenaar and Lexmond [52] calculated a net Zn enrichment of Dutch agricultural soils of 55–800 g ha^{-1} $year^{-1}$ which is in line with later calculations of German (558 g ha^{-1} $year^{-1}$) [79], Danish (300–440 g ha^{-1} $year^{-1}$) [7] and Swiss soils (100–40,000 g ha^{-1} $year^{-1}$) [44]. De Vries et al. [27] demonstrated that Zn accumulation varied up to 50-fold between fields with different soil texture (sand-clay-peat) and up to tenfold in a single field depending on the agricultural practice (arable vs. grassland). For reference, a ploughed topsoil (25 cm and 1.3 g cm^{-3}) with 50 mg Zn kg^{-1} contains 160 kg Zn ha^{-1}.

17.4 The Fate of Zinc in Soils

17.4.1 Soil Chemical Reaction Mechanisms: Mineral Dissolution, Adsorption and Solution Complexation

Zinc is present in the +II oxidation state in soil. The Zn concentration in solution can be affected by precipitation-dissolution, sorption and solution complexation reactions. The distribution of Zn over the solid and solution phase can be quantified by the solid-liquid distribution coefficient K_d (K_d is the ratio of the total Zn concentration over the soluble Zn concentration [l kg^{-1}]). These K_d values reflect the net result of all soil chemical reactions and should not be considered as a constant.

The Zn^{2+} concentrations in soil solution can be controlled by sorption and/or mineral dissolution reactions. There are conflicting views as to which of these dominate and as such has practical consequences in modeling Zn solubility. In a precipitation- controlled model, Zn concentrations are unaffected by total soil Zn concentrations, whereas a concentration dependency is predicted for sorption-controlled reactions. Solubility calculations predict that Zn precipitates are only formed at high total Zn, beyond the typical range of soil Zn concentrations (<200 mg Zn kg^{-1}). Common Zn precipitates are smithsonite ($ZnCO_3$; solubility product K_{sp} $10^{-10.9}$), hydrozincite ($Zn_5(CO_3)_2(OH)_6$; K_{sp} $10^{-8.7}$) or zincite (ZnO; K_{sp} $10^{-11.2}$). Jacquat et al. [41–43] and Voegelin et al. [74] determined Zn speciation in 51 soils (total Zn 251–30,090 mg kg^{-1}; mean 5,000 mg Zn kg^{-1}) contaminated with Zn-rich runoff water from galvanized structures using EXAFS and sequential extraction methods. Both techniques confirmed the presence of Zn precipitates in these soils, logically due to the high soil Zn concentrations. However, Zn solubility and the reversibly adsorbed Zn (labile Zn) increased with increasing total Zn, suggesting that dissolved Zn was not controlled by precipitation or, at least, not by a single mineral phase (Fig. 17.1) [30]. In addition, the pH dependent solubility was in line with a sorption and not precipitation-controlled reaction. A precipitation-controlled Zn solubility has been recently reported in overbank sediments contaminated by historic mining activities. These pH neutral soils contained >4,300 mg Zn kg^{-1} and absolute Zn concentrations and pH dependent solubility were in line with smithsonite controlled solubility [72]. Moreover, the adsorbed (labile) Zn concentrations were about 1,000 mg kg^{-1}, irrespective of the total Zn concentration as predicted by mineral solubility (An Van Damme, personal communication) and the presence smithsonite in these soils was confirmed by EXAFS.

Sorption of Zn^{2+} is, in general, the principle reaction that controls instantaneous Zn^{2+} in solution. Specific sorption of Zn^{2+} ('inner sphere complexes') is possible on organic matter and on oxyhydroxides of Fe, Al and Mn. A generalized sorption reaction reads

$$S - OH + Zn^{2+} \rightleftharpoons S - OZn^{+} + H^{+} \tag{17.1}$$

with S-OH a surface hydroxyl group of organic matter or oxyhydroxides. This reaction illustrates that protons are orders of magnitude more selective than Ca^{2+} on humic

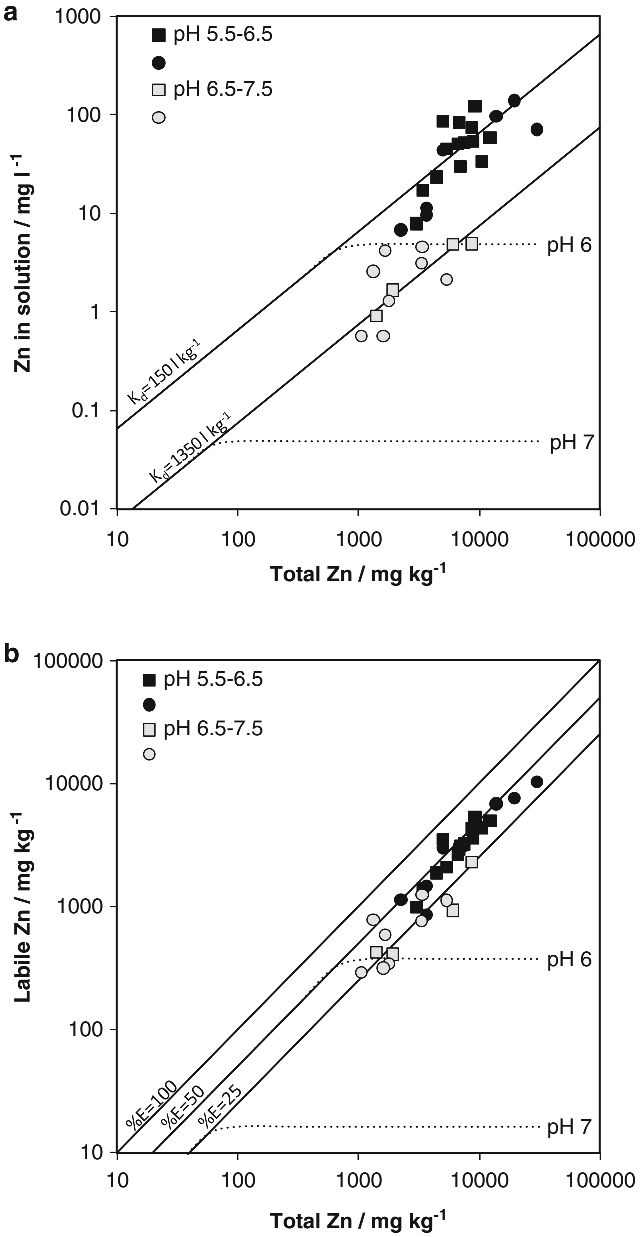

Fig. 17.1 Solution concentration of Zn (**a**) or labile Zn concentration (**b**) as a function of total Zn for soils collected under galvanized pylons with pH >5.5. In all soils, Zn precipitates were identified by EXAFS (circles: only Zn-layered double hydroxides (LDH); squares: Zn-phyllosilicates (+Zn-LDH)). The *straight lines* show the relationships for a 'sorption control' model, i.e. constant K_d or %E (fraction of Zn present as reversibly sorbed Zn), and the *dotted line* the expected concentration in case of 'precipitation control' at pH 6 or 7 (using the solubility product of Zn-phyllosilicate in equilibrium with quartz). The observed increase in solution and labile Zn concentrations with increasing total Zn concentrations is in contrast with a precipitation control model and indicates that there is no thermodynamic equilibrium with a single mineral phase (From Degryse et al. [30])

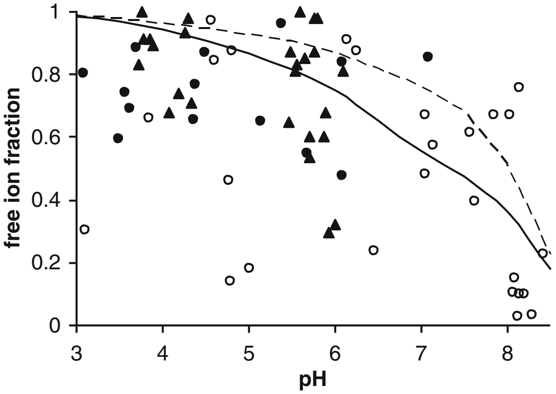

Fig. 17.2 Free-ion fractions of metals in soil solution measured with Donnan dialysis by different authors (●, ○, ▲) or ISE (Δ). The *lines* show prediction with WHAM6 for a generic composition of solution for either 'low' (*full line*) or 'high' (*dotted line*) concentration of the trace metals (From Degryse et al. [29])

acids or oxyhydroxides. Alternatively, Zn can also adsorb non-specifically by ion exchange on clay mineral surfaces or on the ionized groups of organic matter. These reactions are weakly selective, reversible and weakly pH dependent. Speciation calculation predicts that such reactions only contribute to Zn sorption at total Zn concentrations well above background.

Complexation of Zn^{2+} in soil solution with inorganic (e.g. sulphates) or organic ligands (e.g. citrate or humic acids) reduces the charge of Zn and renders Zn more soluble. In general, the free ion fraction (Zn^{2+}/dissolved Zn) decreases with increasing pH (Fig. 17.2). Zinc speciation was determined in 66 uncontaminated and Zn contaminated soils (pH 4.1–7.9; total Zn concentration 11–3,600 mg kg^{-1}), and organic Zn-complexes were on average 88% of the total dissolved Zn (range 60–98%). Free Zn^{2+} ions were, on average, only 8% of total dissolved Zn (range 0.1–21%) [68]. If the soil pH is higher than 7, $ZnOH^+$ becomes a dominant Zn species in soil solution with the neutral species $Zn(OH)_2$ dominant at $pH > 9$.

17.4.2 Slow Reactions of Zinc in Soil: Beneficial for Zn Toxicity but Unwanted for Fertilizer Applications

When Zn is added to soil, there is an initial reaction in which Zn adsorbs onto the solid phases. This reaction is fast, and instantaneous equilibrium between the reversibly sorbed (labile) pool and solution phase can usually be assumed. This initial fast reaction is followed by slower reactions that remove the metal from the labile pool into a pool from which desorption is slow, a process referred to as 'fixation' or 'ageing'. The ageing reactions logically increase the K_d and the Zn fraction that is fixed, i.e. not readily exchangeable with the solution phase, and is no longer (bio)available. It has been suggested that ageing reactions are due to an

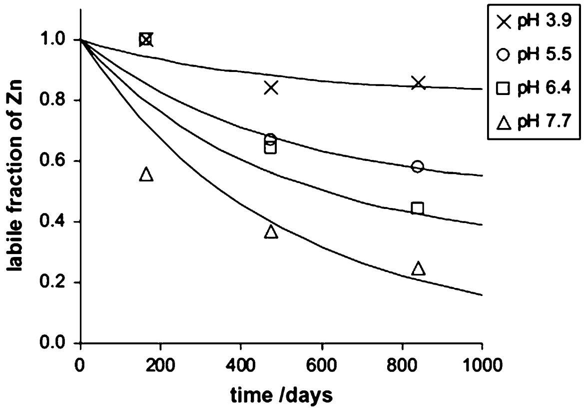

Fig. 17.3 The fraction of radio-labile Zn as a function of the incubation time for 4 $Zn(NO_3)_2$ amended soils with different pH. Soils were incubated under field conditions. Data show a decrease of the radio-labile Zn over time, and an inverse relationship between pH and the extent of Zn fixation (Data from Buekers et al. [14])

intraparticle diffusion of divalent metals in amorphous oxyhydroxides, and this process depends on electrostatic forces of attraction. Zinc fixation generally increases with pH due to the increasing number of reactive sites on oxides (Fig. 17.3) [15]. Fixation is important in reducing the Zn bioavailability.

This ageing reaction is a well known, beneficial reaction to explain the larger Zn toxicity in freshly spiked soils compared to field contaminated soils. At the lower Zn concentration range where Zn acts as an essential plant nutrient, such ageing reactions are logically negative. Here; ageing decreases the residual effects of fertilizer Zn [5, 12]. The work of Brennan [12] is perhaps the most comprehensive biological study to date of ageing reactions on Zn in soil. Fifty four soils varying widely in chemical properties (pH 4.8–8.6, clay 1.5–59.0%, org. C 0.3–3.5%) were incubated for 30 days at 30°C with three rates of Zn as $ZnSO_4$ (0, 133 and 266 mg kg^{-1}). Growth and Zn uptake of subterranean clover were determined using freshly added Zn as a control. The relative effectiveness of incubated versus fresh Zn was defined as the ratio of the slopes of the linear regression relationships between Zn uptake by plants and Zn added. Relative effectiveness varied from 0.47 to 0.80, with a strong negative relationship with soil pH i.e., greater ageing (lower relative effectiveness) at high pH values (Fig. 17.4).

Ageing reactions can be indirectly inferred from the difference in Zn solubility between freshly $ZnCl_2$ amended soils and a corresponding long-term Zn contaminated soil at similar total Zn concentrations (Table 17.3). At low Zn doses, K_d values are comparable but at higher Zn doses, K_d values indicate larger differences. These differences are, however, not only related to ageing but also to the associated increased ionic strength in Zn^{2+} salt amended soils compared to soils in which Zn was slowly added over time, allowing leaching to recover the ionic strength.

17.4.3 Fractionation and Speciation of Zn in Soils

The presence of selected minerals phases of Zn in soil, i.e. Zn speciation, is now being possible to detect down to a few 100 mg Zn kg^{-1} with synchrotron based

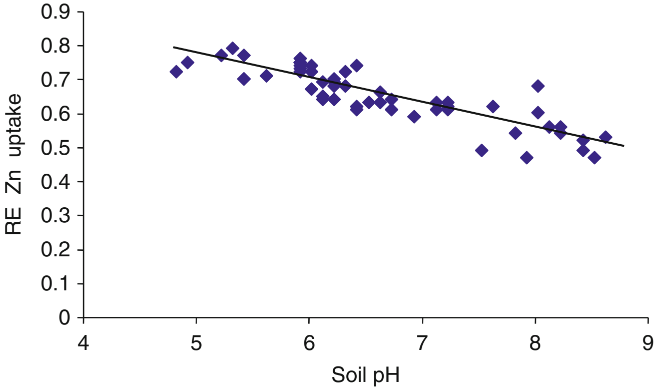

Fig. 17.4 Ageing effects on fertiliser Zn use efficiency: the relative effectiveness of incubated versus fresh Zn was defined as the ratio of the slopes of the linear regression relationships between Zn uptake by clover plants and Zn added. Ageing was 30 days incubated (30°C) of Zn added as $ZnSO_4$ to 54 soils (Drawn from data in Brennan [12])

Table 17.3 Soil solution composition of long-term field-contaminated soils and of freshly $ZnCl_2$ spiked soils at equal total Zn concentrations

	Field contaminated			Freshly spiked		
Total soil Zn (mg kg^{-1})	pH_{pw}[a]	Ca (mM)	Zn (mg l^{-1})	pH_{pw}[a]	Ca (mM)	Zn (mg l^{-1})
83	4.3	6.2	1.2	4.3	6.2	1.2
284	4.6	9.6	8.8	4.6	9.1	8.2
340	4.7	6.8	4.5	4.5	10.3	12
784	4.4	11.5	35	4.3	31.9	375
2,055	4.7	11.0	67	4.3	33.2	677

Data are from Smolders et al. [65]

[a] pH in the soil pore water

techniques (EXAFS). Alternatively, extraction based techniques allow to fractionate Zn into operationally defined fraction from which solubility can be estimated. The isotope exchange technique is a sensitive and conceptually attractive method to determine the reversibly sorbed (labile) pool but does not allow to determine the speciation of the remainder of the Zn in soil. For Zn, a radioactive isotope (e.g. $^{65}Zn^{2+}$) is added to soil and equilibrated for a short period (hours to days) after which the specific activity in solution ($^{65}Zn/Zn$) is determined. A higher ratio in solution than in soil means that a fraction of the soil Zn has not equilibrated with the added isotope, i.e., some (old) Zn has not equilibrated with freshly added Zn. The fraction that is isotopically exchangeable is the called the ‘labile’ fraction and is the fraction that has the same availability as freshly added Zn, also conceptually defined as the reversibly sorbed fraction. Alternative methods to determine labile fraction are extraction methods (e.g. 0.43 M HNO_3 or 25 mM EDTA). Results for the 25 mM EDTA extraction method and the isotope exchange method are highly comparable, but the 0.43 M HNO_3 extracts more at larger pH.

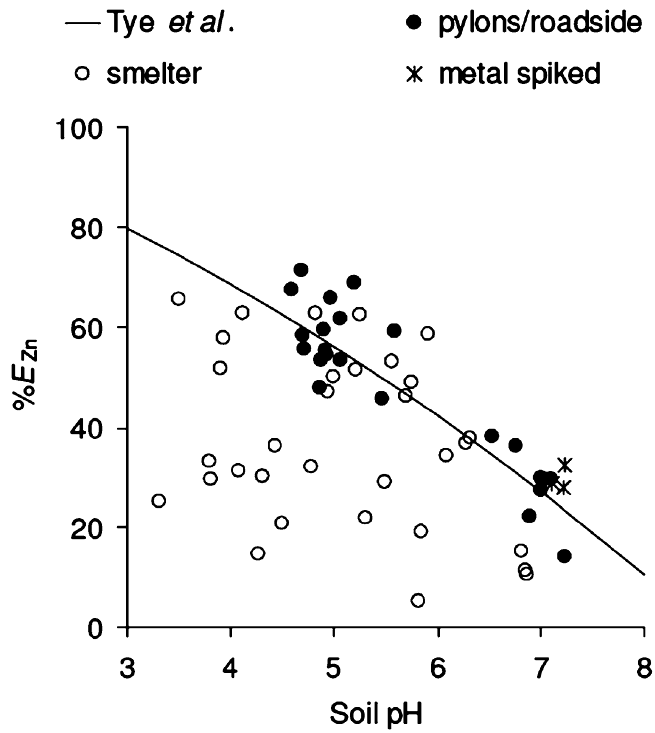

Fig. 17.5 Lability of added Zn for soils amended with Zn salts ('spiked'), soils sampled near pylons and crash barriers and soils near smelters. The line describes the relation between pH and % E in 23 Zn salt spiked soils after 3 years laboratory incubation. Labile fractions below this line may be related to insoluble Zn sources (Data from Degryse et al. [28])

This is likely attributed to the dissolution of carbonate complexed/bound Zn by the acid extractant [29].

Results of a survey of fixed and labile fractions in Zn contaminated soils are illustrated in Fig. 17.5. Zinc solubility depends on the origin of the added Zn; if Zn is added to soil as a soluble Zn salt, the median E value (radio labile Zn) is 55% whereas this value is only 30% for uncontaminated soils, sludge amended soils or soils near metal smelters. Over all soils, E values varied between 3% and 100% with a median value of 29% [28].

17.4.4 Models and Data of Zinc Solubility in Aerobic Soils

Based on previous considerations, it is clear that pH is the dominant factor affecting the solid-liquid distribution of Zn in soil with largest Zn mobility found in acid soils. This is due to the combined effect of pH on adsorption of Zn^{2+}, on fixation of

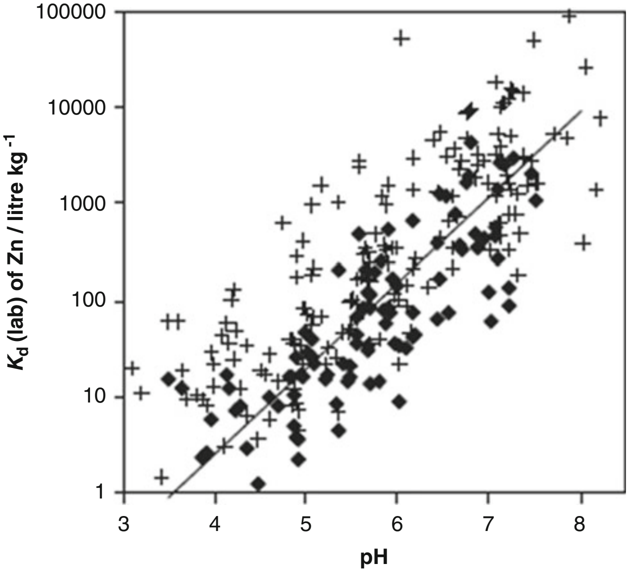

Fig. 17.6 Pore-water based K_d values of Zn, representing the partitioning between total (+) and soil solution Zn concentration or between labile (=adsorbed) metal (◆) and soil solution Zn concentration. The *full line* shows the regression equation of Anderson and Christensen [4] based on adsorption K_d values in 1 mM $CaCl_2$. The data illustrate that pH is the major driver for Zn solubility in soil (Data from Degryse et al. [29])

labile Zn inside minerals and the generally faster weathering of insoluble sources at lower pH. Most pore water based K_d values of Zn range between 10 and 10^4 l kg^{-1}. At an average total Zn concentration of 50 mg kg^{-1}, this is equivalent to a pore water Zn concentration of 50/10 to 50/10,000 mg l^{-1}, i.e. 0.005 mg Zn l^{-1} to 5 mg Zn l^{-1}. As a reference, the fraction of total Zn present in soil solution at a K_d = 1,000 l kg^{-1} is only 0.02%. The compilation of Fig. 17.6 also illustrates that the K_d increases with about a factor 5 (Zn solution decreases with about a factor 5) per unit pH increase. This zinc partitioning in soil can be described with two types of models: multisurface models and empirical models. Multisurface models consider soil as a collection of independent reactive surfaces (oxyhydroxides, clay and organic matter) to which ions can bind. A set of surface specific models is combined to describe Zn sorption on all reactive surfaces, and speciation calculations are preformed with common geochemical programs such as ECOSAT or WHAM. Multisurface models are conceptually attractive, and a powerful tool for scientific research. They are demanding a large number of parameter values and it assumes that sorption surfaces are additive s, i.e. no interaction occur. Empirical models are usually multiple regression equations. In general, regression models are calibrated against a wider range and suited for a larger number of soils [29].

The sorption reactions and the parameters affecting the partitioning of Zn are similar to those of Cd. As for Cd, most of the reported K_d values for Zn are based on measurements in dilute salt extracts. Considerable fractions of Zn in soil may be in non-labile form [28] due to ageing reactions or incomplete dissolution of Zn minerals or insoluble Zn contamination products (see Sect. 17.4.3). If K_d values are expressed as the solid–liquid distribution of the indigenous metal (i.e., including the fixed Zn fraction), values are obviously higher than adsorption K_d values only considering the reversibly sorbed (labile) Zn fraction on the solid phase (Fig. 17.6). Based on the plotted regression lines, the difference between both concepts is about one order of magnitude. The regression equations based on adsorption K_d values are in good agreement with K_d^{lab} values (i.e. labile Zn/solution Zn and not total Zn/solution), indicating that adsorption measurements of Zn (at low concentration) in a dilute salt extract give a reasonable estimate of the *in situ* distribution of labile zinc. Using large datasets, best fitted regression models were

$$\log K_d = -1.77 + 0.66\ \mathrm{pH} + 0.79\ \log(\%\mathrm{OC})(n = 143) \tag{17.2}$$

and

$$\log K_d^{lab} = -2.48 + 0.69\ \mathrm{pH}\ + 0.67\ \log(\%\mathrm{OC})(n = 97) \tag{17.3}$$

in which OC is the organic carbon content in % [29].

17.4.5 Fate of Zinc in Reduced Soils

Waterlogging may initiate a suite of reactions that affect Zn mobility in contrasting ways. The soil pH generally increases under anoxic conditions to values close to 7 when Mn(IV), NO_3^- and Fe(III) act as electron acceptors. The pH increase promotes Zn^{2+} sorption mainly on organic matter, since H^+ is the major competing ion for trace metal sorption (See above). This is mainly important in acid(ic) soils. In contrast, reductive dissolution of Fe oxides can mobilize metals [23]; metals that are sorbed on or embedded in iron oxides are released to the soil solution. These reactions are not infinite, and are governed by the solubility of Fe and Mn oxyhydroxides and carbonate minerals. For Fe, crystalline minerals such as Fe_3O_4 (magnetite) or $FeCO_3$ (siderite) can be formed if the maximum Fe solubility is exceeded, and the dissolution becomes more a conversion of an amorphous iron mineral to a crystalline mineral rather than the pure dissolution reaction. The formation of new minerals implies that previously released Zn can be re-occluded in the new minerals as a substituting ion (Zn^{2+} instead of Fe^{2+} or Mn^{2+}) or as an inherent component such as franklinite-like solids ($ZnFe_2O_4$). These re-occluded Zn ions are no longer bioavailable within a reasonable timeframe. Alternatively, dissolved Fe^{2+} ions can mobilize sorbed Zn^{2+} due to competition effects [62, 75, 80]. Waterlogging may also promote the

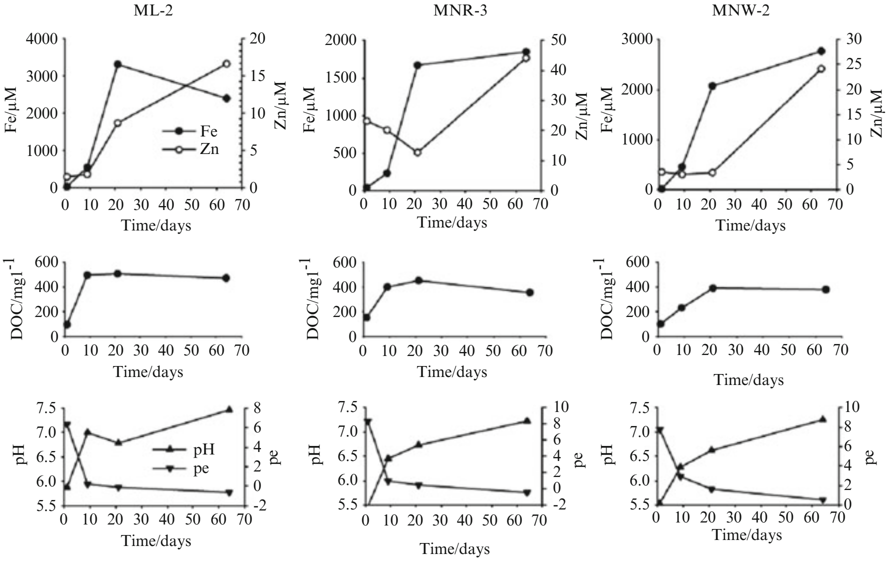

Fig. 17.7 Evolution of the soil solution Zn, iron and dissolved organic carbon concentration, and pH and pe upon waterlogging three Zn contaminated riparian soils. Despite an initial decrease or plateau, Zn is mobilized in all soils after 20 days waterlogging (Data from Van Laer et al. [73])

anaerobic degradation of organic matter, thereby increasing Dissolved Organic Matter (DOM) concentrations in solution [59], which can complex and mobilize metals [37]. In prolonged reduction reactions, Zn can be immobilized due to the formation of sulphide (e.g. sphalerite) or carbonate (smithsonite) precipitates if the solubility product is exceeded [10].

Zinc mobility has been shown to change upon waterlogging; Olivie-Lauquet et al. [59] reported a fivefold seasonal change of the Zn concentration in groundwater of wetlands. The net effect of waterlogging on the soil solution Zn is variable, and is explained by these counteracting mechanisms. In general, the Zn concentration in solution decreased upon waterlogging [20, 32, 62] and Zn deficiency may be induced by soil chemical reactions in irrigated rice. Exceptions have been reported; Weber et al. [75] observed a mobilization of Zn in riparian floodplain soils with high levels of Cd and Zn whereas the Cd concentration decreased due to CdS formation. Recently, it was described that Zn was surprisingly released by, on average, a factor of 18 (range 0.6–80) when 12 Zn soils sampled from riparian soils (i.e. soil that are periodically waterlogged) were submerged and incubated under N_2 (Fig. 17.7). The Zn mobilization was largest at lowest total soil Zn. The mobilization was neither explained by the pH increase (average of 1.8 units) nor by the increased DOM concentration. Modeling and pore water composition suggests that Zn mobilization was attributed to the desorption of Zn^{2+} ions by Fe^{2+} and by the release of Zn from Fe-minerals that dissolve upon reduction [73].

17.5 Zinc Deficiency in Plants

17.5.1 Zinc Deficiency in Soils and in the Human Food Chain

From an FAO study carried out in 30 countries, it was estimated that about 30% of the agricultural soils are Zn deficient and, associated with that, that about 1/3 of the world population suffers from mild to severe Zn deficiency (Fig. 17.8) [64].

The problem of Zn deficiency is mainly attributed to the low Zn bioavailability in soil. Total Zn is not a robust predictor for plant available Zn concentrations, and soil extraction procedures have been developed to determine Zn availability. Diethylenetriaminepentaacetic acid (DTPA) was originally developed to assess Zn phytoavailability in near-neutral and calcareous soils [47], and is still the most widely used soil extractant. Critical soil Zn concentrations for healthy growth of plant species have been derived by assessing the maximal soil Zn concentration above which Zn fertilization did not promote plant growth anymore (see example in Table 17.4).

Critical thresholds are typically 0.1–1 mg DTPA-extractable Zn kg^{-1} [13]. Soils associated with Zn deficiency have typically a low total soil Zn, high $CaCO_3$ content, high organic matter content, neutral or alkaline pH, high P or Mg concentration and/or prolonged waterlogging [1, 16]. Zinc deficiency can be induced by P-fertilization and is likely related to the increased Zn^{2+} sorption on Al and Fe oxyhydroxides on which P sorption reduces the positive charge.[9]. The use of the DTPA protocol to assess Zn phytoavailability has been criticized as having been validated for near-neutral or calcareous soils only. Alternative extractants are Mehlich I, Mehlich III, 0.1 M HCl and, especially, neutral salt solutions

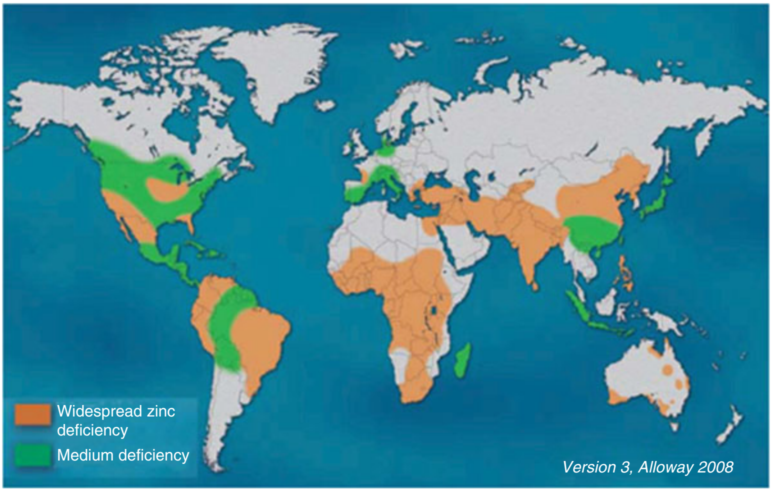

Fig. 17.8 Global distribution of reported Zn deficiency in crops (From Alloway [1])

Table 17.4 Effect of soil Zn application (23 kg Zn ha^{-1}) on wheat grain yield (cv. Gerek-79) grown in various locations in Central Anatolia (Turkey) with different levels of DTPA-extractable Zn in soils

Location	DTPA-Zn (mg kg^{-1})	Grain yield (t ha^{-1})		Yield increase (%)
		−Zn	+Zn	
Konya (Centrum)	0.13	2.8 ± 0.7	5.9 ± 0.5	109
Konya (Comakli)	0.11	0.2 ± 0.1	1.4 ± 0.5	554
Eskisehir	0.15	2.5 ± 0.9	3.3 ± 0.2	31
Sarayönü (Cesmelisebil)	0.25	1.1 ± 0.5	2.3 ± 0.5	16
Sarayönü (Gözlü)	0.38	1.1 ± 0.1	1.5 ± 0.3	27
Cumra	0.64	5.4 ± 0.1	5.6 ± 1.1	5

Data from Cakmak et al. [19]

Wheat yield did not respond to Zn fertilization at 0.6 mg DTPA-extractable Zn kg^{-1} anymore, and the threshold for Zn deficiency was 0.4 mg DTPA-extractable Zn kg^{-1}

Table 17.5 Relative sensitivities of selected crops for Zn deficiency

High sensitivity	Medium sensitivity	Low sensitivity
Bean	Barley	Wheat
Maize	Potato	Pea
Rice	Soybean	Grass
Fruit trees	Lettuce	Clover
Sorghum	Tomato	Alfalfa

Adapted from Alloway [2]

(0.1 M $NaNO_3$ or 0.01 M $CaCl_2$). In general, soil Zn extracts using latter extractants correlate well with plant Zn concentrations [51].

Crop sensitivity to Zn deficiency varies widely with maize, rice, beans and sorghum the most sensitive crops (Table 17.5).

Zinc deficient soils produce food products that are low in Zn and human Zn deficiency may occur. For example, bread wheat grain Zn typically contains 30 mg Zn kg^{-1} and decreases to below 15 mg Zn kg^{-1} in deficient crops [1]. There is some uncertainty and variability surrounding the recommended daily intake of Zn below which human health effects start to occur. The Reference Daily Zn Intake (RDI, set by the FDA in U.S.A) is 15 mg Zn for an adult. The Recommended Nutrient Intake (RNIs) defined by a FAO/WHO/IAEA working group ranges 4–17 mg Zn for adolescents, depending on food Zn bioavailability (low in unfermented cereal products and high in non-vegetable sources such as meat and fish; [78]). Adults may have lower Zn requirements and pregnant women have higher ones. Dairy products and meat consumption are rich sources of Zn. Subsistence farmers living in Zn deficient areas may have a Zn deficient diet if meat or dairy products are not frequently consumed, and this is often aggravated by low Zn bioavailability in high phytate products such as grain products. For example, a daily consumption of 250 g meat and 500 g dairy products contributes >20 mg Zn. In many Central Asian and Middle Eastern countries, however, wheat provides ±50% of the daily energy intake and the proportion can exceed 70% in rural areas [16]. A daily portion of 400 g rice or tubers for subsistence farmers contributes less than 10 mg Zn day^{-1} (Table 17.6).

Table 17.6 Zinc content (fresh weight based) of some typical food items

High Zn (25–50 mg kg^{-1})	Moderate Zn (10–25 mg kg^{-1})	Low Zn (<10 mg kg^{-1})
Whole grain cereals	Processed cereals (low extraction rate)	Fish
Unpolished rice	Polished rice	Milk
Pulses	Chicken	Roots and tubers
Lean red meat	Pork and meat with high fat content	Green leafy vegetables
Legumes		Fruits

Data from WHO [77]

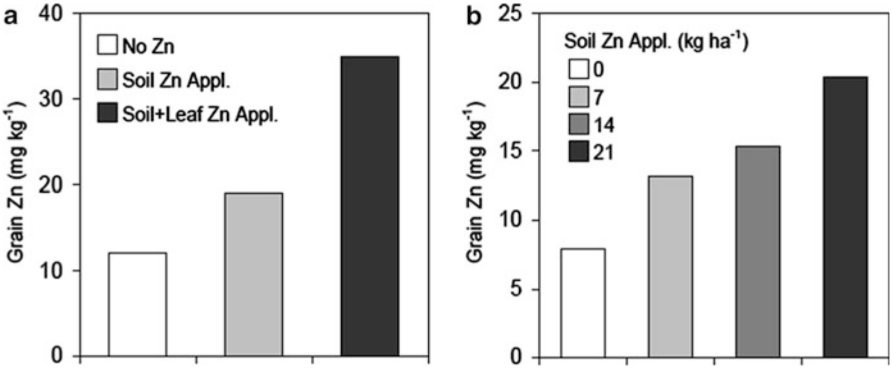

Fig. 17.9 Grain Zn concentration of durum wheat subjected to soil and soil + foliar application of $ZnSO_4$ (**a**) and increasing concentrations of soil applied $ZnSO_4$ (**b**). Plants were grown in a highly Zn deficient calcareous soil under field conditions in Central Anatolia, Turkey. The grain Zn concentration increased with Zn fertilization (Data from Cakmak [17])

17.5.2 Managing Zinc Deficiency: Biofortification

There are two options to increase the plant Zn content: Zn fertilization or Zn biofortification. Zinc fertilization can occur via application of Zn on or in soil, seed coating or via foliar spraying (Fig. 17.9). The most frequently used fertilizers are Zn salts such as $ZnSO_4$, ZnO (less effective when applied in soil with high pH) or chelated forms such as $Na_2ZnEDTA$ (mainly for foliar spraying). Zinc application rates are typically 10 kg Zn ha^{-1} (range 4.5–34 kg Zn ha^{-1}) and depend on site and crop characteristics. Zinc application in soil has the advantage that residual Zn remains present for future crops, whereas residual Zn from foliar application is removed from the site after harvesting. Zinc deficient soils, however, are mostly characterised by an extremely low (e.g. sandy soils) or and extremely high (e.g. calcareous soils) Zn binding potential, and foliar Zn application is advised in these soils.

Biofortification is the process of increasing Zn concentrations in grains and pulses of growing crops by plant breeding (genetic biofortification) or judicious use of fertilizers (agronomic biofortification) [2]. Agronomic biofortification is essential to create and maintain a sufficiently large bioavailable Zn pool in soil, to optimize Zn transport to seeds during the reproductive growth stage, and to improve grain Zn bioavailability for humans. Numerous studies report promising data on increasing grain yields on fertilized Zn deficient soil, but specific fertilization strategies are required to increase the grain Zn content. Cakmak [17] applied soil Zn and soil Zn+ foliar Zn to wheat. Soil applied Zn slightly increased grain Zn content, but the combination of soil Zn and foliar Zn at two different growth stages increased grain Zn content threefold compared to the unamended plants. The additional application of soil Zn and/or N fertilizers (e.g. urea) maximized the grain Zn content, and concentrations were >100 mg Zn kg^{-1} in grain, The interaction of N × Zn is explained by proteins that facilitate Zn uptake, root-to-shoot transport and Zn sequestration in the grain [18].

Genetic biofortification involves plant breeding to develop new cultivars capable of accumulating relatively high concentrations of Zn in grains [2]. It is the most cost-effective strategy to alleviate Zn deficiency, but it is a time and resource-consuming process. There is a huge variation in grain Zn concentrations between plant species and cultivars (reviewed by [76]). A few wild emmer wheat accessions were identified with a very high Zn (up to 125 mg kg^{-1}), Fe (up to 85 mg kg^{-1}) and protein (up to 250 g kg^{-1}) content in grain. At the same time, some of these accessions showed a simultaneous high tolerance for drought stress and for growth under Zn deficient conditions [60]. Most maize and rice cultivars have somewhat lower maximum grain Zn contents, but a fourfold variation between cultivars has been observed [76]. There is little information about the exact molecular or genetic mechanisms underlying grain Zn accumulation, but the development of transgenic plants with increased grain Zn content is very promising; it suggests a high potential for genetic biofortification to reduce Zn deficiency [16]. One of the main challenges to successfully introduce these Zn efficient cultivars is to make them tolerant to other chemical and physical problems in Zn deficient areas next to the low Zn bioavailability. For example, vertisols are often Zn deficient (high pH and $CaCO_3$ content), and are clay rich soils with a typical swell-shrink behaviour, whereas other Zn deficient areas suffer from salinity stress due to inappropriate irrigation practices. For this reason, Zn-efficient cultivars often do not perform well when grown in these areas [16]. To overcome severe human Zn deficiency on the short term, it is advised to combine techniques and use an optimal fertilizer strategy on most Zn-efficient crops [2, 18].

17.6 Toxicity of Zinc in Soil

17.6.1 Toxicity as Affected by Ageing and Soil Properties

Although Zn is an essential nutrient for plants, exposure to elevated Zn concentrations might cause plant toxicity. Typical Zn concentrations in healthy plants are 60 mg Zn kg^{-1} dm [26], and 10% reductions in plant yield are found

Table 17.7 Toxic (critical) Zn concentrations in plant leaves at a 10% yield reduction

	Critical level (mg kg^{-1} dry matter)
Maize	<200
Barley	290
Wheat	108–224
Lettuce	380–520
Cabbage	100
Bush beans	130–200

Data adopted from Macnicol and Beckett [50]

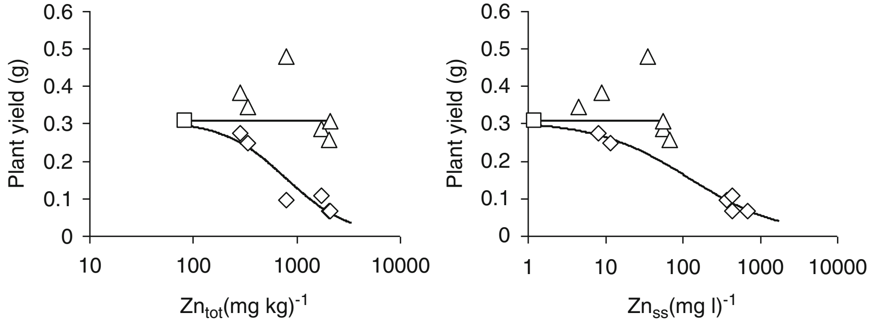

Fig. 17.10 Difference in Zn toxicity between freshly spiked (*diamonds*) and long-term contaminated soils under a galvanized pylon (*triangles*). The uncontaminated control soil is indicated with a square. Toxicity is larger in freshly spiked soils than in soils when expressed as total soil Zn (Table 17.8), but differences disappear when expressed on a soil solution (Znss) basis (Smolders and Waegeneers, unpublished data)

at 100–500 mg Zn kg^{-1} dm (Table 17.7). Increased plant Zn concentrations cause reduced root growth or stunted shoot growth, and may induce Fe and Mg deficiency.

Zinc toxicity to plant or soil (micro-)organisms is readily assessed by adding soluble Zn salts to an uncontaminated soil (‘spiking’) at increasing doses. Zinc toxicity is assessed within a short time frame (hours to weeks) after Zn spiking. The dose-response relationship represents the endpoint (e.g. plant growth) at increasing Zn concentrations either expressed as total soil Zn, added Zn or Zn in soil solution, and toxic concentrations can be inferred (EC_X = Zn concentration causing x% reduction of the endpoint compared to the control treatment; No Observed Effect Concentration (NOEC) = highest Zn concentration at which no inhibitory effect is observed). Zinc toxicity is often determined in such straightforward laboratory experiments, but the relevance for field conditions is questionable (Fig. 17.10). First, adding a Zn salt solution to soil affects the soil solution composition. The added Zn^{2+} desorbs H^+, Ca^{2+}, Mg^{2+} (Table 17.3) and part of the toxicity may be related to soil acidification [67].

Second, anionic Zn ligands such as chlorides or sulphates will be added to the soil solution and logically increase ionic strength and may induce salt effects [69]. To avoid these side effects, Zn toxicity thresholds can be derived using long-term

Table 17.8 Difference in Zn toxicity between freshly spiked (FS) and long-term (LT) contaminated soils of three sites

	Wheat		PNR		F. candida		E. fetida	
Soil	FS	LT	FS	LT	FS	LT	FS	LT
Rhydtalog (83 mg kg^{-1})	185	>2,101	600	>2,101	171	>2,101	569	747
De Meern (155 mg kg^{-1})	411	>2,520	591	>2,520	458	>2,520	902	>2,520
Zeveren (76 mg kg^{-1})	275	217	282	>3,741	165	507	1,120	1,100

Data from Smolders et al. [65], Smolders and Waegeneers (unpublished data) and Lock (unpublished data). Background Zn concentrations are indicated

The Zn concentrations causing 10% reduction of the endpoint (EC10 value), expressed as total soil Zn (mg kg^{-1}), for wheat growth, Potential Nitrification Rate (PNR), Glucose Respiration Rate (GRR), Maize Residue Respiration (MRR) and reproduction of *Folsomia candida* and *Eisenia fetida*

Zn contaminated soils. These can be either Zn spiked soils that are leached and/or aged to mimic field conditions, or field sites that are historically enriched by Zn (e.g. sites are sides under galvanized structures). Soils collected at different distances from the contamination source may yield such a Zn contamination gradient, however such gradients are often confounded by mixed metal contamination or an accumulation of organic material near the contamination source [35]. Selected pair-wise comparisons between long-term Zn (only) contaminated soils in laboratory spiking studies illustrated a discrepancy in Zn toxicity between both systems (Table 17.8).

Leaching and ageing reactions explain the discrepancy in Zn toxicity between freshly spiked soils versus long-term contaminated soils. In the long-term, Zn ions can be fixed on the soil solid phase and become unavailable for plants/(micro) organisms within a reasonable time frame (see Sect. 17.4.2). As a consequence, Zn concentrations in solution of freshly spiked soils are larger than in long-term field contaminated soils at similar total Zn concentrations. If Zn in soil solution is used as an indicator for toxicity, the difference between both Zn addition modes disappear (Fig. 17.11).

Toxicity of Zn also differs widely among different freshly spiked soils (Table 17.8). It was shown before (see Sect. 17.4.3) that Zn solubility largely depends on soil characteristics. As a consequence, adding a single dose of Zn to soils with different physicochemical characteristics implies a different Zn concentration in soil solution depending on the soil specific Zn adsorption characteristics. It was empirically found that total soil Zn thresholds for plants and invertebrates (e.g. EC50 values) of Zn increase with increasing effective CEC (Smolders et al. [66] and references therein).

17.6.2 Toxicity of Zinc in Sewage Sludge-Amended Soils

Sewage sludge application is one of the major routes through which Zn is added to soil via agricultural practices, particularly on a field-scale (Table 17.2). There is a general consensus that spiking soil with soluble Zn salts overestimates toxicity due

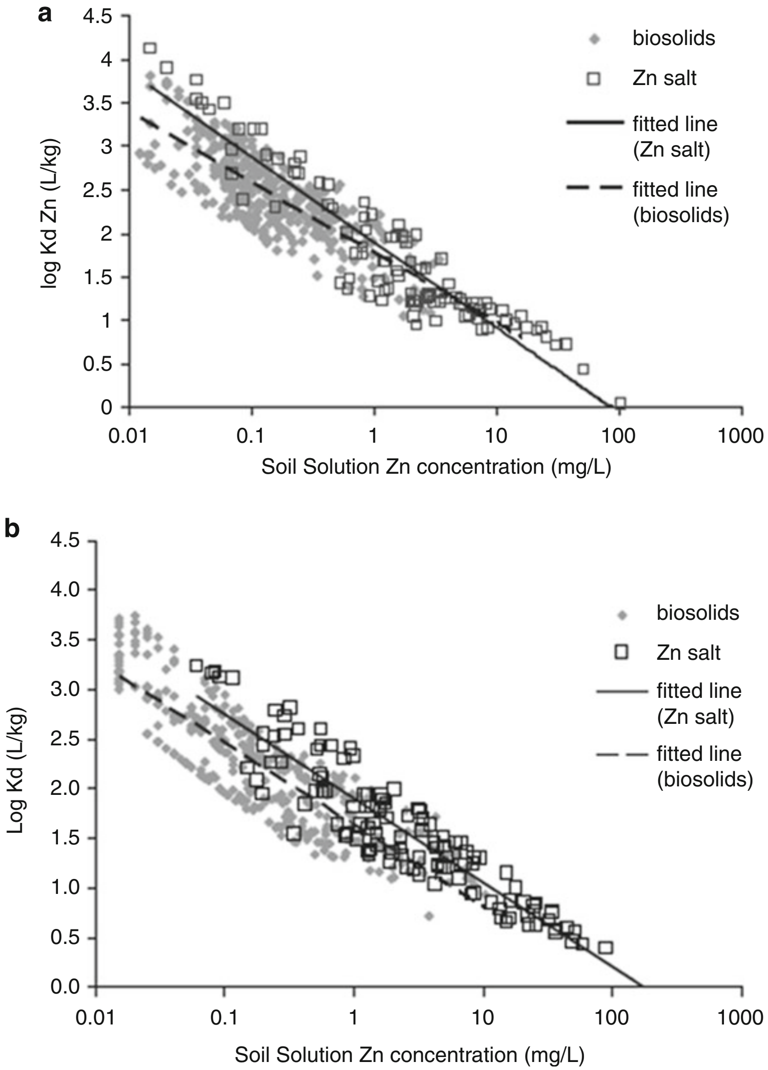

Fig. 17.11 Partitioning coefficient (K_d) for Zn versus the soil solution Zn concentration at the start of the experiment (**a**) and after the third harvest (i.e., after 3 years incubation in the field); (**b**). Zinc was added either in biosolids or as a soluble Zn salt. The regression lines for Zn salts and biosolids differed significantly ($p < 0.001$), but data of both treatments overlapped suggesting a similar Zn availability (Data from Heemsbergen et al. [38])

to bioavailability reasons discussed earlier (see Sect. 17.6.1). In contrast, sludge associated Zn is present in a matrix with a high metal binding capacity and high nutrient concentrations, the latter being beneficial to soil processes and plant growth. Comparing toxicity between either metal salt or sludge amended soils is important to predict the ecological consequences of sludge associated Zn.

Heemsbergen et al. [38] applied biosolids on 12 different field sites in Australia, and Zn chemistry and bioavailability were compared with corresponding Zn salt spiked plots. Zinc solubility, assessed by the K_d (Fig. 17.11), and plant availability were comparable between Zn spiked or sewage sludge-amended soils immediately after the experimental set-up and after 3 years incubation in open air. This suggests that Zn bioavailability in soil is similar if applied either as metal salt or via sewage sludge, and that the sludge matrix does not strongly exert protective effects.

17.7 Risk Assessment of Zinc in Soil

Zinc contaminated soils are unlikely to pose a risk to humans because the phytotoxic effects limit transfer of excessive Zn to the human food chain. Therefore, risk assessment of Zn contaminated soils focuses on its ecotoxicological effects on soil organisms. Toxic Zn concentrations vary widely between soils and Zn addition methods (salts versus aged) (Smolders et al. [66]), complicating the derivation of a single and general threshold for different soils.

So-called ‘soil Zn screening levels’ have been defined to regulate Zn emissions to soil. The ECOSSLs (Ecological Soil Screening Limits), derived by US-EPA in 2005, range from 46 mg Zn kg^{-1} for avian wildlife to 160 mg Zn kg^{-1} for plants. A European risk assessment, performed in 2008, derived a generic PNEC (Predicted No Effect Concentration) of 26 mg added Zn kg^{-1} which, after corrections for bioavailability and soil natural background, is equivalent to 28–286 mg total Zn kg^{-1} depending on soil characteristics (see below for more details). These values are not soil clean up standards but are derived as protective values to regulate the current emissions. Differences of soil Zn limits are large when contrasting different legislations (Table 17.9) and depend on the margins of safety applied, on the risk pathways considered and on political choices.

To illustrate a risk assessment, we briefly illustrate the effects assessment of Zn that was concluded in a European Zn risk assessment in 2008 [34]. Zinc toxicity data were taken from studies in which Zn salts were added to soil at increasing doses, and the No Observed Effect Concentrations (NOECs), expressed as added Zn to soil, were calculated (Table 17.10).

All NOECs were plotted in a cumulative probability curve, and the 5th percentile of the curve (HC_5) was derived (Fig. 17.12). At this Zn concentration, 95% of the species are protected from Zn toxicity. If only microbe-mediated processes are considered, the HC_5 is 27 mg added Zn kg^{-1}. This means that all soils with a total Zn concentration equal to the background Zn concentration plus 27 mg Zn kg^{-1}, are potentially affected. If invertebrates and plants are considered, a value of 52 mg added Zn kg^{-1} is derived. This value was considered not sufficiently protective based on the experimental data, and an assessment factor (AF) of 2 was used yielding a Predicted No Effect Concentration ($PNEC = HC_5/AF$) of 26 mg added Zn kg^{-1}. Soil bioavailability corrections were subsequently included [66]. First, the total added Zn concentrations was allowed to increase by a factor 3 to correct for differences in Zn toxicity between freshly spiked laboratory experiments and

Table 17.9 A selection of soil Zn limits (mg kg^{-1}) and their basis. Ecological Soil Screening Limits (ECOSSLs) or predicted no-effect concentrations (PNEC) are derived to evaluate current emissions and should not be considered as clean-up values since the degree of protection is large (i.e. conservative limits)

Legislations	Protection goal	Limit (and name)	Note
US-EPA-2005	Plants	160 mg kg^{-1} ECOSSL	[71]
US-EPA-2005	Soil invertebrates	120 mg kg^{-1} ECOSSL	[71]
US-EPA-2005	Mammals	79 mg kg^{-1} ECOSSL	[71]
US-EPA-2005	Birds	46 mg kg^{-1} ECOSSL	[71]
EU-risk of chemicals -2008	Plants, invertebrates, soil microorganism	26 mg kg^{-1} PNEC	[34] added Zn only and not including bioavailability corrections (see Table 17.11)
EU countries, Switzerland, USA and Canada	Unknown	100–23,000 mg kg^{-1} clean up values for residential areas 360–100,000 mg kg^{-1} clean up values for industrial landuse	[61]
UK sludge	Soil microorganism	200 mg kg^{-1}	Based on survival data of rhizobia [21, 31]
EU-sewage sludge limits 86/278/EEC	Unknown	150–300 mg kg^{-1}	[33]
US-EPA 1993 (biosolids)	Plants	2,800 kg ha–1, equivalent to about 900 mg kg^{-1}	Ceiling concentration [70]

Table 17.10 The NOECs (No Observed Effect Concentrations = highest Zn dose at which no inhibitory effect is observed) expressed as added soil Zn (mg kg^{-1}), for invertebrate, plant and microbial assays [34]

	NOEC range
Oligochaetes	85–1,000 (n = 27, 3 species)
Insects	32–1,000 (n = 18, 1 species)
Plants	32–400 (n =29, 16 species)
Microbial processes	
C mineralization	17–1,400 (n = 39)
N mineralization	38–1,000 (n = 26)
Enzyme activity	30–2,623 (n = 32)

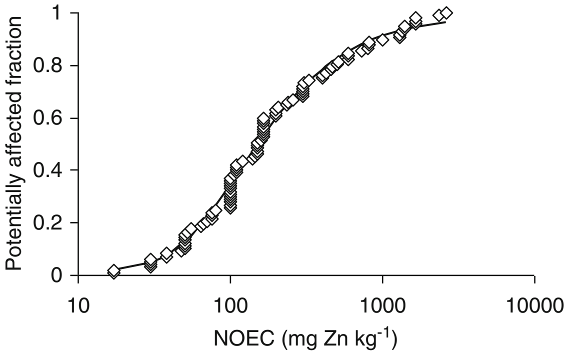

Fig. 17.12 Sensitivity distribution of No Observed Effect Concentrations (NOECs) of microbe mediated processes, not corrected for bioavailability. Based on this curves, the hazardous concentration affecting 5% of the microbial processes (HC_5) was derived [34]. At this concentration, 95% of all microbial species are protected from Zn toxicity (Redrawn from EU [34])

Table 17.11 Soil specific Predicted No Effect Concentrations (PNEC) for Zn as derived in the EU risk assessment of Zn in 2008

	Highly sensitive soil[a]	Medium sensitive soil[a]	Weakly sensitive soil[a]
added Zn (mg kg^{-1})	24	94	246
total soil Zn (mg kg^{-1})	28	111	286

PNEC values corrected for bioavailability as explained in Nicholson et al. [54]

[a] Properties for these three soils are, respectively, effective cation exchange capacity (eCEC), 4, 15, and 35 cmolc kg^{-1}; pH, 4.5, 5.5, 7.0; % OC, 1.0%, 2.9%, and 12%; % clay, 5%, 15%, and 30%; background Zn, 8, 51, and 155 mg Zn kg^{-1}

long-term field contaminated soils. Second, a correction was made considering soil physicochemical properties (effective CEC, background Zn and pH) that mitigate toxicity, yielding a final soil PNEC that varies with the soil properties; (highly-medium-weakly sensitive; Table 17.11).

Concerns about sludge-borne metals for soil application have been recognized since the 1970s. Current regulations for the use of sewage sludge as soil fertilizer are focused on preventing the build-up of metals in soils. Critical sludge limits are set for sludge and soils to which sludge can be applied (Table 17.9). In the EU, countries are allowed to apply sludge if the maximum allowable soil concentrations are not exceeded and will not be exceeded due to sludge application, or if the 10-year mean metal loading rate of added metals through sludge application is not exceeded. The US and the Netherlands made a risk assessment to determine which soil and sludge metal concentrations and metal loading rates are acceptable [25, 70]. Depending on e.g. the used approach or databases, both countries ended up with highly variable values; the maximum allowable Zn concentration for agriculturally used sludge in the Netherlands is 300 mg kg^{-1}, well below the US-EPA rules (Table 17.9).

17.8 Remediation of Zinc Contaminated Land

Zinc contaminated land that is considered harmful for the environment has to be managed to prevent long-term negative effects. There are a few options that are frequently applied. *Removal* is only suited for small scale point source contaminations. *Phytoremediation* by extraction has been often tested, but the time required to remove excess metals is long (years to eras) [46]. *Additives* can be mixed into soil to reduce zinc bioavailability. If soils are acid with high bioavailable Zn concentrations, lime can be applied to raise soil pH and reduce metal solubility. Liming needs to be repeated at regular time intervals to maintain soil pH. Alternative additives such as bauxite (red mud) residues or beringite, an alkaline aluminosilicate, have a high metal fixing capacity and will effectively fix metals on the long-term, even when soil acidify in the case of bauxite residue [48]. Lombi et al. [49] compared liming and bauxite or beringite application to remediate two heavy metal contaminated soils due to sewage sludge application (UK soil – 1,760 mg Zn kg^{-1}) or to smelter activity

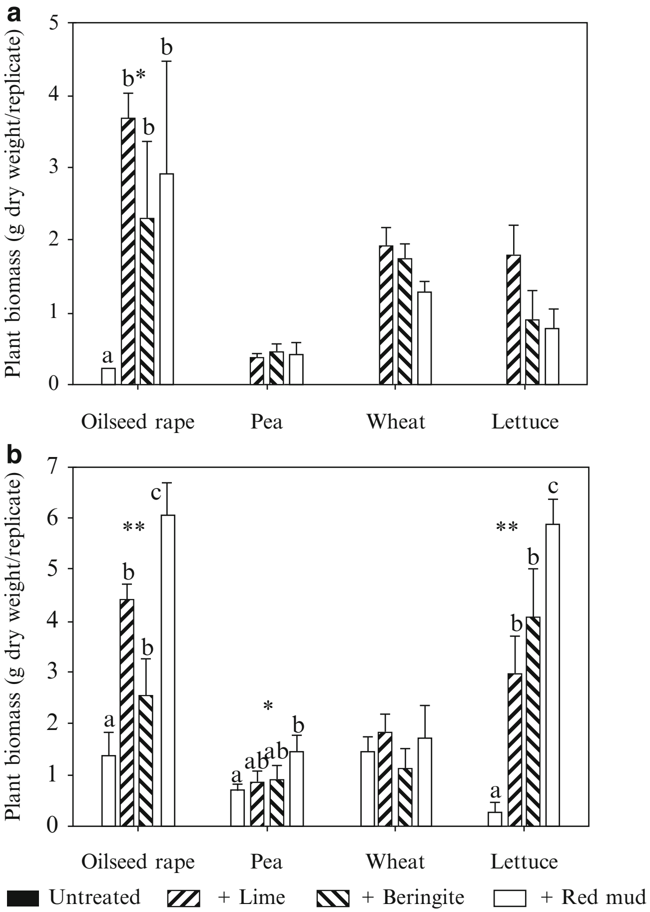

Fig. 17.13 Shoot biomass of oilseed rape and lettuce, and weight of pea seed and wheat grains grown on a Zn contaminated French (**a**) and UK (**b**) soil with and without soil amendments (0.25% $Ca(OH)_2$, 5% beringite or 2% red mud). Different letter represent significant differences at $p < 0.01$ (*) and $p < 0.001$ (*). All amendments were effective in reducing Zn toxicity, but effects differ between soils and plant species (Data from Lombi et al. [49])

(French soil – 2,920 mg Zn kg^{-1}). Effects between additives varied between soils and plant species, but performed well in reducing trace metal toxicity to plants (Fig. 17.13).

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Part III

Other Heavy Metals and Metalloids of Potential Environmental Significance

Chapter 18
Antimony

Rafael Clemente

Abstract Antimony (Sb) is a naturally occurring metalloid that has a wide range of industrial applications. There exists an increasing interest in this metalloid as it is likely to be a pollutant in industrialised environments. It is now known that Sb has fewer geochemical and toxicological similarities with As than previously believed. It has low mobility and bioavailability in soils, and presents low toxicity to plants, although where Sb is present in more mobile forms in the soil it can be accumulated by plants and affect their growth.

Keywords Antimony • Alloys • Ammunition • Flame-retardant • Metalloid • Semiconductor • Smelter • Stibnite • Valentinite

18.1 Introduction

Antimony (Sb) is a naturally occurring metalloid element. It can exist in a variety of oxidation states (−III, 0, III, V), but is mainly found in two oxidation states (III and V) in environmental, biological and geochemical samples [18]. The abundance of Sb in the Earth's crust is in the order of 0.2–0.3 mg kg^{-1} [21]. The concentration of Sb in soils is higher than that in parent rock materials. In unpolluted (background) soils, the concentration range is from 0.3 to 8.4 mg Sb kg^{-1} [28]. In Europe, natural background concentrations in soils range from 0.1–1.9 mg kg^{-1} (10–90th percentile for EU soils) [49].

In 2007, Sb was mined as a principal product or was a by-product of the smelting of base-metal ores in ten countries [11]. Nearly all the world's primary Sb was mined in China (88%), Bolivia (3%), South Africa (3%), Russia (2%), and

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Tajikistan and Australia (1% each). Current world production of Sb is about 160,000–170,000 t per year [12]. In 2008, the USA consumption of Sb was 23,800 t and the estimated distribution of Sb used was as follows: flame retardants, 40%; transportation, including batteries, 22%; chemicals, 14%; ceramic and glass, 11%; and other, 13% [12]. Antimony is therefore not a major pollutant, but local accumulation or dissipation by incineration or dumping (e.g., Sb mining areas) must be controlled. The present day enrichment factor (relative to elements/Sc ratios of typical crust rocks) is of the order of 70 times (for comparison, it is 20 for As, 130 for Pb) [51].

For years, the major industrial use of Sb was the production of alloys, but now the main industrial applications include flame retardants, a catalyst in plastics production, pigment in paints or in production of glassware [45]. In its 'metallic' form, its major use is as a hardener for Pb, e.g., in Pb-acid batteries, cable sheathings and ammunition, and it is also an important component in semiconductors. Large amounts of Sb (as antimony trioxide Sb_2O_3) are used in flame-retardants in textiles, papers, plastics and adhesives and there is no perspective on the development of alternative materials. It is also used as a ceramic opacifier (to make the material opaque) and as a mordant (fixing colours). Antimony tetroxide (Sb_4O_8) is used as an oxidation catalyst (oxidative dehydrogenation of olefins) [60]. Antimony is also commonly used in products such as brake linings, antiparasitic agents, polyethylene terepthalate (PET) plastics, and as an additive in the tyre vulcanization process [37, 53].

18.2 Lithogenic Occurrence and Geochemistry

Antimony is a chalcophile element and as such mainly occurs in nature as Sb_2S_3 (stibnite, antimonite) and Sb_2O_3 (valentinite) [9]. In addition to those major forms, the most important ores of Sb include kermesite (Sb_2S_2O) and cervantite (Sb_2O_4) [42]. These compounds are commonly found in ores of Cu, Ag, and Pb. Antimony is also a common component of coal and petroleum. Many sulphide and oxide minerals containing Sb (in particular Sb(III)) have been identified in rocks and mineral deposits, yet very little is known of secondary minerals that may form in sediments and soils under ambient conditions [25]. Antimony has been observed to have relatively low mobility in soils [23, 37, 43]. Direct chemical oxidation of the primary Sb ore antimonite by environmental oxygen is negligible. Instead, the process is carried out by specific autotrophic bacteria. These are common in oxidation zones of Sb deposits, and take an active part in the formation of their oxidised products [63]. Biogenic degradation pathways of antimonite and Sb sulpho-salts are quite specific [47].

Antimony is a metalloid which has chemical and toxicological properties similar to As owing to its position in the periodic table. Its toxicity depends on factors like oxidation state, compound solubility, and interactions with ligands [31]. Numerous papers on the distribution, cycling and mobility of Sb confirm the increasing interest in this metalloid, which is one of the important anthropogenic contaminants [32, 37, 38]. Only recently Sb has become the focus of environmental concerns about trace element inputs into shooting range soils [48]. Filella et al. [19] have also recently reviewed (i) how much is present in the different environment compartments; (ii) in which form it is actually present; (iii) its toxicity; and (iv) its cycling between the different compartments.

18.3 Chemical Behaviour in Soil and Availability to Plants

In soil environments Sb has shown less mobility and bioavailability than As or Cu [20, 62]. A very low percentage is extracted by using mild extractants and, when sequential extraction procedures are applied, some Sb is present in the 'Fe oxide' fraction, but most is present in the so-called residual fraction [19]. Even in heavily polluted soils in the proximity of mines and smelters, Sb is essentially immobile in soils. It is generally believed that Sb is mainly present as Sb(V) in soils. In fact, solid phase speciation in environmental systems containing concentrations high enough for X-ray absorption spectroscopy (XAS) (around smelters, mine pits or shooting ranges) have shown that Sb was present exclusively as Sb(V), and Fe(III) hydroxide was the apparent host phase [41, 50, 58]. Although the oxidation of Sb (III) in homogeneous solution with O_2 is kinetically hindered and extremely slow [34], oxidation of Sb(III) to Sb(V) is fast in both natural water and soil in the presence of amorphous Fe and Mn oxyhydroxides [5, 46], while the mechanism is unclear [25]. Most Sb is emitted as Sb_2O_3 from smelting operations, and around 70% of it can be oxidized to Sb(V) in the soil in 2 days [46].

The low mobility of Sb in soil is reflected in all the relevant studies to date and is a function of speciation. Adsorption and further oxidation of Sb(III) by amorphous Fe and Mn oxyhydroxides has been reported [5]. Studies have indicated the adsorption of Sb by other agents such as humic acids (HA) [8] or hydroxyapatite [35]. Amorphous components have an important role in soil adsorption of Sb(V). Generally, Sb(III) binds to solids more strongly and over a wider pH range than Sb (V). Andosol soils rich in amorphous components have a high capacity for Sb(V) adsorption [57]. In these soils, the contribution of Fe-related surface base groups is higher than the aluminol and silanol groups. The adsorption of Sb(V) has been shown to be closer to that of As(III) than As(V) [57]. A significant fraction of Sb in the <0.5 mm fraction of shooting range soils was found to be oxalate-extractable, indicating an association with amorphous ferrihydrites, but also possibly with solid phases, such as carbonates, that are soluble at pH 2 [25]. The mobile fraction appeared to be Sb(V) and the precipitation of Ca antimonite may play a role controlling the solubility. McBride [40] also reported adsorption of soluble Sb by clays and Fe or Mn oxyhydroxides, these processes markedly affecting Sb mobility and availability.

Only a minor role for pH in the mobilisation of Sb has been reported [36]. Jones et al. [26] described strong adsorption of Sb(V) by hematite below pH 7, and rapid desorption at higher pH. The dominant solution species was $[Sb(OH)_6]^-$. Depending on experimental conditions Sb(V) is almost completely sorbed at pH values below 7, while Sb(III) sorbs to pH values of at least 10 [25]. In three different mine soils in Spain, low soil Sb mobility was encountered with no significant influence of the measured general soil characteristics on Sb mobility [42]. Relatively low Sb extractabilities (<6% of total soil concentration) have been also reported by Lintschinger et al. [37].

Antimony association with soil organic matter in environmental samples has only been confirmed in recent years [13, 14]. A significant correlation ($P < 0.05$) between Na_2HPO_4-extracted Sb and TOC was observed in different highly polluted soils and sediments [17], indicating that it could be specifically sorbed onto organic matter. Weak sorption on organic matter may be dominant for oxyanions especially under acidic conditions. Tighe et al. [59] reported sorption of Sb(V) by HA decreased as the pH increased. When a liming-induced pH increase is applied, the mobilisation of soluble Sb needs to be considered [30]. The importance of humic substances, particularly soil humic acids, in converting inorganic Sb(III) species to a less toxic species (i.e., Sb(V)) as well as arresting Sb movement through the soil by complexing with it has been reported [55]. Klitzke and Lang [30] suggested that Sb does not bridge to non-mobile or aggregated organic matter to the same extent as As, because of different accessibility of negative charge. In the $Sb(OH)_6^-$ complex the negative charge is located at the Sb atom which is coordinated by six octahedral OH-groups [29], with these OH-groups shielding the negative charge [30].

Nakamaru et al. [43] found that in a range of Japanese agricultural soils, soil solution distribution coefficient (K_d) values of Sb, and therefore sorption, increased with decreasing pH and decreased with increasing phosphate concentration, suggesting pH-dependent specific sorption of Sb species. In a Japanese mine tailings soil, under reducing conditions, the concentration of As in the soil water increased whereas that of Sb decreased showing different redox properties of Sb and As [41]. In that study, Sb(V) was the stable oxidation state over a wide range of Eh in soil and it was mainly associated with Fe(III) hydroxide; dissolved Sb concentrations did not increase with decreasing redox potential [41].

Plants are generally more tolerant to soil Sb than soil fauna and particularly high plant Sb concentrations occur in Sb mining areas [60]. Hammel et al. [23] extracted Sb from contaminated soils from a historical mining area in Germany using 1M NH_4NO_3 to assess the mobile fraction which is bioavailable to plants, and reported levels of 0.02–0.29 mg kg^{-1}, representing between 0.06% and 0.59% of the total Sb content. Other studies have found relatively low concentrations of Sb in local flora and fauna even in highly contaminated areas, indicating that low soluble or mobile fractions reflect low availability and uptake into biological systems, and a lack of bioaccumulation in food chains [1, 27, 36]. The large size of the $Sb(OH)_6^-$ anion, the predominant form in well aerated soils [50], may prohibit its passage through the root endodermis into the xylem, thus limiting its translocation to the aerial portions of the plant [48]. However, evidence shows that where Sb is present in more mobile forms in the soil, it can be accumulated by plants [4, 23] and affect their growth [24]. Markert [39] reported an average Sb level of 0.1 mg Sb kg^{-1} (dw) in plants. Potential phytotoxicity of Sb has been described as moderate [7], although no environmental cases have been reported.

Overall, plant Sb accumulation increases with the Sb concentration of soil over a very wide range of concentrations. That was observed in a combination of published data from field studies which produced a relationship with a significant correlation between plant and total soil Sb. With soluble instead of total soil Sb concentrations, a closer relationship was obtained despite the variety of analytical methods used and very different plants examined [60]. This fact suggests a very general and rather simple mechanism. Passive transport by convection with the stream of transpirational water into and through the plant would easily explain it. In fact, evidence suggests that Sb is translocated within plants primarily along the apoplastic pathway through the xylem, but some symplastic transport may also occur [60]. Atmospheric deposition of Sb onto plant surfaces may in addition be an important pathway in the soil-to-plant transfer of Sb under field conditions [60].

18.4 Soil Contamination

Although Sb is a naturally occurring trace element in most soils, it is likely to be a pollutant in industrial environments [38]. Reported soil concentrations have ranged from 0.17 mg kg^{-1} in organic soils in Norway to 1,489 mg kg^{-1} in the vicinity of a Sb smelter in NE England [2]. Input to soil ecosystems was estimated at 26,000 t year^{-1} of Sb [10]. This anthropogenic contribution of Sb is tenfold higher than emissions from natural sources (around 2,600 t year^{-1}) reported by Nriagu [44]. Antimony is ubiquitous throughout the environment as a result of both natural processes and human activities [19]. Patterns of Sb concentrations in cores from peat bogs in remote areas of Switzerland and Scotland reflect the history of anthropogenic air pollution over the past two millennia [15, 52].

Mining operations are assumed to be the greatest emission source of Sb into the environment [57]. Other important anthropogenic sources of Sb in the environment are emissions from vehicles (as a consequence of its use as a fire-retardant in brake linings), waste disposal and incineration, fuel combustion, metal smelters and shooting activities [3, 10]. The current trend to avoid the use of Sb in Pb alloys towards its use in fire-retardant treatments and other applications, which do not permit recycling, have caused lesser amounts of secondary Sb to be produced, which is of environmental concern [18].

Antimony is used in bullets to harden them, so shooting ranges are hotspots of soil pollution by Sb [25]. Bullets generally have cores made of Pb-Sb alloy with an Sb content of between 2 and 5 wt.%. Once in the soil, the bullet fragments gradually oxidise through the weathering actions of air, water, organic acids and microbial activity [25]. As the bullets corrode, metals are released to the soil. In Switzerland, for example, it is estimated that 10–25 t of Sb annually enter the soil as a result of shooting practice at more than 2,000 ranges [25]. The highest contamination in shooting ranges tends to occur in the surface soils [25] and decreases with soil depth [18]. The organic-rich soil humus layer may act as a repository for anthropogenic Sb [55].

18.5 Risk Assessment

The real environmental risk posed by Sb is still largely in need of assessment and proof. The case of the comparison of Sb(III) versus Sb(V) toxicity is paradigmatic. In addition, although it has been generally assumed that the geochemical behaviour and toxicity of Sb are similar to those of As [59], Sb might behave less like As than previously believed. Most investigations into mining spoils have not focused on Sb, yet it is often a major constituent, is a suspected human carcinogen [22] and a priority interest pollutant in both the USA and the EU [16, 61]. Systematic reviews are lacking on many environmental topics such as: Sb in the atmosphere, ecotoxicology, and soil-plant transfer, among others. Integrating existing data into a global cycling model should be a priority task today [19].

Indirect evidence suggests that Sb(III) is somewhat more toxic than Sb(V) and that Sb(III) forms could be used as a worst case scenario for testing the toxicity of environmental Sb [45]. Toxicity tests with soluble Sb salts have shown little relevance for predicting the risk of Sb_2O_3 emissions to soils. At full equilibrium, all Sb_2O_3 is likely to be transformed, i.e., dissolved, oxidised and adsorbed [46]. The preferred exposure regime for terrestrial toxicity tests is via long-term equilibrated Sb_2O_3-amended soils. Based on the data available at present, only a generic predicted no effect concentration (PNEC) value of 37 mg Sb kg^{-1} dw can be derived in soils [45].

Naturally occurring Sb has no known function in living organisms and has no known biological role [55]. Exposure to Sb species, especially trivalent, has been reported to produce injury in organ systems such as the lungs, heart, liver and kidney [21]. In its trivalent form, Sb may have a level of genotoxicity similar to trivalent As [22]. The mechanism of Sb toxicity seems to include interactions with functional thiol (SH) groups of glutathione and proteins [56]. Toxicity of water insoluble Sb sulphate was found on average to be higher than that of Sb-tartrate (very soluble in water), with a reproduction LOEC (lowest-observed-effect-concentration) for earthworm, potworm and collembolan of around 100 mg Sb kg^{-1} [33].

Antimony in contaminated soils does not seem to be readily bioavailable, its concentration in source-receptor pathways has been measured and no significant increase compared to uncontaminated soils has been observed [1, 54]. Flynn et al. [20] found in five different locations in SW England that soil contamination by Sb due to mining and smelting operations was not a severe risk to the environment or human health provided that it was present as immobile species. In that study, total Sb of up to 700 mg kg^{-1} was shown to be biologically unavailable over a wide range of pH values (3.72–8.07), with no relationship between pH and water soluble levels or percentage solubility.

A possible danger is the low Sb toxicity to plants. It is difficult to assess the health risks of exposure to elevated concentrations of Sb. Acute Sb poisoning of humans or animals via ingestion of Sb-contaminated soil or consumption of plants grown on Sb-contaminated soil is extremely unlikely. The threshold of Sb intake considered to be critical is 100 mg day^{-1} [6].

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Chapter 19
Barium

Paula Madejón

Abstract Barium (Ba) is a common element in the Earth's crust and is present at higher concentrations than most other trace elements, and naturally occurs in one oxidaton state (+II). Industrial uses of Ba are wide and variable including: oil and gas drilling muds. The most common minerals of Ba are barite and hollandite and in geochemical processes it is usually associated with K^+. Barium is not very mobile in most soils although plants may take up Ba easily from acid soils, but there are few reports of toxic concentrations of Ba in plants.

Keywords Barium • Barite • Biosolids • Brines • Drilling muds • Radium • X-ray

19.1 Introduction

Barium (Ba) is a common and ubiquitous element with a mean content in the Earth's crust of 425 mg kg^{-1}, and a range from 550 to 668 mg kg^{-1} in the upper continental crust [32]. It is 14th in order of abundance in the earth's crust and occurs at higher concentrations than most other trace elements [29].

In nature Ba occurs in only one oxidation state, +II. In aqueous environments, Ba occurs primarily as the dissolved divalent ion, Ba^{2+} [38]. The neutral ion-paired species, $BaSO_4{}^0$, forms in the presence of high sulphate concentrations. Similarly, $BaCO_3{}^0$, becomes the dominant species in the presence of carbonate at pH >9.3 [39]. Solid phase barite ($BaSO_4$) and witherite ($BaCO_3$), exhibit fast precipitation kinetics and very low solubilities, limiting Ba concentrations in aqueous solutions [4]. Therefore when it is released by weathering is not very mobile because it is easily precipitated as either sulphates and carbonates [21].

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According to Bowen [6], the mean content of Ba in soils is 500 mg kg^{-1}. The reported range for soil Ba, on a world scale, is from 19 to 2,368 mg kg^{-1}. Schroeder [33] reported Ba in soils at concentrations ranging from 100 to 3,000 mg kg^{-1}. Mean values in Chinese soils are 370 mg kg^{-1} [9] and in United States the mean values correspond to 440 mg kg^{-1} [35]. (See also Chap. 2, Table 2.1).

Industrial uses of Ba are wide and variable, including: oil and gas drilling muds, automotive paints, stabilizers for plastics, case hardening steels, bricks, tiles, lubricating oils, and jet fuel as well as in various types of pesticides [4, 45]. The largest use of mined barite, which accounts for 94% of the total output, is oil and gas well drilling. Other Ba compounds are important in the brick, ceramic, photographic, and chemical manufacturing industries [2, 4]. One of the major uses of $BaCO_3$ is as a rodenticide [2]. Barium and its compounds have several important medical uses as well. Barium is frequently utilized as a benign, radio-opaque aid to X-ray diagnosis in colorectal and some upper gastrointestinal examinations, because it is normally not absorbed by the body after oral intake [2], although $BaCl_2$ is no longer used to treat heart block due to its toxicity.

Barium is an ideal analogue of radium (Ra) as Ba and Ra are alkaline earth elements, and possess similar ionic radii ($Ba^{2+} = 1.34$ Å and $Ra^{2+} = 1.43$ Å) [36]. For this reason Ba has been used to study migration of radioactive radium (^{226}Ra) in soil, due to environmental concern about Ra, especially in areas adjacent to U deposits [47].

19.2 Lithogenic Occurrence and Geochemistry

Barium has a lithophilic affinity and is likely to concentrate in acid igneous rocks and argillaceous sediments, ranging from 250 to 1,200 mg kg^{-1} [22].

The most common minerals of Ba are barite ($BaSO_4$), and hollandite ($Ba_2Mn_8O_{16}$). Witherite ($BaCO_3$), another ore of Ba, is not as common as the others minerals and can form deposits in association with barites [3]. This element is also found in possible host minerals of K-feldspar, micas, apatite, calcite [32]. In geochemical processes, Ba is usually associated with K^+ due to their similar ionic radii, and thus usually follows the fate of K in geochemical processes and therefore its presence is linked with alkali feldspar and biotite [21, 22].

Barium is concentrated in Mn and P concretions and is specifically adsorbed onto oxides and hydroxides [21]. Barium is easily sorbed by other alkaline earth metals from some oxides (MnO_2, TiO_2), although it is displaced from Al_2O_3 by alkaline earth metals (Be, Sr) [4].

19.3 Chemical Behaviour in Soil and Availability to Plants

Barium is not very mobile in most soils. The rate of transport is dependent on the characteristics of soils, such as cation exchange capacity (CEC) and $CaCO_3$ content. In soils with high CEC values (such as clay minerals, finely textured mineral soils, or soils with high organic content) the mobility of Ba is limited by adsorption. High $CaCO_3$ contents limit mobility by precipitation as $BaCO_3$ or in presence of SO_4^{2} ions, Ba precipitates as $BaSO_4$. In the presence of Cl^- ions, Ba is more mobile and more likely to be leached from soil to groundwater [39].

Barium acetate, nitrate, and chloride are all quite soluble, whereas the arsenate, carbonate, oxalate, chromate, fluoride, sulphate, and phosphate salts are very poorly soluble. Concentration of Ba in the soil solution and therefore potential uptake is controlled by the nature of the soil, pH of the extractant [5] and by solution SO_4^{2-} concentration [16]. All Ba salts, except for $BaSO_4$, become increasingly soluble as the pH decreases. These salts dissolve partially in carbonic acid and completely in hydrochloric or nitric acids. Strong sulphuric acid is required to dissolve $BaSO_4$ [44]. Barite has been considered as a very stable and inert material. Carbonell et al. [7] studied the influence of pH and redox potential in barite sediments. These authors found that a combination of low pH and highly anaerobic conditions resulted in a release of Ba to the sediment solution.

Different studies have reported very low exchangeable-Ba levels in soils (0–185 mg kg^{-1}) despite rather high total Ba contents (50–3,000 mg kg^{-1}) [13]. Leaching experiments indicate that the formation of soluble complexes of Ba with fatty acids from domestic wastes and other, unidentified organic Ba complexes can contribute to Ba mobility in soils [23]. During studies with a soil column, a small quantity of Ba, 18–39%, was leached out, probably as organic Ba complexes, while the remaining Ba (added in the form of $BaCO_3$) was adsorbed and precipitated, and remained at the original place of application [23]. Hatipoglu et al. [17] studied sorption properties of Ba on kaolinite, montmorillonite, chlorite + illite type of mixed clay, being the mixed clay with the best sorption of Ba.

Sultan and Shazili [40] studied Ba levels in tropical soils in Malaysia. They found that under humic tropical conditions most of the metals from the top soil layer, especially alkali and alkali earth metals, such as Ba, are significantly depleted by preferential leaching/or plant uptake.

The USEPA [41] has published an amended list of 15 "candidate pollutants for exposure and hazard screening" with regard to biosolids land application, and this includes Ba. Ipolito et al. [19] studied Ba accumulation in soils amended with biosolids (sewage sludges) and found that biosolids additions increased Ba accumulation in the 0–20 cm soil depth. They also reported DTPA-extractable values declining with time; this supports the idea that insoluble Ba precipitates are forming due to biosolids addition in soils.

Soluble Ba, e.g., in the form of BaS, is extremely toxic to humans and animals, although due to its low absorption in the gastrointestinal tract, sparingly soluble $BaSO_4$ can be orally supplied as a contrasting reagent in radiological exploration without health risk. Because most of Ba in the environment is present in forms with low solubility, mainly as sulphate or carbonate, the risk of Ba toxicity is considered to be very low [25, 26].

Barium is taken up by plants although it has no known plant or animal physiological functions, and usually undergoes biodiminution as it is transferred along the food chain [15, 31, 34]. On the other hand, in the ionic form, Ba is considered to be toxic to humans, animals, and plants at moderate concentrations [8].

Bowen and Dyamon [5] found that Ba contents of plants from normal soils vary from 0.5 to 40 mg kg^{-1} with a mean value of 10 mg kg^{-1}. Other authors reported normal Ba values in plants from 10 to 150 mg kg^{-1} [13].

Plants may take up Ba quite easily from acid soils, but there are few reports of toxic Ba concentrations in plants [21]. Wyttenbach et al. [46] studied correlations between soil pH, EDTA-extractable Ba in soil and Ba contents in needles of Norway spruce. They found a significant negative correlation between Ba in plant and pH and a positive significant correlation with extractable Ba in soils.

19.4 Soil Contamination

Davis et al. [14] report that Ba and Mn are consistently associated with natural sources in both urban and rural areas. Raghu et al. [30] studied the soil on a barite deposit, in an area in India, and they found a range of values in soils from 171 to 802 mg kg^{-1}. Shock et al. [37] studied the Red Dog Mining District in western Alaska and reported that Ba concentrations in ore concentrates were found to range from 2,400 to 2,700 mg kg^{-1}.

Contents of Ba in coal range from 75 to 330 mg kg^{-1} [10]; other authors reported concentrations of $<$3,000 mg Ba kg^{-1} [6]. It also occurs in fuel oils, the Ba content varying with the petroleum source.

Despite relatively high concentrations in soils, only a limited amount of Ba accumulates in plants. It is actively taken up by legumes, grain stalks, forage plants, red ash leaves, and the black walnut, hickory, and Brazil nut trees [31]. In plants on a barite-rich soil (760 mg kg^{-1} Ba in *aqua regia* extract) shoot Ba concentrations ranged from 21 mg kg^{-1} in grass species to 320 mg kg^{-1} in *Rubia peregrine* (Wild Madder) [24]. The highest concentrations (10,000 mg kg^{-1}) have been found in Brazil nut trees (*Bertholletia excelsa*), a Ba-accumulating species [38].

Pais and Jones [28] found that Ba contents of 200 mg kg^{-1} could be moderately toxic, and an excess of 500 mg kg^{-1} could be considered toxic for plants. Barium toxicity has been studied in *Phaseous vulgaris* (red kidney bean) and *Hordeum vulgare* (barley) on an experimental soil spiked with 2,000 mg kg^{-1} Ba as nitrate. Internal concentrations associated with growth inhibition were found at 10,000 and 20,000 mg kg^{-1} in foliar levels [8]. Plant yield decrease and phytotoxic effects were related to the suppression of K uptake by Ba. Llugany et al. [25] studied *Phaseous vulgaris* in an experiment using a culture solution with different doses of Ba and found that Ba interfered with both the SO_4^{2-} transport from roots to shoots and the import of Ca into leaves. Similar results were found previously by Wang [43] and Wallace & Romney [42]. However, according to Llugany et al. [25] the most Ba-sensitive parameter is the K concentration in leaves, which is reduced even at concentrations that do not affect plant growth. Raghu [30] found a concentration of 3,500 mg kg^{-1} in shoots of

Indigofera cordifolia (a legume 'True Indigo') and also concluded that the presence of *Indigofera cordifolia* on a Ba mine dump area and its absence away from this area shows its indicator characteristics for Ba from the geobotanical point of view.

19.5 Risk Assessment

Environmental problems associated with Ba are due to well drilling and the on-site disposal of brines with high Ba contents. Cipollini and Pickerink [11] studied the effect of Ba in plants from high-Ba well sites. They found that, although there was a high Ba content in soils (2,000 mg kg^{-1}), there were no detectable effects upon plant yield and in general, plant Ba levels did not exceed the normal range in plants. Coscione and Berton [12] evaluated the Ba extraction potential of *Brassica juncea* (Indian mustard), *Helianthus annuus* (sunflower) and *Ricinus communis* (castor bean) growing in a soil artificially contaminated with increasing Ba additions (0, 150, 300 mg kg^{-1} rates). None of the plants tested presented toxicity symptoms, decreased nutrient accumulation or decreased dry matter production in response to Ba treatments. The largest accumulation was with sunflower at 300 mg kg^{-1} of Ba added to the soil. They concluded that none of the three species studied was efficient as a Ba accumulator.

Monaci and Bragagli [27] showed that in urban environments unwashed *Quercus ilex* (Holm Oak) leaves had a significantly higher Ba content compared with those from suburban or control areas. This study also found a significant relationship between normalized concentrations of Pb and Ba and the presence of the latter element in diesel and unleaded gasoline. Therefore these authors consider Ba to be a valuable tracer for vehicle emissions, in the place of Pb.

Hope et al. [18] studied Ba accumulation at different ecosystems levels. The study area exhibited a mean Ba content in soil of 105 mg kg^{-1}. Vegetation analysed showed a mean Ba concentration of 30 mg kg^{-1}, the mean concentration in terrestrial invertebrates was 16 mg kg^{-1} and the Ba content in small mammals analysed was around 2 mg kg^{-1}. According to these results Hope et al. [18] concluded that although Ba appears capable of bioconcentration and bioaccumulation in terrestrial and aquatic environments, its bioaccumulation factors were low in the terrestrial receptors examined (Ba levels decreased by an order of magnitude with each successive increase in the tropic levels). Other authors have studied the possible toxic effect of Ba in soils on pheasant populations. Anderson and Stewart [1] speculated that Ba in the diet might be a factor limiting the pheasant establishment in habitats adjacent to areas of long-term sustaining populations in Illinois, however Jones [20] did not find any relation between Ba content in soils and pheasant abundance. Even more, the present of these birds were higher at the maximum Ba values in soils.

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Chapter 20
Gold

Rafael Clemente

Abstract Gold (Au) is a noble, relatively scarce metal, highly valuable for its beauty, resistance to corrosion and as a long-term investment. Demand for it has increased steadily and it has become vital in different technological fields. Gold nanoparticles have also attracted broad interest. Despite being chemically inert towards most naturally occurring substances Au may be subject to biological interactions in soils. The impact of Au concentrations in different environmental compartments is not known with certainty.

Keywords Gold • Cyanide • Electronics • Jewellery • Monetary • Nanoparticles • Noble • Precious metal

20.1 Introduction

Gold (Au) is a precious and noble metal (resisting corrosion) and one of the ten least abundant elements in the Earth's crust with an average concentration of 0.004 mg kg^{-1} [35], and a concentration range from 0.02 to 0.20 μg L^{-1} in natural waters [42]. Despite being a relatively scarce element, it is widely distributed through the Earth's crust and global waters. Gold is a highly valuable metal, which since ancient times has been valued for its scarcity, beauty, resistance to corrosion and as a long-term store of value [12, 18]. Throughout the centuries, Au has been used for a variety of purposes and demand for it has increased steadily with the advancement of technology. Due to its special chemical and physical properties [40], Au has become vital in such diverse fields as dentistry, photography, medicine, electronics, and nanotechnology [53].

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Gold is used in three principal ways: as a manufactured product in industry and the arts, as an investment good, and as a monetary metal. Of the Au supplied to the international market yearly, about 88% is destined for fabrication, and 12% for investment and bullion stocks [12]. Jewellery is by far the most demanding activity and accounts for 85%, by weight, of world Au fabricated each year [12]. In the twentieth century, many different applications that take advantage of its unique physicochemical properties were developed, adding great technological importance to Au (almost always alloyed), especially for the electronics industry [12]. Gold nanoparticles have attracted extensive attention in interdisciplinary research because of their potential applications in electronics, optics, catalysis and drug delivery [15].

Gold is a noble (reluctant to combine chemically with non-metallic elements, remarkably oxygen) and precious (a combination of rarity, durability, and beauty) metal [12]. It is the most malleable of metals, is soft and highly ductile, has a bright pleasing colour, is highly reflective, alloys readily with common metals, is readily joined by soldering or brazing, and has high electrical and thermal conductivity. It is also chemically inert towards most naturally occurring substances [12].

World total mine production from 2003 to 2009 varied from 2,540 to 2,330 t year^{-1}, respectively. The leading commercial producers of Au are currently the People's Republic of China, the Republic of South Africa, the United States, the Former Soviet Union, Canada, Australia, and Peru [21, 22]. Worldwide, mined, secondary (recycled) Au, and outflow from above-ground bullion stocks mean a world market supply of Au of nearly 3,900 t year^{-1} [12].

The concentration of Au in ore deposits can vary from about 0.2 mg kg^{-1} (possibly the lowest content that can be economically extracted) to around 30 mg kg^{-1} in some of the richest South African mines; several hundred mg kg^{-1} can be found in some parts of certain deposits called 'bonanzas' [26, 54].

In addition to the Au found in precious-metal deposits, Au is commonly found in or associated with base-metal ores and is recovered during their smelting or refining. The vast amount of base metals mined makes these deposits important sources of Au. Worldwide, by-product Au accounts for around 5–15% of total Au mined and is likely to remain an important source of Au in the future [12]. Other possible sources of secondary Au could be certain abiotic materials such as sewage sludge [18]. For example, sewage solids from a south-eastern Australian community with a long Au mining history contained 0.18 to 2.35 mg Au kg^{-1} dw [18]. These concentrations are similar to those in ore deposits mined for Au [39].

The geochemical properties of Au condition the forms in which it is found in ore deposits and the formation of the deposits themselves. The electronic configuration of its atom provides Au with a very strong resistance to oxidation and a weak bonding ability with most anionic elements. Gold has six oxidation states (+1, +2, +3, +4, +5, and +7) but only the +1 (aurous) and +3 (auric) states are common [12]. Although the complex compounds of Au(III) are markedly more stable than those of Au(I), ore-forming fluids tend to have low oxidation potentials; therefore, +1 is the dominant Au oxidation state in them [58].

20.2 Lithogenic Occurrence and Geochemistry

The Earth's core contains on average 150–300 times more Au than does the crust. Native primary Au is commonly present as alloys with Ag, Cu, Al, Fe, Bi, Pb, Zn, Pd or Pt, with Au concentrations ranging from 50% to 80% wt [11]. Gold occurs principally as flakes, scales, or crystals of native metal [12]. The average Au content of soils is about the same as the crustal abundance. The concentration in sedimentary rocks tends to be above the crustal average, especially in sandstones [12]. Gold can concentrate in iron-rich exogenetic horizons such as laterites (Brazil, Cameroon, Indonesia) or gossans (Canada, USA, France) [10].

Gold forms relatively few minerals. Aside from the native alloys (most commonly with Ag, Cu, and Fe, only aurostibite ($AuSb_2$), calaverite ($AuTe_2$), and sylvanite ($[Au, Ag]Te_2$) are important ores of Au [12]. Small amounts of Au substitute for other metals in some more minerals, which are sometimes also considered as Au minerals. Chemical (and biological) weathering of Au deposits can lead to the dissolution of Au from the primary Au deposit (hosted by sulphides or quartz), transportation in solution, and re-precipitation elsewhere in the weathering (regolith) profile [27]. Sorption of Au complexes and colloids to organic matter, clays, Fe and Mn minerals as well as bioaccumulation and biomineralisation may also lead to the formation of secondary Au particles [25, 34]. Secondary Au is generally much finer (up to 99% weight of Au) compared to primary Au, and the individual Au aggregates are often larger than in potential source rocks [44, 63].

Under surface conditions, Au occurs in aqueous solution mainly as a metal colloid and aurous or auric complexes. Standard redox potentials of Au^+ (1.68 V) and Au^{3+} (1.50 V) exceed that of water (1.23 V), which makes the existence of free Au ions thermodynamically unfavourable [11, 61]. In hydrothermal fluids Au is chemically mobile as complexes with sulphide and bisulphide (for example, $[Au(HS)^0]$, $[Au(HS_2)^-]$, $[Au_2S_2{}^{2-}]$) [9, 23, 52]. Deposition from these solutions leads to the formation of Au-containing sulphide minerals (for example, pyrite and arsenopyrite) [11, 30]. The chemical mobility of Au in the supergene zone is linked to the weathering of these sulphide minerals, and its subsequent oxidation and complexation [11, 59]. Oxidizing groundwater with elevated dissolved chloride concentrations may also solubilise Au through the formation of chloride complexes ($[AuCl_2{}^-]$, $[AuCl_4{}^-]$) [25].

The mobility of Au increases with increasing degree of weathering of host materials [48]. For example, in the Ah-horizon overlying the mineralized zone at a Au mine in south eastern New South Wales, approximately 50% wt of the total Au was associated with the most easily extractable fractions; in contrast, in the unweathered quartz-vein material more than 95% wt of the Au was extractable only with concentrated *aqua regia* [50].

Microorganisms are capable of actively solubilising and precipitating Au and they may play a key role in the dispersion and concentration of Au under surface conditions, in the deep subsurface and in hydrothermal zones [51]. Therefore, many environmentally relevant groups of microbes may be involved in the biogeochemical cycling of Au [51]. Microorganisms intervene in Au solubilisation via excretion of certain metabolites (e.g., thiosulphate, amino acids and cyanide), are able to deal with toxic Au complexes, and to precipitate Au intra- and extra-cellularly, and in products of their metabolism (e.g., sulphide minerals) [51]. Lintern et al. [38] also reported that Au may be subject to biological influences in natural soil samples. In regolith materials from tropical and semi-arid areas in Australia, Au was shown to be mobile through the mediation of auriferous soils indigenous microbiota [48]. The microbially mediated solubilisation was highly influenced by environmental factors such as climate, soil geochemistry and substrate quality and availability [48].

Bacteria have been linked to pure Au precipitation in natural environments [49, 51]. However, the concentrations of amino-acids and other biogenic reductants necessary to induce size and shape control of experimental Au nanoparticle growth are quite high, and it is more likely that an inorganic reduction of Au-bearing solutions is the cause of the majority of Au precipitation in natural environments [27].

20.3 Chemical Behaviour in Soil and Availability to Plants

The significance of Au concentrations in various environmental compartments, Au's mode of action, and mechanisms governing its uptake, retention, and translocation are not known with certainty [18]. The solubility of Au in natural environments is controlled in part by adsorption reactions at mineral surfaces [57]. Soluble concentrations of Au in natural soils are usually very low when compared with predictions of Au dissolution using equilibrium thermodynamic calculations [10].

Traditional views of Au being a relatively inert metal contrast with its ability to be mobilised in the soil. Evidence for soluble Au in soil has been known for many years [24], although it has been unclear whether Au naturally occurs in ionic form or is dissolved by a substance in the soil (like cyanide or organic acids) that was first mobilised. Lintern et al. [38] showed for the first time that ionic Au is present in soil samples and that it is the most likely Au form to be dissolved by water. Tests on natural soil samples containing pedogenic calcrete, from a soil profile overlying a Au deposit in Western Australia, indicated that up to 20% of the Au present in soil was water soluble and thus potentially mobile. X-ray adsorption near edge spectrometry (XANES) indicated that a significant proportion of the Au was in an ionic form, most likely as Au (I), while the remaining Au was present as nanoparticulates [38].

Under most conditions, the prevalent dissolved Au complex has been suggested to be $AuOH{\cdot}H_2O^0$ [61]. But near oxidizing sulphide minerals, complexes such as $Au(HS)_2^-$, $AuHS{\cdot}H_2O^0$ [52] and $Au(S_2O_3)_2^{3-}$ [45, 65] may be the dominant species and aid Au mobility and dispersion. At high Cl^- concentrations that exist in many arid regions, Au may be mobilized as Au(I)- or Au(III)-chloride complexes which are stable under acidic and oxic conditions [47]. Other important forms of transportable Au may include Au complexes with organic matter and CN^-, and elemental colloidal Au [47]. The strong complex that Au(I) forms with cyanide

$[Au(CN)_2^-]$, which is stable over a wide range of Eh-pH conditions, is of great relevance [11, 25].

Gold has the ability to strongly bind to organic matter [24, 62]. Organic Au complexes may be important in soil solutions with high concentrations of dissolved organic matter [51]. The major role of organic matter, including humic substances, can be the reduction of ionic forms of Au to Au^0 causing its precipitation. Vlassopoulos et al. [62] demonstrated that "soft" N- and S-donor ligands form much stronger bonds with Au(I) than "hard" O donor ligands such as carboxylic acids. Where humic substances have a relatively high portion of N- or S-donor binding sites, then strong complex formation may lower the standard reduction potential of the Au species sufficiently to prevent reduction and carry out aqueous transport [47]. Citrate- and acrylate-stabilised Au nanoparticles have shown increased stability against pH induced aggregation as a consequence of interactions with humic acids, which increases Au stability [15]. Gold species present in solution can equally be reduced to metallic Au after exposure to oxidisable mineral surfaces such as metal sulphides [10]. Gold can also be reduced and can precipitate by reacting with Fe^{2+}-bearing minerals or with Fe^{2+} released by the dissolution of such minerals [64].

The different forms in which Au is available for transport (e.g., monovalent Au solution complexes, colloidal metallic Au, Au-sulphide/sulphite complexes interacting with organic matter, biogeochemical forms of Au in plants, etc.) are subjected to various adsorption reactions. Adsorption onto mineral surfaces is therefore important in determining the extent of Au mobilisation, dispersion and deposition [47]. The interactions of Au(III)-bearing solutions with fine-grained minerals such as Fe and Al-hydroxides are among the most important of those reactions [10]. For instance, Au concentrates in Fe-rich exogenetic horizons such as laterites through retention onto highly reactive soil components such as Fe oxyhydroxides [13]. Numerous studies suggest that Au(III)-chloride complexes are adsorbed specifically (inner-sphere coordination) onto hematite and goethite surfaces, while the adsorption of thio Au(I) complexes on Fe oxide surfaces is supposed to occur through a nonspecific (outer-sphere) mechanism [47]. Using extended X-ray absorption fine structure (EXAFS) information and titration experiments the adsorption of aqueous Au(III) from chloride solutions onto goethite surfaces has been described as inner-sphere square-planar complexes (Au(III)(OH,Cl)(4)), with dominantly OH ligands at $pH > 6$ and mixed OH/Cl ligands at lower pH values [13]. Berrodier et al. [10] demonstrated through EXAFS spectroscopic studies that Au(III) adsorbs from chloride solutions on ferrihydrite, goethite, and boehmite surfaces dominantly as innersphere, square-planar complexes, with relatively low degrees of distortion. Adsorption of Au complexes on oxidisable mineral surfaces such as metal sulphides, thioarsenides, and Fe(II)-containing oxides and silicate minerals often involves the reduction of aqueous Au(I) and Au(III) species to elemental Au, which is subsequently sorbed [47].

Dunn [16] reported a background level of Au in plants of 0.2 $\mu g\ kg^{-1}$ dw, although this author stated that values up to 100 $\mu g\ kg^{-1}$ could be found. Typically, the background level of Au naturally occurring in plants is below 10 $\mu g\ kg^{-1}$ [4].

Gold accumulator plants, such as *Artemisia persia*, *Prangos popularia*, and *Stipa* spp. grasses, routinely contain >0.1 mg Au kg^{-1} and may contain as much as 100 mg Au kg^{-1} dw [18]. Microorganisms in the plant roots may be responsible for solubilising the Au, allowing ready uptake by these species. Plants readily take up Au and accumulate it within their tissues and specific reactions which influence the mobility of Au have been reported to take place in the rhizosphere [37]. Conifers are known to accumulate Au [6]. Bioaccumulation of Au from metal-contaminated soils has been documented in stems and needles of Corsican pine trees (*Pinus laricio*) [46]. *Pinus radiata*, *Cassinia aculeate*, and *Eucalyptus* have shown elevated Au in outer bark (*Pinus* and *Eucalyptus*) and in twigs and needles/leaves [6]. Gold has been also detected in aquatic macrophytes from streams draining abandoned base-metal mines, suggesting the potential use of these plants in bio-recovery [55]. In Poland and the Czech Republic, aquatic bryophytes reflected increasing amounts of Au in former Au mining areas; highest values recorded were in *Fontinalis antypyretica* (18.8 μg Au kg^{-1} dw) and *Chiloscyphus pallescens* (20.2 μg Au kg^{-1} dw) [56].

Gold is absorbed and present in plants in reduced Au(0) form (more than 90%) and only in very small amounts as Au(I) and Au(III) forms [8]. Plants are able to take up Au as Au(III) and then this is reduced to Au(0) in root tissues; Au mobility in tissues is probably very limited [8]. However, in undigested *Brassica juncea* plant material, Au was found in approximately equal quantities as the metallic (Au^0) and oxidised (Au^{+1}) states [41]. Similarly, the formation of Au nanoparticles within desert willow tissues has been reported [53]. In field experiments, carrot (*Daucus carota*, Apiaceae) in comparison with other crops (red beet, onion and radish), demonstrated the highest ability to accumulate Au [14].

20.4 Soil Contamination

The current processes used for Au recovery from ores are not only expensive, but also harmful to the environment, due to the use of toxic compounds containing cyanide [31]. These processes devastate the soil where mine tailings are deposited, damage ecosystems and alter the environment [7]. The production of primary Au affects the physical environment mostly at the mining and ore processing stages. Both take place at the mine site, and the very low content of Au in all its ores means that extremely large volumes of ore must be excavated and processed for each unit of Au recovered [12]. The smelting/refining stage poses no appreciable threat to the environment because of the very small volumes of material treated. In the case of mining, environmental disturbance is much greater where the Au is obtained from surface mines than where Au is obtained from underground mines; around 50% of the world's primary Au is currently produced from surface mines [12]. But the environmental concerns about ore processing come mainly from the use of cyanide (CN^-), which is used to extract Au from ores because it forms the stable complex $Au(CN)_2^-$, that allows for chemically efficient and inexpensive leaching by dilute aqueous solutions [40]. Ore leaching is carried out in large vats or by dripping the solutions onto ore heaps built on impermeable pads [28]. After the precious metal has been extracted from ore, cyanides are discharged as effluents and as solid mine tailings [66]. Although the cyanide radical tends to decompose rather quickly, some metal cyanides can persist long enough in ground water to cause concern [12].

20.5 Risk Assessment

Although Au has traditionally been considered to be relatively harmless, it is now known that it is a relatively common allergen that can induce dermatitis around the face and eyelids and at sites of direct skin contact [17]. Patch tests indicate that the incidence of Au allergy might be as high as 13% worldwide [19]. The main exposure sources of Au contact dermatitis are personal jewellery and dental alloys [1, 60].

Research into microbial processes affecting the cycling of Au as well as the physiological and biochemical responses of microorganisms to toxic Au complexes has been limited, and as a result its biogeochemical cycling and geomicrobiology are poorly understood [51]. Due to their high oxidation potentials, most Au(I) and Au(III) complexes can act as strong bactericides even at low concentrations [29]. The aerobic spore forming soil bacterium *Bacillus cereus* has been used as an indicator organism for Au in studies of different locations. It has been suggested as an effective biogeochemical exploration technique when used as a pre-screening method to target areas suitable for further sampling and complete geochemical analysis; the suppression of competing microbial species by mobile Au complexes provoked the increase of *B. cereus* spores in Au-bearing polymetallic soils [50]. In agreement with this, Au was almost completely removed from a 50 mg l^{-1} solution within 72 h through bioaccumulation, provoking toxic effects and decreasing fungi growth [43].

Due to the negative environmental effects of current Au-recovery techniques, alternative recovery processes such as phytoremediation have caught the interest of scientists and engineers. The discovery of significant Au uptake by plants has long been a "philosopher's stone" [2]. The concentration of Au from ores by plants (phytomining) is a proposed alternative method of recovering Au [4, 20, 32]. Gold could be a candidate for phytoreclamation as it is a valuable metal that is often found in relatively high concentrations in spent heap leach pads and waste dumps [5]. To make Au phytoreclamation viable, the research target is to harvest a crop with a dry biomass of 10 t from 1 ha of land, and to induce a Au concentration in the dry biomass of 100 mg kg^{-1}. This would yield 1 kg $ha^{-1}$of Au [5].

At this point phytoreclamation is not considered competitive with conventional recovery processes such as heap-leaching for low-grade materials. Only for the reclamation of a spent heap-leach pile or for a small tonnage ore deposit, it is suggested that phytoextraction could be a useful approach to set up revegetation practices that would also recover residual Au in the pile [5].

The possible role of vegetation in the formation of Au anomalies in soil has also been described [36]. Although plants are able to take up Au from soils, there are limitations of Au uptake [8]. Gold, in natural conditions, has very low solubility. The supplementation of the soil with Au chelating agents significantly increases Au uptake by plants. Cyanate seems to be a good Au chelator and it has demonstrated higher efficiency to promote Au uptake when compared to thiocyanate [8]. Other solubilising agents such as cyanide, iodide, bromide, and thiosulphate have been examined in Au-accumulation studies [33]. Anderson et al. [2, 3] reported induced hyperaccumulation of Au by Indian mustard (*Brassica juncea*) plants after soil amendment with ammonium thiocyanate (NH_4SCN). They defined Au hyperaccumulation as a concentration above 1 mg kg^{-1} dw of plant tissues. Elevated Au concentrations (maximum 19 mg kg^{-1} dw) have been reported in *B. juncea* plants grown in a mine ore containing natural colloidal Au [3]. An average Au concentration of 39 mg kg^{-1} was achieved in *B. juncea* after treatment of a 0.6 mg kg^{-1} Au ore with NaCN [5].

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Chapter 21
Molybdenum

Brian J. Alloway

Abstract Molybdenum (Mo) occurs at relatively low concentrations in most rocks and soils, but in relatively high concentrations in soils developed on black shales. It is present as an oxyanion in soil solution and, unlike most other heavy metals, is most mobile and plant available in alkaline conditions. Its main ore mineral is molybdenite, but it is also produced as a by-product from the processing of copper (Cu) ores. It is used mainly for making alloys and stainless steels. It is essential for plants and deficiencies can occur in brassicas, legumes, wheat, sunflowers and some other crops in many parts of the world, mainly on acid and sandy soils. It was recently proved to be essential for animals and humans, but deficiencies are rare. Molybdenum-induced copper deficiency (molybdenosis) in cattle and sheep is a serious problem on Mo-rich pasture soils in several countries.

Keywords Molybdenum • Steels • Black shales • Oxyanions • Nitrates • Acid soils • Deficiency • Molybdenosis

21.1 Introduction

Molybdenum (Mo) is a heavy metal belonging to Group 6 (previously called Group V1b) of the periodic table, along with chromium (Cr) and tungsten (W). It has an atomic mass of 95.9, a density of 10.28 g cm^{-3} and exists in the lithosphere in oxidation states ranging from Mo(III) to Mo(VI), with Mo(IV) predominating in reducing conditions and Mo(VI) in oxidising environments. It is much less toxic to humans and animals than many other heavy metals such as Hg, Tl and Pb and this

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makes it an attractive substitute for more toxic metals in several uses [10]. Unlike most heavy metals, Mo (together with Cr and W) usually forms oxyanions (and not cations) and coordinates only weakly with ligands such as Cl^- and OH^- [14]. As a consequence, it is most mobile and bioavailable under alkaline conditions (>pH 6.5) and least available in acid conditions. In plants, it plays a key role in nitrogen (N) metabolism being a constituent of the enzyme nitrate reductase. This reduces NO_3^- to NH_4^+ which can then be assimilated [15]. In animals, it is an essential constituent of several enzymes, including xanthine oxidase, xanthine dehydrogenase and aldehyde oxidase [17].

Molybdenum is mined primarily as the ore molybdenite (MoS_2), but also produced as a by-product from sulphide ores of Cu, especially in 'porphyry Cu' deposits. World mining production totalled 234,000 t in 2010, with mines in China producing the most (77,000 t) followed by the US (50,000 t) [22].

Molybdenum is primarily used in the manufacture of various alloy steels and stainless steel. Around 70% of total of Mo is used for steel, 22% for production of cast iron and various alloys and 8% for catalysts, lubricants, pigments and other uses [1, 10]. Molybdenum has a high melting point (2,610°C) and its incorporation in steels gives them a high melting point, high strength at high temperatures and good resistance to wear and corrosion. In addition, the coefficient of expansion and thermal conductivity of Mo-containing steels and alloys makes them valuable to the electronic industry. Examples of uses of Mo-containing steels and alloys include: cutting tools, aircraft components, forged automobile parts, industrial furnaces, support wires for filaments in incandescent light bulbs, glass melting equipment and machines for forming metals and plastics [10]. About 10% of stainless steel contains Mo (at about 2% W:W) and this is primarily used for industrial processes, such as chemical, petrochemical, oil and gas, paper, power, water, food and pharmaceutical industries [10]. The most important Mo chemicals include the disulphide (MoS_2), molybdic oxide (MoO_3) and several molybdate salts, such as sodium molybdate ($NaMo_4$) and ammonium molybdate ($(NH_4)_2Mo_2O_7$) which are variously used as catalysts (especially for S removal), corrosion inhibitors, pigments, additives to lubricating oils and fertilisers [1].

Concentrations of Mo in soils are generally quite low and usually reflect the composition of their parent materials, with a world mean total concentration in soils of around 1.8 mg kg^{-1} and a commonly observed range of 0.2–5 mg kg^{-1} [1, 13]. However, concentrations (in mg Mo kg^{-1}) of <30 have been reported for soils in the USA, <24 for vegetable growing soils in British Columbia, Canada, and <74 in topsoils in the Baltic region [13, 18]. On a global scale, deficiency of Mo in crops is more important than potential excesses from contamination because it is a micronutrient for plants. Concentrations of Mo in soils are generally the lowest of all the essential trace elements for plants (B, Cl, Cu, Fe, Mn, Mo, Ni and Zn) (see Chap. 7). It is generally considered that soils with total concentrations of Mo of <0.5 mg kg^{-1} are more likely to be associated with deficiencies in crops even when the pH is >7.

21.2 Lithogenic Occurrence and Geochemistry

In most rock types, the concentrations of Mo are relatively low (1–2.3 mg kg^{-1}) with an average of around 1.1–1.2 mg Mo kg^{-1} in the upper earth's crust, making it 56th in order of crustal abundance, similar to W and slightly lower than arsenic (As) [3, 14]. Authors differ in the range of concentrations given for Mo in rocks but Adriano [1] gives the widest range (in mg kg^{-1}): igneous rocks 0.9–7.0, phosphorites 5–100, shales 5–90, black shales <300 limestone and dolomite <3–30 and sandstones <3–30. Granites and other acid igneous (felsic) rocks tend to have slightly higher Mo contents than basic igneous (mafic) rocks. Organic-rich sedimentary rocks, such as black, bituminous or oil shales tend to contain the highest levels of Mo (<570 mg kg^{-1}) together with high levels of other heavy metals such as U, Cd and Zn (see Chap. 2, Table 2.2 and Sect. 2.3.1.1) [7]. Garret [8] describes Cretaceous age black shales outcropping in Manitoba, Canada, with Mo contents in the different beds varying by around two orders of magnitude, being highest in the deep-water shales, where anoxic sulphide and organic-rich sediments sequestered Mo. In Ireland, the Clare Shales, (Upper Carboniferous black shales) have been found to contain <200 mg Mo kg^{-1} (as well as high selenium (Se)) and are known to cause problems with livestock health, especially Mo-induced Cu deficiency [6].

21.3 Chemical Behaviour in Soil and Availability to Plants

Unlike the other trace metals essential for plants (Cu, Fe, Mn, Ni and Zn), Mo is present in the soil solution as an oxyanion ($MoO_4{}^{2-}$) which means that it is least available in acid soils (<pH 5.5) and most available above pH 6.5. Molybdenum more closely resembles phosphate or sulphate than other metals in its behaviour in soils [5]. In acid soils, $MoO_4{}^{2-}$ is strongly adsorbed on hydrous oxides of Fe and this is at a maximum at pH 4.0. However, this adsorption depends on the Eh-pH conditions which control the precipitation of Fe. Molybdenum adsorbed on freshly precipitated hydrous Fe oxides ($Fe(OH)_3$) is readily exchangeable, but with time it ages and becomes less available due to the formation of an Fe-Mo mineral (ferrimolybdite $Fe_2(MoO_4)_3.8H_2O$), which is only slightly soluble. A high proportion of the total Mo in soils is likely to be associated with organic matter and hydrous Fe oxides. As a result of its affinity for organic matter, Mo can accumulate to relatively high concentrations in forest litter [13].

Plants appear to take-up Mo readily when it is present in the soil in soluble forms. Therefore the availability of Mo in soils is dependent on soil pH and the drainage status (redox conditions). It is most easily taken up by plants from alkaline soils with poor drainage (gleying). This is partly the result of the high activity of $MoO_4{}^{2-}$ at higher pHs, and also its ability to form thiomolybdates under reducing conditions. When plants transport oxygen from the stem to the roots, the

Mo compounds close to the root surface are likely to be more oxidized and therefore more soluble and available for uptake. Normal Mo concentrations in plant leaves are 1 mg kg^{-1} or less, but tissue concentrations of 0.03–0.15 mg kg^{-1} DW are considered to be adequate for nutritional requirements. However, some native plants, especially legumes, growing on Mo-rich soils with favourable pH and redox conditions can accumulate much higher concentrations (<350 mg Mo kg^{-1}). Fodder plants with high Mo contents may induce Cu deficiency in ruminants (molybdenosis) [13]. Soil factors which increase the availability of Mo to plants can have an inhibitory effect on Cu uptake by plants and the physiological barrier to Mo uptake is less effective than the barrier to Cu uptake. The nutritional effects of Cu:Mo ratios in herbage on livestock are controlled by the sulphate concentration in plants and increased levels of SO_4^{2-} can reduce Cu uptake with even small amounts of Mo. A value of 5 mg Mo kg^{-1} in soils and/or >2 mg Mo kg^{-1} DM in herbage and/or a Cu:Mo ratio of $<2{:}1$ in herbage are generally considered to be indicative of potential Cu deficiency-related problems such as growth retardation and infertility in cattle due to a Cu/Mo imbalance. Other factors such as the sulphate intake and total Cu and Mo contents in the animal diet also need to be considered [2, 13].

In acid soils ($<$pH 5.5) with a low total Mo content and high concentrations of hydrous Fe oxides, Mo is likely to have a very low availability to plants and these are the circumstances under which Mo deficiency in plants most often occurs. Liming soils to raise their pH can often be an effective way of remedying deficiencies. However, with very heavy liming, Mo availability can decrease again owing to its adsorption on $CaCO_3$. Molybdenum can also be relatively unavailable in acid peaty (highly organic) soils due to the formation of complexes with the soil organic matter. Soils in arid and semi-arid regions generally have higher Mo concentrations than soils in more humid temperate conditions [13].

A Mo-Mn antagonism can arise in acid soils where Mn is highly available (and can be toxic) and Mo unavailable. Liming the acid soil reverses this situation remedying Mn toxicity and Mo deficiency. Interactions between Mo and P are commonly observed and P can enhance the availability of Mo in acid soils, due to the higher mobility of the phosphomolybdate complex and the higher Mo mobility in plant tissues. The effects of P fertilisers on Mo may be affected by their SO_4^{2-} content. Sulphate containing superphosphate fertiliser reduces Mo uptake, but high P fertilisers without SO_4^{2-} enhance it [13] .

There are four key enzymes in plants in which Mo is a co-factor. These are: (1) nitrate reductase, required for the assimilation of NO_3 into plants; (2) aldehyde oxidase which is involved in the synthesis of the hormones indole-3 acetic acid (IAA) and abscisic acid, (3) xanthine dehydrogenase, involved in the catabolism of purine and synthesis of ureides in soya bean and cowpea, and (4) sulphite oxidase which mediates the biochemical oxidation of sulphite ($-SO_3^{2-}$) to sulphate ($-SO_4^{2-}$). In addition to green plants, Mo is also required by N-fixing bacteria in root nodules in legumes, where it is a component of the enzyme nitrogenase which is involved in the biological fixation of N_2. Other (non-symbioitc) soil microorganisms have been found to benefit from Mo additions to soil. Positive responses have included increased decomposition, higher non-symbioitc

N-fixation, increased numbers of actinomycetes and elevated enzyme activity [2]. Foliar applications of Mo to rice have been shown to stimulate various rhizosphere bacteria. In general, plants with mycorrhizal infection benefit from a greater Mo uptake. It has been shown that <0.16% of Mo in a range of soils occurred in the microbial biomass [2]. Molybdenum is also involved in the assimilation and metabolism of C through its role in photosynthesis, including the quantity of chlorophyll and the health of chloroplasts [15].

21.4 Soil Contamination

Molybdenum is used in steelmaking and various other industrial uses which have resulted in atmospheric pollution and soil contamination around some major industrial sites and urban complexes [10]. Nevertheless, the total concentrations found in these soils tend to be relatively small in comparison with other heavy metal contaminants such as Pb and Zn, with <35 mg Mo kg^{-1} near processing plants in the USA and <38 mg Mo kg^{-1} in Chile [13]. The UKSHS survey of soils at selected industrial sites in the UK found significantly elevated Mo concentrations (<24 mg Mo kg^{-1}) in soils near a steel works, an incinerator and mineral workings [19]. Sewage sludges commonly contain 5–50 mg Mo kg^{-1}and if high Mo sludges are applied to pastures they could cause molybdenosis problems in livestock [13].

Soils with high available Mo concentrations from either geochemical, or anthropogenic origins can pose a problem due to possible toxicity in plants and/or animals, but it is very rare for plants to exhibit Mo toxicity symptoms under field conditions. Toxicity can occur at Mo concentrations in leaf tissue of 10–50 mg kg^{-1} [2]. The symptoms caused by acute Mo toxicity are frequently similar to those due to P deficiency such as red bands along leaf margins but there are usually no root abnormalities [4, 5]. Application of elemental S to acidify soils is an effective way of reducing available concentrations of Mo. Plants growing on contaminated soils have been reported to contain <200 mg Mo kg^{-1} [13].

21.5 Risk Assessment

Molybdenum deficiencies are most likely to occur on acid and severely leached soils, which include unlimed tropical soils and sandy-textured soils, including Podzols. Molybdenum deficiency is mainly a problem in brassicas and legumes, such as peanuts, subterranean clover and soya beans, but other crops, including wheat and sunflowers can also be affected. In many crops, the reproductive phase is more sensitive to Mo deficiency than the vegetative phase, causing poor crop yield [15]. Molybdenum deficiency has ‘striking’ effects on pollen formation in maize. Tasselling is delayed, a large proportion of the flowers fail to open and the capacity of the anther for pollen production is reduced. The emergence of maize cobs is delayed and these are severely condensed, the styles are poorly developed and fail to emerge out of the leaf sheath [15].

In an international study for the FAO involving field trials in 15 countries, Sillanpää found that Mo deficiencies were primarily hidden (or latent) i.e., revealed by yield effects with no obvious symptoms of stress, and that deficiencies of Mo were the third highest in occurrence (15% of crop experiments) after Zn and B [20]. In northern Alabama, USA, Mo deficiency in soya beans is a widespread problem on acid soils [5]. In Australia, Mo deficiency is the second most ubiquitous micronutrient deficiency problem affecting large areas of cropland with acid soils [9]. In China, Mo deficiency has become an important factor limiting yields in winter wheat and soya beans and affects 47% of agricultural soils [24]. On the predominant acid sandy soils in Africa, Mo deficiency is a widespread problem, particularly in maize, sunflower, ground nuts, dry beans and peas [23].

Not all Mo deficiencies in crops can be rectified by liming, especially in sandy soils with low total Mo contents. In these cases it is necessary to apply Mo compounds as fertilisers to supply sufficient amounts of the element. Legumes, cruciferous crops, grasses and several vegetable crops have responded to Mo fertilisation [16]. On acid soils in Brazil, responses of beans to Mo fertilisers were only observed after the soil pH had been raised to above 5.5 by liming [5]. The most commonly used fertiliser compounds are ammonium molybdate ($(NH_4)_6Mo_{24}.4H_2O$) and sodium molybdate ($NaMoO_4.2H_2O$). These are applied to soils at a rate of 0.1–1.0 kg Mo ha^{-1} or as foliar sprays ($<1\%$ solutions) directly onto the crop to supply 100 g Mo ha^{-1}, but proprietary molybdate complexes are also used as foliar sprays. Molybdenum trioxide (MoO_3) is insoluble, but is used as a seed dressing for grass and legume seeds when establishing pastures on deficient soils.

In Australia, Mo is added to superphosphate fertilisers in many areas and is also applied with Cu and Zn fertilisers on acid, sandy and gravely soils in Western Australia [9]. Usually, Mo-fortified superphosphate is only applied to pastures in Australia every 3–4 years, typically supplying Mo at a rate of 50–100 g ha^{-1}. In India, soil applications or foliar sprays containing 0.05–1% $NaMoO_4$ are applied three times to green gram (*Phaseolus aureus*). Basal applications of Mo are applied to peanuts on calcareous soils and the seeds of soya beans and peanuts are also treated with an Mo formulation [21]. Seed treatments combining Mo with *Rhizobium* (symbiotic N-fixing) bacteria inoculants are commonly used for legumes such as groundnuts.

Molybdenum was confirmed as essential for humans and animals in 1976 [17]. It acts as a cofactor for the enzymes sulphite oxidase, xanthine oxidase and aldehyde oxidase which are involved in the catabolism of sulphur amino acids and heterocyclic compounds including purines and pyridines in animals and humans [11]. The main dietary sources of Mo are legumes, nuts and grain products. The only people known to have Mo deficiency are those with a genetic defect which prevents the synthesis of sulphite oxidase and causes severe illness except when Mo was administered. However, there is also inconclusive epidemiological evidence that low Mo intakes may be associated with the occurrence of oesophageal cancer in humans.

Care must be exercised when applying Mo fertilisers to pastures, because excess Mo relative to Cu can induce molybdenosis in cattle and sheep. In Sweden, Mo-induced Cu-deficiency in wild moose (*Alces alces*) has been found in an area where widespread liming of pastures was undertaken to offset the effects of acid rain [12].

21.6 Concluding Comments

Although only occurring at relatively low concentrations in most soils, Mo is an important heavy metal because of its role as a micronutrient in plants and animals and the problems with its antagonism with Cu in ruminant diets. The fact that soil physicochemical factors such as pH and redox conditions affect the availability of molybdate anions and Cu cations differently needs to be born in mind when managing soils, especially pastures with elevated Mo contents. Contamination of soils and/or plants with Mo in atmospheric deposition or applications of sewage sludge also needs to be considered. Nevertheless, on a global scale, Mo deficiency in a wide range of important crops such as maize, wheat, soya beans growing on soils with low available Mo contents is of greater economic significance than contamination problems.

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Chapter 22
Silver

Rafael Clemente

Abstract Silver (Ag) is a precious metal that has recently become a valuable industrial metal and Ag nanoparticles are being increasingly used in a wide range of applications. In soils, Ag is strongly sorbed but may cause environmental concern. Both monovalent Ag ion and Ag nanoparticles have antimicrobial properties that have found different uses, but could also provoke adverse effects in soil beneficial bacteria. Silver toxicity to plant species varies from highly toxic to easily inactivated by the plant.

Keywords Silver • Acanthite • Biocide • Decorative • Industrial • Photographic manufacturing • Plating • Proustite

22.1 Introduction

Silver (Ag) is one of the eight precious and noble metals along with Au and the six platinum-group metals [8]. Silver and Au are commonly found together in nature and were almost certainly the first metals known and prized by man [8].

Silver has always been valued because of its colour (it is the whitest of all metals), its brilliant lustre, its non-corrodible nature, and the relative ease with which it can be worked. Several other useful properties have recently transformed it from a decorative and monetary metal to a predominantly industrial metal. Silver is soft, malleable, it is the most ductile of metals and possesses the highest electrical and thermal conductivities of any element [8]. It has also the highest reflectivity in the visible spectrum of any metal [12]. Its photoreactive and conductive properties make it indispensable to photographic manufacturing (25–50% of all industrial

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demand) [31]. Chemically, Ag is a 4d transition element, atomic number 47, atomic weight 107.87, and electron configuration [Kr]$4d^{10}5s^1$. Silver, like Cu and Au, is a member of Group 11 (1B) of the periodic table. It is the most reactive of the noble metals, forming three cationic species, Ag^+, $Ag^{2+}$and Ag^{3+}, of which only the monovalent form is environmentally significant [8]. Of the elements in earth's crust, Ag, at 0.075 mg kg^{-1} ranks 65th in abundance, just below Hg and above Se [26]. The normal range of Ag in soils varies from <0.01 to 5 mg kg^{-1} with an average of 0.1 mg kg^{-1} [5].

World mine production of Ag in 2001 was 18,700 t. The largest producer was Mexico, followed by Peru, Australia, and the United States [8]. This production increased moderately to 20,900 t in 2008, when China and Chile joined the group of main producers in the world. Around 80–85% of the world's Ag is recovered from sulphide and oxidized sulphide ores, frequently recovered as a by-product of the base metals Ni, Pb and Zn. The other 15–20% is produced mainly from Au and Au-Ag ores, which are predominately oxide ores, and also from Cu and Pt ores by a number of processes including cyanidation, smelting and electrolysis. Secondary Ag (recovered from scrap) is an important part of the total Ag supply. Most of the scrap (more than 80%) is generated from the manufacture and use of photographic materials, electrical switchgear, and catalysts [8].

Silver has been used in three principal ways: a fabricated product (more than 97% of Ag supplied to the market is destined for fabrication), an investment good, and, until the 1970s, a monetary metal [8]. Some of the most important uses are: Ag and Ag salts in photography; Ag-Hg dental amalgams; production of silvered glass mirrors; high-energy-density batteries; sleeve bearings in high-performance military aircraft engines; catalysts for the large-scale production of formaldehyde and the oxidation of ethylene; switch and relay contacts and conductors. For industrial products, cost restricts Ag to those uses for which it is strictly necessary. Commercial Ag is used in metallic form for many applications and as the starting material for the production of Ag compounds. In many applications, however, alloying the Ag with one or more other metals (e.g., Cu, Au) is desirable and sometimes necessary [8]. Total world consumption of Ag is expected to continue to grow slowly, especially regarding its consumption for industrial uses [8].

Most Ag compounds are based on Ag (I), and range from insoluble to at best moderately soluble in aqueous environments. Silver (I) and (II) form complexes with ammonia, cyanide, halide ions, thiosulphate and thiourea and with many organic aromatics and olefins [8]. Silver nitrate ($AgNO_3$) is the intermediate chemical from which all other Ag compounds are made and thus is, by far, the most important commercial compound. Silver bromide (AgBr), chloride (AgCl) and iodide (AgI) are photosensitive and are used extensively in photographic materials [9]. Silver nanoparticles have a wide range of current and potential future applications, including spectrally selective coatings for solar energy absorption [32], chemical catalysts [44], surface-enhanced Raman scattering for imaging [43], and in particular, antimicrobial sterilisation [30].

22.2 Lithogenic Occurrence and Geochemistry

Goldschmidt [14] estimated Ag terrestrial abundance as 0.2 mg kg^{-1} in the lithosphere. Igneous rocks contain on average 0.1 mg Ag kg^{-1}, sedimentary rocks 0.05–0.25 mg kg^{-1}, and organic-rich shales up to 1 mg kg^{-1}. Sediments may contain slightly higher concentrations than soils and are prone to enrichment near mineralised zones or anthropogenic sources. Silver is always present in Au ores and also tends to be present in sulphide ores of Pb, Cu, and Zn and sometimes with Bi and Sb [8]. Silver is often highly enriched in the oxidized parts of sulphide deposits, in mineralised veins as the native ore [41] and in various natural alloys. It occurs most frequently as a secondary component of a great variety of minerals. As many as 248 minerals can have Ag as a structural component [17], acanthite (Ag_2S), argentian galena (Pb,Ag)S, proustite (Ag_3AsS_3) and pyargyrite (Ag_3SbS_3) being some of the principal ones.

Although Ag is almost inert to atmospheric oxygen, it is very permeable to atomic oxygen, readily reacts with sulphurous gases to form surface tarnish, and dissolves in oxidizing acids and in aqueous potassium or sodium cyanide solutions in the presence of oxygen [12]. Knowledge of the forms of Ag in soils is of importance to both mineral exploration and environmental management [24]. Crystalline Fe oxide (57%) and residual (43%) phases were found to be the dominant hosts of Ag in natural soils, but when soluble Ag was added to these soils, much Ag was found in the crystalline Fe oxide fraction (66%) and only a relatively small proportion of Ag was in the residual fraction [24]. Jones et al. [22] tested a range of chemical extractants on soils from a mineralised area of Wales, and found that no single extractant removed more than 10% of the pseudo-total soil Ag for any of the soil samples.

22.3 Chemical Behaviour in Soil and Availability to Plants

Silver sorbs strongly to soils, especially those rich in organic matter; which may play an important part in controlling its cycling, mobility, and sorption in soils. Both humic and fulvic acids have been shown to have strong retentive capacities for Ag [21]. Among the different functional groups on soil organic matter, Ag^+ forms especially strong complexes with thiol groups to the extent that it can displace or replace metals more weakly complexed to thiols such as Fe in >S-Fe-S< groups [27].

Exchange reactions are also supposed to play an important role in Ag^+ adsorption to soils [2]. The mobility and bioavailability of Ag is ultimately affected less by the sorptive capacity of the soil than by the ease with which this element desorbs from soils [18]. Silver is believed to be so strongly sorbed to soil surfaces, or to readily form such insoluble salts and/or compounds that desorption is assumed to be negligible [18]. In addition, both live and dead biomass has shown the ability to take up Ag^+ [15]. Iron and Mn oxides and soil OM have substantial capacities to adsorb Ag ions from solution [10]. In fact, one of the reasons given for Ag immobility in soils with pH >4 is that Ag sorbs readily to oxides, particularly Fe and Mn oxides, largely by exchange processes [2, 36].

Li et al. [25] studied the mobility and bioavailability of Ag in the environment in terms of the desorption behaviour of Ag from some environmentally relevant soil components. These authors found that a significant proportion of Ag^+ sorbed by Fe-oxides, humic acids (HA), and charcoal could not be desorbed readily back into solution. Two-site adsorption models gave good fits to experimental data, except for Ag^+ desorption from charcoal, where data fitted to a 1-site model better. This suggests that Fe-oxides, HA, and charcoal could be very important sinks for Ag in the soil. For goethite and HA, the longer the interaction time, the less mobile (and thus less toxic and bioavailable to living organisms) Ag became. For ferrihydrite and charcoal, such residence time effects were not obvious. The observed trends could be explained by assuming that Ag^+ moved from reaction sites associated with fast desorption reactions to sites associated with slower reactions as reaction time increases (solid-state diffusion within oxide particles, incorporation into mineral structure recrystallisation, or diffusion into micropores or intraparticle spaces) [25]. Possible mechanisms for long-term Ag retention in soils may also include reduction by organic matter functional groups such as quinones or phenolics to metallic Ag, or fixation in the interlayers of clay minerals [18].

Jacobson et al. [19] found that a peaty-muck soil sorbed Ag more strongly than a range of mineral soils, confirming that Ag sorption to soils is dominated by soil organic matter either through exchange or complexation. Amounts of Ag adsorbed on to the soils increased after a 1-year incubation period. These same authors, in a different experiment [18], found that more Ag was desorbed from a sandy soil than from a peaty-muck soil or a range of mineral soils with higher clay contents. The observed release of Ag from sandy soils and even from organic matter-rich soils suggests that Ag may pose an environmental concern when present in soils at elevated concentrations [18].

Silver has been reported as a trace constituent in many plant forms, including higher plants [5, 23]. Concentrations are very variable, but usually <1 mg kg^{-1} ash [5]. Data on Ag in plants have mainly been gathered to aid biogeochemical exploration for ores [5, 40] and few ‘baseline’ data exist for Ag concentrations in plants.

22.4 Soil Contamination

The anthropogenic loading of Ag in soils is of concern. Silver concentrations in soils impacted by industry (2.3 ± 2.2 mg kg^{-1}) or by smelter activity (<2.4 mg kg^{-1}) may be 3–20 times the background [28, 38] (see also Chap. 2, Sect. 2.3.3.2.3). An estimated 2×10^6 kg Ag $year^{-1}$ is lost in the US of which 68% ends up on land as solid waste [31]. Silver plating is extensively used by various industries for production of durable and decorative products. The metal is normally plated from alkaline cyanide solutions [4] that usually generate Ag dicyanide

[$Ag(CN)_2^-$] as a contaminant in the waste water. Silver dicyanide may be accompanied by other Ag species and is a chemically stable and extremely toxic metal complex of high mobility in the environment [15].

Due to the value of the metal and environmental concern, there is an increasing trend to reclaim Ag from waste. For economic reasons, virtually all the Ag in spent thiosulphate photographic processing solutions is routinely recovered [9]. The use of Ag ions in industry to prevent microbial growth is increasing and Ag is a new and previously disregarded heavy metal contaminant in sewage sludge amended soil [6, 39]. In fact, Ag in concentrations known to occur in soil amended with sewage sludge can seriously affect soil microbial activity [20].

22.5 Risk Assessment

Silver is a non-essential element that can be highly toxic to a number of biota even when present in the environment at trace levels [19]. Silver is almost unique in combining very low solubility of most of its compounds with exceedingly high toxicity of the soluble fraction [11]. Silver is included in the US EPA list of priority toxic pollutants; the monovalent Ag ion is more toxic to fish than Cu or Hg, and it is an extremely effective bactericide [36]. Antimicrobial activity of Ag is due to its complexation to membranes, enzymes, nucleic acids, and other cellular components [35]. The antimicrobial properties of Ag nanoparticles have found use in a range of products, including textiles, bandages, air filters, and vacuum cleaners [37]. However, these biocidal properties have also the potential to adversely affect beneficial bacteria in soils and waters [34].

Silver is relatively harmless to higher life forms. Because Ag^+ is very easily reduced it is not readily accessible to living organisms in the natural environment. Most Ag compounds, aside from those containing toxic anions, such as arsenate or cyanide, are essentially nontoxic [8]. In the United States, the level of Ag in drinking water is not regulated, but the U.S. Environmental Protection Agency recommends that to avoid possible skin discoloration, Ag should not exceed 0.01 mg L^{-1}.

Despite low Ag solubility, in contaminated soils the available fraction may be enough to adversely affect soil microbial populations [19]. Denitrification has been identified as being sensitive to Ag in soil; Ag^+ inhibits this activity in soil [39]. Compounds that dissociate in solution and provide significant concentrations of free Ag ions can be toxic to bacteria and to freshwater aquatic organisms, but compounds and complexes in which the Ag is tightly bound, such as Ag sulphide and thiosulphate complexes, are innocuous [8]. Evidence for microbial uptake and accumulation of Ag often suggests a certain Ag resistance and detoxification [35].

Silver nanoparticles have been used as a bactericide and microbicide since ancient times. They attach to the cell membrane of gram-negative bacteria creating lethal pores and producing bacteria lysis [3]. At concentrations $<0.1\ \mu g\ ml^{-1}$, Ag nanoparticles are toxic to viruses, prokaryote and mammalian cells [7, 16]. Silver nanoparticles have been found to exert considerable toxicity in the soil nematode *Caenorhabditis elegans*, decreasing drastically its reproduction potential, mainly through oxidative stress; nanoparticles were slightly more toxic than Ag ions in terms of reproduction potential [34].

Silver has no known physiological function in humans [13]. Most of the Ag that enters the human body is breathed in or ingested in foods; a lesser amount enters through the skin. Tests in animals show that Ag compounds are likely to be life-threatening to humans only when large amounts (grams) are swallowed, and that skin contact with Ag compounds is very unlikely to be life-threatening [1].

The toxicity of Ag to plant species varies, with sensitive cultivars being impacted at aqueous concentrations as low as 75 mg Ag L^{-1}, whereas in sludges spiked with photographic Ag waste at 120 mg Ag kg^{-1} no impact on the growth of several agricultural species was noted [33]. It is known that Ag ions interact metabolically with Cu and Se and replace H from the sulfhydryl groups of the photosynthetic enzymes, changing their structure and inactivating them. Silver also forms complexes with amino acids, pyrimidines, purines and nucleotides, as well as with their corresponding macromolecular forms, suggesting its potential to be either highly toxic or easily inactivated by the plant [29].

Information on the uptake of nanoparticles by plants, as well as on the potential mechanisms of phytotoxicity, remains largely unknown. Nanoparticles may release ions that result in toxicity [37]. During a 15-day hydroponic trial, the biomass of *Cucurbita pepo* (zucchini or marrow) plants exposed to Ag nanoparticles (1,000 mg L^{-1}) was reduced by 75% as compared to control plants and bulk Ag powder solutions [37]. Exposure at 100 mg L^{-1} or lower did not significantly impact zucchini biomass. Increased Ag ion dissolution from the nanoparticles only partially explained the observed phytotoxicity; half the observed phytotoxicity came from the elemental nanoparticles themselves [37].

Low or zero toxicity was observed in germination (cucumber and lettuce), bioluminescent bacteria (*Photobacterium phosphoreum*) and anaerobic toxicity tests for Ag nanoparticles at 16–100 μg ml^{-1} concentrations [3]. Morphological symptoms of senescence phenomena such as chlorosis and damage of chloroplasts and mitochondria were observed in *Potamogeton crispus* L. (curly pondweed) plants exposed to various concentrations of Ag (5–20 μM), which suggested that Ag accelerated the senescence of the tested plants. Silver accumulation in *P. crispus* resulted in disturbances in photosynthetic capacity, oxidative stress and general disarray in the cellular functions [42].

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Chapter 23
Thallium

Paula Madejón

Abstract Thallium (Tl) is widely distributed in the natural environment although at very low concentrations. It mainly occurs in the oxidation state Tl (I), whilst Tl (III) increases under acid and oxidizing conditions. Geochemical behaviour of Tl is analogous to that of potassium. Thallium does not occur in a free state in nature although several minerals contain it as a major constituent. The most common Tl-containing minerals are Lorandite and Crooksite. This element is mobilised by the combustion of fuels and other industrial processes and tends to persist in soils, depending on the soil type. It is considered a non-essential element and highly toxic to living organism. It is relatively easily taken up by plants and enters the food chain and it has been shown to accumulate in fish and other animals, with toxic effects.

Keywords Thallium • Cruciferae • Pollutant • Potassium • Rodenticide • Silicates • Toxicity

23.1 Introduction

Thallium (Tl) is widely distributed in the natural environment, generally present at very low concentrations. The Tl content of the earth's crust ranges from 0.5 to 1.0 mg kg^{-1} [43] and 0.013 mg kg^{-1} in the oceanic crust [8]. Its content seems to increase with increasing acidity (silicon content) of igneous rocks and with increasing clay contents of sedimentary rocks [14, 15].

In nature, the primary oxidation state of Tl is I (thallous species), and it occurs in soil via isomorphous substitution with K^+ in feldspars and silicates. It can also occur in the III oxidation state (thallic species) [25]. Geochemical behaviour of Tl is

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analogous to that of K, the lower oxidation state may predominate in aqueous systems [25]. The most dominant species in nature is Tl (I), whilst the proportion of Tl (III) increases considerably under strongly acidic and oxidizing conditions [23]. Thallium (I) compounds resemble the compounds of alkali metals and are soluble in water. Thallium (I) compounds are easily oxidized by Br, chloride, hydrogen peroxide, or nitrous acid. Thallium (III) compounds are reduced to Tl (I), for example by sulfurous acid. Thallium (III) compounds tend to be appreciably more stable than Tl (I) compounds [17].

Concentrations of Tl in uncontaminated soils generally range from 0.01 to 3 mg kg^{-1}, but most have <1.00 mg kg^{-1} [10]. Marine sediments of different origins show Tl concentrations from 0.14 to 1.13 mg kg^{-1} [43]. There has been little research on Tl concentrations in world soils compared to other elements [27, 38]. Logan [28] reported total values of Tl (HNO_3-extractable) in some British soils in the range 0.03–0.99 mg kg^{-1}. Tremel et al. [46] reviewed several studies on Tl in soils and reported that most arable soils in France contained 0.13–1.54 mg Tl kg^{-1}, with a median value of 0.29 mg kg^{-1}. A slightly lower range of Tl concentrations was found in 460 soil samples from Upper Austria (0.08–0.91 mg kg^{-1}) [11]. A range of 835 soil samples from China contained between 0.29 and 1.17 mg Tl kg^{-1} [49]. Non-polluted soil from the south of Spain contains approximately 0.70 mg Tl kg^{-1} [7]. (See also Chap. 2, Table 2.1).

Although world annual production of Tl does not exceed 15,000 t, it is estimated that about 2,000–5,000 t $year^{-1}$ are mobilised by combustion of fossil fuels, ferrous and non ferrous metal smelting (Pb, Cu and Zn ores) and other industrial processes such as cement production [9, 18]. Due to the high volatility of some Tl compounds, there is considerable enrichment of Tl in the fine particles in dusts and fly ashes that are not efficiently retained by electrostatic precipitators or other emission control facilities. Thus, a large fraction of Tl is released into the atmosphere [9].

In the past, Tl was extensively used for medical purposes and also as a rodenticide. Its main current uses are in the electrical and electronics industries, in the manufacture of semi conductors, scintillation counters and low temperature thermometers, and in mixed crystals for infrared instruments and laser equipment. It is also used with Se in the production of special glasses. Alloyed with Pb, Zn, Ag and Sb, Tl enhances resistance to corrosion and is also used for catalysing organic reactions. Radioactive isotopes of Tl are used in physics, in industry and medicine [18, 36].

23.2 Lithogenic Occurrence and Geochemistry

Thallium does not occur in a free state in nature although several minerals contain it as a major constituent [1]. Thallium is classed as a lithophile element (occurs with or in silicates), forms sparingly soluble sulphides and is a minor constituent of pyrites and other sulphide minerals (e.g., ZnS sphalerite) and thus shows some chalcophile characteristics [36].

It is found in sulphide ores of Pb, Zn and Cu and in coal [18] and the deposits characteristically high in As are usually also high in Tl [1]. Relatively high contents have been found in granite and shale, with intermediate values for limestone, sandstone and coal; however, much higher values have been found in organic-rich shales and coals of the Jurassic period with values of $<$1,000 mg kg^{-1} [43]. Although many Tl-containing minerals have been discovered and described, the following are the most common: Lorandite ($TlAsS_2$) and Crooksite $(Cu, Tl, Ag)_2Se$ (minerals with thallium levels up to 60%); [18], Hutchisonite $(Pb, Tl)_2 (Cu, Ag)As_5S_{10}$, and Urbaite ($Tl_4Hg_3$ $Sb_2As_8S_{20}$).

Thallium occurs naturally as two stable isotopes: ^{203}Tl and ^{205}Tl with relative abundances of 29.5% and 70.5% [41]. The ^{205}Tl/^{203}Tl isotopic ratio of 2.378 varies with geological processes and hence can not be used as a fingerprint for sources of Tl in the environment.

23.3 Chemical Behaviour in Soil and Availability to Plants

Thallium is readily mobilized and transported together with alkaline metals during weathering. However, once deposited, Tl tends to persist in soil, depending on soil type. Greater retention is found in soils containing large amounts of clay, organic matter, Fe and Mn oxides. Thallium is retained in the upper layers of soil, less so in acid soils [18]. Yang et al. [53] found that natural and anthropogenic Tl is distributed differently between soil components; anthropogenic Tl was mainly retained in the labile fractions of soils (~80%) whereas natural Tl is predominantly found in the residual fraction (~98%).

There is little information on the chemical form taken by Tl in soil. In contrast to other pollutant elements (Zn, Pb, Cd, and Cu), extraction with *aqua regia* yielded only 28–74% of total contents [30]. In soil samples from Bulgaria, *aqua regia* and conc. HCl leached about half of the amount obtained with HNO_3/HF. Only 6% of total was found to be exchangeable with NH_4Cl, $pH = 7$, or with KCl [45].

Thallium is considered a non-essential element and highly toxic to living organisms, [38]. Kaplan et al. [16] studied the toxicity of Tl in beans grown in hydroponic culture and showed that Tl was accumulated in roots and not in the aerial part. They also found that micromolar concentrations of Tl added to the nutrient solution altered the concentration of certain nutrients in soybean tissues; drastically reduced plant biomass with severely stunted, unbranched root systems and chlorosis of mature leaves despite the presence of adequate levels of Fe. On the other hand Allus et al. [2] studied rape and barley grown in culture solutions with a range of Tl concentrations and found differences in the susceptibility of the two species to Tl. Thallium content in barley was higher in roots whilst in rape, Tl contents were higher in shoots.

The Tl content of plants seems to be a function of the concentration of the mobile fraction in soils. It is relatively easily taken up by plants because it is generally present as thermodynamically stable Tl (I), an analogue of potassium; through plants, it enters the food chain and it has been shown to accumulate in fish and other animals, with toxic effects [3, 26]. Toxicity of Tl is probably due to its interactions with K (both elements have similar ionic radii) especially by substitution into enzymatic systems, such as (Na+/K+)-ATPase and other monovalent cation-activated enzymes, as well as to its high affinity with sulfhydryl groups of proteins and other biomolecules [6, 24, 29]. Other systems similarly affected include pyruvate kinase [39] and phosphatases [12].

The transfer from soil to plants generally depends on species-specific properties, as well as soil properties, such as soil texture and humus contents, cation exchange capacity, pH and other properties. Madejón et al. [33] showed that the Tl content of plants (*Brassicae*) growing in semi-arid conditions can be significantly influenced by precipitation. In dry years, plant Tl accumulation may be significantly reduced.

The reference content of Tl in plants has been calculated by Markert [34] at 0.05 mg kg^{-1}. Smith and Carson [43] gave Tl levels in various plants (in mg kg^{-1}): vegetables 0.02–0.13 and clover 0.008–0.01. Madejón et al. [31] found Tl levels of 0.005 mg kg^{-1} in sunflower seeds, 0.06 mg kg^{-1} in roots (the pseudo total soil content of Tl was 0.50 mg kg^{-1}) and 0.009 mg kg^{-1} in seeds and 0.32 mg kg^{-1} in roots of sunflowers in soils with a level of 2 mg kg^{-1} due to a mine spill accident. Concentrations of Tl in fruits (seeds) of Holm oak (*Quercus ilex*) were 0.002 mg kg^{-1} in non affected trees and 0.01 mg kg^{-1} in seeds from trees affected by a mine spill [32].

It is well known that the uptake rate of heavy metals can vary between plant species [35]. Some plants, especially in the *Cruciferae* and *Graminae* families, exhibit a special ability to take up Tl. Tremel et al. [47] showed that Tl is accumulated by S-rich plants from the family *Brassicaceae*. Several studies have investigated Tl accumulation in different members of this family. Crop plants such as green cabbage [50, 51], white cabbage (*Brassica oleracea capitata*) and kale (*Brassica oleracea acephala*) [21] have been shown to accumulate Tl in edible parts (shoots and foliage). Soriano and Fereres [44] reported relatively high Tl accumulations in the aerial biomass of *Brassica napus* and *B. carinata*. Other brassicas such as *Iberis intermedia* and *Biscutella laegiviata* have been found to hyperaccumulate Tl in their shoot tissues [5, 22, 42].

23.4 Soil Contamination

There are several cases where soils with naturally elevated Tl contents of >2 mg kg^{-1} have been observed [4, 46–48]. These soils are generally developed on K-rich magmatites (e.g., granites, syenites) where Tl^+ isomorphically substitutes for K^+ or Rb^+, especially in K-feldpars and micas [13, 19]. High Tl concentrations of <73 mg kg^{-1}have been found in soils around old mines [40] due to contamination from Tl-rich sulphide ores of Hg, As and Au (40–124 mg kg^{-1}) [52] from pyrite processing areas (5–15 mg kg^{-1}) [53] and from a zone of Pb-Zn exploitation (9–28 mg kg^{-1}) [27].

23.5 Risk Assessment

Thallium is a highly toxic element and is a US Environmental Protection Agency (EPA) priority pollutant [37]. The ecotoxicological importance of Tl is derived from its high acute toxicity to living organisms, comparable to that of Pb and Hg [19].

The major pathway of Tl exposure for animals and humans is the ingestion of plants grown in Tl-contaminated soils [42]. In Germany, 1 mg kg^{-1} Tl in soils has been established as the tolerance level for agricultural use [20].

Xiao et al. [51] reported a case study drawing attention to the fact that natural processes can mobilize Tl, which may enter the food chain as a "hidden health killer" with severe health impacts on the local human population. The study was carried out in Guizhou Province, China, in which "natural contamination" of Tl in bedrocks/ores was within the range 6–35,000 mg kg^{-1}. This led to enrichment of Tl in the aquatic system (0.005–1,100 μg L^{-1} in groundwaters and 0.07–31 μg L^{-1} in surface waters) and soil layers (1.5–124 mg kg^{-1}). Concentrations of 1–500 mg kg^{-1}Tl were determined in many food crops growing on Tl-contaminated arable soils. The daily intake for inhabitants consuming these crops was 1.9 mg of Tl, showing a latent health hazard with potential risk of toxicity in humans within areas of "natural" contamination of Tl. In fact in a retrospective study, Xiao et al. [52] found that majority of the volunteer subjects from these communities had urinary Tl concentrations above 4.5–6 μg L^{-1}, implying early adverse health effects, and some had over 500 μg L^{-1} urinary Tl, considered to be on the threshold of clinical intoxication.

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Chapter 24
Tin

Brian J. Alloway

Abstract Tin (Sn) is one of the metals of antiquity and its use with copper in the alloy bronze was a major development in human history. It is now mainly used in protective coatings on steel, in electrical solders and in the production of organotin compounds which have a wide range of uses including as biocides. Adsorption of inorganic forms of Sn in soils is positively correlated with pH, organic matter content and cation exchange capacity. Plant uptake is greatest in acid soils and in most species Sn accumulates in the roots. Organotin compounds with three organic groups, such as tributyltin, have the highest biocidal activity and constitute the greatest ecotoxicity hazard. Organotins are more ubiquitous sources of Sn in soils than inorganic forms and can reach soils in atmospheric deposition, fungicidal crop sprays and sewage sludges. They behave as enzyme disruptors in many animal species and there is concern about their possible impact on human health.

Keywords Tin • Tin-plating • Bronze • Organotins • Fungicide • Canned foods • Antifouling • Ecotoxicity • Sludged soils • Plant uptake • Mammalian toxicity

24.1 Introduction

Tin (Sn) is a white, silvery soft metal with an atomic number of 50, atomic weight 118.7, specific gravity of 5.75 and a melting point of 232°C. It is one of the seven metals of antiquity (together with Ag, Au, Cu, Pb, Fe and Hg) and artefacts made of Sn date back to at least 2,000 BC, but Sn smelting only became common after 1,800 BC [7]. However, Sn had been alloyed with Cu to make bronze from around 2,500 BC.

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Bronze, comprising approximately 90% Cu and 10% Sn, is much harder and easier to cast than Cu on its own and was used for artefacts such as weapons and tools during the 'Bronze Age' which lasted for about 1,500 years [7]. Current major uses of Sn (metal) are in protective coatings (tin-plating) on steel (27% of Sn production), especially in cans for food and drink and aerosol containers, electrical uses such as solders etc. (23% of Sn production), in alloys such as bronze (containing 8.5–16% Sn), pewter (with 85% Sn) and other special engineering alloys and in glass treatment. Small amounts of inorganic Sn, such as $SnCl_2$ are used as additives in food and toothpaste [1]. World mine production of Sn in 2010 was 261,000 t (Chap. 1, Table 1.1) [26]. China is by far the largest producer of Sn (44% of mined Sn in 2010), followed by Indonesia (23%) [26].

Tin forms a wide range of organometallic compounds. These 'organotin' compounds (OTCs) have the general formula R_nSnX_{3-n}, where R is an alkyl or aryl group (methyl, butyl, octyl, cyclohexyl, phenyl, or neophyl), Sn is in the +4 oxidation state and X is a singly charged anion or anionic organic group (halides, oxide, hydroxide, carboxylates or mercaptans) [1, 11]. These OTCs were first produced commercially in the 1960s and there are now probably more synthetic organometallic compounds of Sn in commercial use than of any other metal [13]. Uses of OTCs include heat stabilisers in PVC, catalysts and as biocides in marine antifouling paints, agricultural pesticides, industrial fungicides and slimicides and wood preservatives [1, 9]. Around 66% of OTCs are used for PVC production, but their biocidal uses are of greater environmental significance, especially in aquatic ecosystems [1].

The fungicidal and bactericidal properties of OTCs depend on the organic group in the molecule. Those OTCs with three organic groups, such as tributyltin (TBT) and triphenyltin (TPT), are the most important with regard to biocidal properties and ecotoxicity. Chau et al. [4] consider TBT to be the most toxic chemical ever to be used as a biocide in the environment. Organotins with one organic group, such as methyltin and butyltin are used in PVC manufacture. They have no biocidal activity and low mammalian toxicity. Those OTCs with two organic groups, such as dimethyltin (DMT) and dibutyltin (DBT) have many industrial uses, such as heat stabilisers in PVC and as catalysts. Tetraorganotin compounds (with four organic groups) are very stable and have no biocidal properties. World production of OTCs is around 50,000 t $year^{-1}$ [1, 16].

There is a possibility that Sn may be an essential trace element (micronutrient) for mammals [28]. In experiments with rats on purified diets, dietary deficiency of Sn has been reported to cause hair loss, depressed growth, depressed response to sound, decreased feed efficiency and decreases in heart Zn, tibial Cu and Mn, muscle Fe and Mn, spleen Fe, kidney Fe and lung Mn. A typical dietary intake in humans is 1–40 mg Sn day^{-1} [22].

24.2 Lithogenic Occurrence and Geochemistry

Tin concentrations in the earth's crust average around 2.5 mg kg^{-1} and are highest in acid igneous rocks and in argillaceous sediments [6, 15, 18] (see also Chap. 2, Table 2.2). Rocks derived from argillaceous sediments, such as clays and shales normally have higher Sn contents (6–10 mg kg^{-1}) than ultramafic and calcareous rocks (0.35–0.5 mg kg^{-1}). The most important Sn ore mineral is cassiterite (SnO_2) which is found in vein and placer deposits. It is very resistant to chemical weathering which explains its occurrence in placer (coarse sediment) deposits which are derived from the physical weathering of veins of cassiterite. The chemical weathering of Sn is highly dependent on pH.

The concentrations of Sn found in surface soils tend to be in a relatively narrow range, although concentrations in parent material rocks differ considerably. This is probably due to a combination of other Sn inputs. Kabata-Pendias [15] refers to ranges of 1–11 mg kg^{-1}, but with 50–300 mg kg^{-1} in peats. In China, reference soils have a concentration range of 2.5–17 mg kg^{-1} and in the USA 1.7–4.0 (mean 2.4 mg kg^{-1}), but concentrations of $<$800 mg Sn kg^{-1} have been reported in the vicinity of Sn mines and smelters.

24.3 Chemical Behaviour in Soils and Availability to Plants

Tin occurs as stannous (Sn^{2+}) and stannic (Sn^{4+}) ions, and complex anions of oxides and hydroxides [3]. The Sn^{2+} ion serves as a strong reducing agent in acid solutions.

Adsorption of Sn in soils is positively correlated with pH, organic matter content and cation exchange capacity [15]. Norra et al. [23] found that Sn and other heavy metals from diffuse urban sources were more strongly adsorbed in urban soils which had a higher pH, higher contents of organic matter, carbonates and expanding clay minerals than nearby soils developed on the same sandstone parent material under forest.

Most authors report that Sn taken up by plants tends to remain concentrated in the roots [15], but Ashraf et al. [3] found little accumulation in the roots of *Cyperis* species sedges grown on spiked soils. Concentrations in plants from the literature reported by Kabata-Pendias [15] include a common range of 20–30 mg kg^{-1} (Ash weight) in plants and 5.6–7.9 mg kg^{-1} DW in wheat grains. Concentrations of $<$300 mg kg^{-1} (Ash weight) are reported in plants growing in mineralised areas. Sedges and mosses are considered the best accumulators. Tin contents of $<$1,000 mg kg^{-1} (DW) have been found in sugar beet plants growing near a chemical factory and $<$2,000 mg kg^{-1} found in vegetation near a Sn smelter [15].

In pot experiments by Ashraf et al. [3] using soils spiked with inorganic Sn, different species of *Cyperus* sedges showed varying abilities to accumulate Sn. Accumulation increased with Sn concentration in the soil and *Cyperis rotunda* L. showed the greatest accumulation, with *Cyperis fastigiatus* Rottb. and *Cyperis alternifolius* showing lower concentrations. In all three species, soil Sn was translocated to the twigs and leaves and did not accumulate in the roots. It was concluded that plants of *Cyperis* species (especially *C. rotunda* L.) have considerable potential for the phytoremediation of soils contaminated with Sn, but the plants would need to be harvested annually to prevent the recycling of Sn bound in the leaves and twigs [3]. Kabata-Pendias [15] considers Sn to be highly toxic to higher plants and fungi, but Ashraf only found growth to be inhibited in the soil with the highest Sn spike (60 mg kg^{-1}).

Inorganic Sn appears to be methylated in the aquatic environment to various methyl forms [16]. However, it is not known to what extent this methylation occurs in soils.

Commercially produced OTCs can reach soils and terrestrial ecosystems in atmospheric deposition and accumulate in topsoils. Other inputs to soils include OTCs used as fungicides on crops and the recycling of sewage sludge containing Sn. Huang and Matzer [14] found that adsorption of OTCs in soils correlated with carbon content and cation exchange capacity. The strength of adsorption was in the order: mono-> di-> tri-substituted OTCs and butyl > methyltin compounds. The OTC adsorption coefficients were much larger in organic soils than in mineral soils. Adsorption and desorption showed a pronounced hysteresis. Trimethyltin (TMT) adsorption was partly reversible in all soils, but DMT, TBT and DBT only showed reversible adsorption in mineral soils. Trimethyltin was more mobile and bioavailable in soils than the other OTCs (which were strongly sorbed) and this suggests that it might be more readily leached and enter aquatic ecosystems [14].

In experiments with lettuces grown on sewage sludge-amended soils spiked with TBT and TPT compounds, Lespes et al. [19] showed that these OTCs were taken up into the roots and translocated to the shoots. In the plants, the degradation of tri-organotin compounds via DBT and DPT appeared to be reduced. Crop plants growing in soils amended with OTC-containing sewage sludge and/or sprayed with OTC-based biocides do take up these compounds and ultimately humans consuming them may be exposed to increasing amounts of OTCs. Although OTC concentrations in the lettuces in these experiments were not very high, other plant species or cultivars which accumulated OTCs to a greater extent could pose a potential risk to health. The WHO Admissible Daily Intakes (ADIs) of OTCs are 0.25 μg SnTBT and 0.5 μg SnTPT kg^{-1} (body weight) for a human of 70 kg.

24.4 Soil Contamination

Norra et al. [23] reported that urban soils in Pforzheim, Germany had higher total Sn contents compared with nearby forest soils developed on the same (sandstone) parent material. The mean Sn concentrations (in mg kg^{-1}) were: forest 3.6, urban green space 5.7, low density urban development 6.6 and medium density urban development 8.0. It was concluded that the Sn (and other heavy metals) had accumulated in clays and carbonates in the urban soils and that these minerals, like the heavy metals, were of anthropogenic origin from diverse sources. The maximum Sn content found was 18.3 mg kg^{-1}. Soils contaminated by Sn smelting works have been found to have concentrations of $<$1,000 mg kg^{-1} [16].

Most sewage sludges contain Sn from both inorganic and organic sources. Senesi et al. (1999) reported a range of Sn in sewages sludges from European and US treatment works of 40–700 mg kg^{-1}. McBride et al. [20] worked with a sewage sludge containing 95 mg Sn kg^{-1}(DM), but many values in the literature for sewages sludges are lower than this. The mean Sn content in Swedish sewage sludges is around 23 mg kg^{-1}(DM) (<40 mg kg^{-1}). Given normal sewage sludge application rates, Eriksson [10] calculated that it would take around 200 years to double the Sn content in the top 25 cm of soils in Sweden. In Canada, MBT was found in all sewage sludge samples analysed, but DBT and TBT were only found infrequently and octyltin was not found in any samples [4].

Vouvoulis and Lester [27] worked with a sample of sewage sludge containing 18 mg kg^{-1}(DM) TBT and showed that there was little degradation of this compound during anaerobic sewage treatment and subsequent thermal drying. A study for the EU proposed a PNEC for TBT of 2.5 μg kg^{-1} which could cause problems for soil on land receiving sludges with relatively high TBT contents. Other authors have reported the slow decomposition of TPT in soils following its use as an agricultural fungicide [17].

Organotin compounds are more ubiquitous sources of Sn contamination of soils than metallurgical industry sources such as mines and smelters. Tributyltin oxide (TBTO) is used as a fungicide, timber preservative and industrial biocide. Until recently, it was also widely used as a marine antifouling agent on boat hulls, but it is now banned from this use on account of its ecotoxicity. Triphenyltin acetate (TPTA) is used as a sterilant in insect control and as a fungicide. Triphenyltin chloride is used as a biocide and an intermediate. Triphenyltin hydroxide is used for sterilising insects and as a fungicide. The use of TPT has not been as strictly regulated as TBT although they produce similar levels of toxicity [13].

Apart from OTCs in sewage sludges applied to land, the most significant inputs to soils are in OTCs used as fungicidal sprays on agricultural crops. Triphenyltin acetate (Fentin) and triphenyltin hydroxide (Fentin hydroxide) are used as fungicides especially on potatoes to control blight (*Phytopthora infestans*) and other fungal diseases in sugar beet, celery, carrots, onions, rice, pecan nuts, hops and coffee. Current application rates of TPTA are 0.16–0.42 kg ha^{-1} as foliar sprays and these can be applied <15 times year^{-1}. Until a few years ago, it was often the practice to apply larger doses of this fungicide (0.33–0.67 kg ha^{-1}) several times a year. Application rates for TPT hydroxide are 0.21–0.24 kg ha^{-1}. It has been estimated that the inorganic Sn residues in soils after the degradation of organotin applied to potato crops are around 1.1 kg Sn ha^{-1} year^{-1} [24]. Degradation of organotins to less toxic forms of Sn depends on the organotin compound. It is mainly brought about by microbial processes and is accelerated by sunlight and higher temperatures. Degradation of TBT can take from several months to more than 2 years, depending on conditions [8]. The degradation of TPT is thought to be via di- and monophenyl intermediates brought about by microbial processes [24]. However, it is considered that monophenyltin (MPT) may inhibit methanogenic bacteria at lower concentrations than DPT [24]. Experiments have shown half lives of 27 and 33 days for amendments of 10 and 20 mg Sn kg^{-1} as TPT, respectively. In the early stages of degradation, there was an increase in toxicity to microorganisms from metabolites produced during the microbial degradation process, but this decreased with time [24].

24.5 Risk Assessment

With regard to risks to human health, inorganic forms of Sn are considered to be relatively non-toxic because of their low solubility and absorption by the oral route, but divalent Sn salts are more toxic than tetravalent ones causing GI irritation, abdominal pain and anaemia [5]. Short-chain alkyltin compounds are easily absorbed from the GI tract and are more toxic than long chain alkyltin compounds. Triethyltin acetate (Et_3, SnOAc) is the most toxic. The human toxicity of OTCs increases in the order $R_3Sn^+ > R_2Sn^+ > RSn^{3+}$ [16]. Diorgaontins are used in PVC food packaging materials and are a potential (but very small) dietary source together with residues of triorganotin agricultural biocides.

In Australia, the National Pollutant Inventory states that there is no evidence of the accumulation of OTCs in the environment, although they do refer to the highly toxic effects of TBT and TPT compounds in anti-fouling paints on many species of aquatic organisms. In mammals, high levels of TBT oxide can affect the endocrine glands upsetting hormone levels and also cause damage to the reproductive and central nervous systems, bone structure, and immune system. They are also moderately toxic to birds [8].

Leaching of Sn from Sn-coated cans, cooking utensils and other food containers may contaminate foods and beverages. Canned foods, especially fruits and vegetables are considered to be the main source of Sn in the human diet [1]. Some canned juices and fruit may contain <2,000 mg Sn kg^{-1}. Most Sn-plated cans used for food products are lacquered and this reduces the leaching of Sn into the contents.

Both TBT and TPT are known to be enzyme disruptors in aquatic organisms. They are also known to be associated with certain tumours in humans and are dermal irritants (especially in occupationally exposed people) [8, 16, 21]. There is considerable concern about the risk to people consuming a large amount of sea food on a regular basis due to the accumulation of TBT in marine ecosystems. One of the explanations for the mammalian toxicity of OTCs is their lipophilicity which enables them to penetrate and damage cell membranes and mitochondria, interrupt oxidative phosphorylation and inhibit the synthesis of heme oxygenase. They can also be immunotoxic and genotoxic (damage DNA) [5]. According to Grun et al. [12], TBT is the first example of an environmental endocrine disruptor that promotes adipogenesis and that long-term exposure to OTCs may act as a chemical stressor for obesity and related disorders. A Tolerable Daily Intake (TDI) for TBT by humans adopted by the World Health Organisation is 0.25 μg kg^{-1} (body weight) [2].

Fromme et al. [11] reported a median total OTC content of 1.66 mg kg^{-1} (<7.18) in household dusts from 28 apartments in Berlin. They refer to other surveys in European countries showing a range of total OTC levels of 0.14–5.18 mg kg^{-1}. These OTCs were derived from a variety of products used in the houses and absorbed by the dust. Although it was not possible to make a reliable risk assessment, the authors concluded that the presence of OTCs in houses could, under certain circumstances, be a significant source for intake by children.

Turner [25] refers to median levels of total Sn in household dusts in urban-suburban environments in Dhahran (Saudi Arabia), Ottowa (Canada) and Plymouth (UK) ranging from 13 to 31 mg kg^{-1}. Estimates of the bioaccessibility of Sn using a physiologically-based extraction test (PBET) showed that it was higher with dust from the hot arid environment of Dhahran than in dust from the cooler and more humid environment of Plymouth.

It would appear that the behaviour and long-term fate of inorganic Sn and OTCs in the soil – plant system needs further investigation in order for meaningful risk assessments to be made.

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Chapter 25
Tungsten

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Abstract Tungsten (W) is a lithophile element that occurs naturally in small concentrations in soils and sediments. Its hardness and resistance to corrosion (alone, alloyed with other metals, or combined with carbon) makes it an important strategic element with a wide range of both common and specialised applications. Concerns over adverse environmental effects of W have recently arisen and its designation as a non-toxic and environmentally benign metal is being reconsidered. Tungsten speciation and the formation of polytungstates in acid conditions may be important in ecotoxicology.

Keywords Tungsten • Ammunition • Carbide • Light bulb filaments • Metallurgy • Pellets • Polytungstates • Scheelite • Wolframite

25.1 Introduction

Tungsten (W) is a relatively rare constituent of the earth's crust, ranking 54th in the abundance of the elements on earth [10]. Tungsten is a dense, corrosion-resistant metal and has the highest melting point among metals (3,422°C). When alloyed with other metals or combined with carbon (C), it increases hardness, durability, and resistance to corrosion for the resultant alloy or compound [25]. Tungsten is therefore an important strategic element. Tungsten-based products are used in different

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applications ranging from daily household necessities to highly specialized components of modern science and technology [9]. It is used in metallurgy, abrasives, lamp filaments and cathodes, high-speed steels, textile dyes, paints, x-ray tubes, and as an industrial catalyst [25]. Recently W has been the focus of several military applications. Concerns over adverse environmental effects [15] have also led to the substitution of Pb shot ammunition (or bullets) and Pb fishing weights by W-based materials [9]. Notwithstanding, most W is used to make W carbide and W alloys for use in machine tools and drilling equipment.

The use of W is strongly influenced by general economic conditions [19]. The world's metallurgical and chemical industries annually use some 33,000 t of W [25]. World tungsten mine production is estimated at 61,000 t (2010) with an approximate value of \$150–180 t^{-1} [20]. World W resources are geographically widespread. China ranks first in the world in terms of W resources and reserves and has some of the largest deposits. Canada, Kazakhstan, Russia, and the US also have significant W resources [20]. World W supply is dominated by Chinese production and exports. China's government regulates its W industry, as it is also the world's largest W consumer [20].

Scheelite ($CaWO_4$) and wolframite ($(Fe,Mn)WO_4$) are the predominant ore minerals of W. Both occur in hard-rock deposits; wolframite is also recovered from placer deposits [25]. Tungsten is produced both from surface and from underground mining operations. Underground mines account for about 50% of the W resources in the major deposits. Tungsten is also recovered as a co-product or by-product of mining operations in deposits that are mined primarily for other metals, such as tin (Sn), Mo, Cu, Pb, Zn, or bismuth (Bi) [25].

25.2 Lithogenic Occurrence and Geochemistry

The earth's crust is estimated to contain an average W concentration of 1.3 mg kg^{-1} [9]. Tungsten is a lithophile element that occurs naturally in soils and sediments usually in small concentrations; average concentration values in the lithosphere are in the range 0.2–2.4 mg kg^{-1} [17, 22].

Tungsten is capable of forming a large number of soluble complexes with a variety of inorganic and organic ligands because it has oxidation states ranging from -2 to +6 and coordination numbers from 5 to 9 [11]. The reactions of W with water play a major role in the behaviour and mobility of this element and its compounds in the environment. A number of potential-pH equilibrium diagrams and pertinent reactions of W-water systems, under conditions of thermodynamic equilibrium at 25°C, have been generated by Pourbaix [12]. These diagrams clearly indicate the complexity of W chemistry in aqueous solutions even in the absence of complexing/precipitating agents, alloyed metallic elements or interfaces (e.g., soil particles). Because W is a base metal with a domain of stability less than that of water, under alkaline conditions it has a tendency to dissolve into WO_4^{2-}while forming non-protective oxide layers. Once W dissolves, its chemistry assumes a greater degree of complexity as the tungstate anion occurs monomerically only in alkaline or neutral solutions. When conditions are only slightly acidic, tungstates tend to polymerize to form isopolytungstates with implications for toxicity [23, 24]. Koutsospyros et al. [9] illustrate the relationship of W speciation to pH, based on several published sources. Tungstate can be considered as the principal soluble species in alkaline environments, whereas there are a number of possibilities for polymerisation in acid conditions. The situation becomes highly complex in different redox conditions and in the presence of chelating and precipitating agents, interfaces with fixed charged sites and organic compounds [9].

25.3 Chemical Behaviour in Soil and Availability to Plants

Studies on the sorption of soluble W species in different soils have demonstrated that greatest sorption occurs in peat-rich soils [3]. The presence of phosphates in solutions containing dissolved W species applied to a range of test soils has been shown to affect W sorption by acting as a competitor for adsorption sites [9]. Competitive adsorption between certain anionic species and dissolved W forms may be of significance in natural environmental systems as this may serve as a mobilisation mechanism for W [9]. There is very little information on interactions between W and DOM in soils, specifically the dissolved fulvic and humic acid fraction, as well as the conditions leading to formation of organotungsten compounds [9]. Tungsten hexacarbonyl ($W(CO)_6$) has been detected in municipal landfill gases, its formation being presumably a result of direct action of carbon monoxide present in anaerobic landfill environments on W originating from light bulb filaments or any other solid waste source [4].

Plants are known to take up and accumulate W, the extent of accumulation being apparently directly related to the W content of the soil and varying widely with the plant genotype [9]. Concentrations of up to 100 mg kg^{-1} were found in trees and shrubs in the Rocky Mountains [18], whereas normal concentrations in other plant types appear to be below 1 mg kg^{-1} [7]. Both growth enhancement and moderate toxicity to certain microbial, plant, and animal species have been associated with the presence of W [8].

25.4 Soil Contamination

The distribution and fate of W in the environment is controlled by both its physical, chemical and biological properties and the prevailing environmental conditions. Ecosystem exposures include release of W by natural processes and anthropogenic processes [9]. Natural transformation of W minerals may result in significant enrichment of environmental systems, and soluble forms of W can be released as the result of chemical transformation of the W-containing minerals [21]. Anthropogenic activities that may contribute to W mobilisation include pollution resulting from mining and industrial operations, military operations using W-containing hardware, application of W-containing fertilisers, and non-sustainable disposal of W-containing substances (e.g., disposal of light bulbs in landfills, land application of wastewater residuals) [9].

There is a lack of data on global background concentrations of W in soils and there are only a limited number of studies on a local scale. Studies in the European Union have reported W concentrations in soils (0.5–83 mg kg^{-1}) and surface soils (0.7–2.7 mg kg^{-1}) [16, 17]. In New Zealand, elevated values in agricultural soils (1.9–21.4 mg kg^{-1}) may be the results of particular farming practices [14]. Tungsten contents ($\leq$2 mg kg^{-1}) determined for agricultural soils in Iowa were in close agreement with a background concentration of 1.3 mg kg^{-1} [6]. High W concentrations have also been reported for topsoil (56 mg kg^{-1}) and deeper soil horizons (78 mg kg^{-1}) in the vicinity of mining/smelting sites in North Queensland, Australia [13]. Tungsten concentrations in the range 10–67 mg kg^{-1} have been detected in top soils collected from four random locations in Fallon, Nevada, adjacent to an abandoned W mine and a smelting location. Elevated W contents ($<$127 mg kg^{-1}) in surface soils (0–5 cm depth) have been reported in areas close to the Saudi Arabian–Kuwait border as a result of combat operations during the First Gulf War (1990–1991) compared to W content of surface soils (3.3 mg kg^{-1}) from areas 300 km away that were unaffected by discharge of W-containing munitions [9]. Other sites where potentially high W concentrations may be expected are shooting ranges using W-based ammunition. Recent approval of the use of W-based shot in ammunition used to hunt migratory birds may also be of concern. There is very little data in existence, but the US Department of the Interior estimates that environmental concentrations based on the use of W-based shot may result in soil concentrations falling in the range of 26–58 mg kg^{-1} in exposed terrestrial ecosystems, based on the current rate of Pb shot discharge [5].

25.5 Risk Assessment

Tungsten and its compounds have been traditionally considered environmentally benign [9]. A clear example is the fact that W alloy shotgun pellets have been considered as environmentally safe, non-toxic substitutes for Pb pellets [1, 2]. Despite its widespread use, the potential environmental effects of W are essentially unknown [22], and the ecotoxicological effects of W on environmental systems have not been thoroughly investigated [21]. Over the last decade the toxicological and environmental effects of W have received significant attention in relation to different research programs. In recent years, the W industry has increased its monitoring of proposed legislation and scientific research regarding the impact of W on human health and the environment [20]. Overall, studies indicate that the historical view of W as a “nontoxic” and “environmentally inert” metal must be re-evaluated and environmental regulations for W are needed [21]. Reportedly some W compounds exert adverse biological effects on humans and animals [8].

In general, the literature suggests that toxicity depends on the chemical form of the W compounds and the exposure pathway [22]. In one of these reports, W powder mixed with soils at rates higher than 1% on a mass basis caused the death of a substantial portion of the bacterial component of the soil microbial community and an increase of the fungal biomass. It also induced the death of red worms and ryegrass plants, these effects being related to soil acidification as direct biological effects of W on soil microorganisms, plants and animals could not be concluded [22]. In that experiment, an enrichment of W in the plant rhizosphere was observed, an indication that W compounds may be introduced into the food chain and suggests the possibility of development of phytoremediation-based technologies for the restoration of W contaminated sites [22].

Tungsten is now the focus of study of various regulatory, health and environmental agencies, and remains one of the least regulated metals [9]. There are no environmental regulations for W in either the USA or the EU, and ecotoxicological risk of W is being intensely debated. Recent discoveries indicate that W speciation may be important to ecotoxicology.

Polymeric W compounds emerging via self-assembly mechanisms from monomeric anions appear to be common in environmental and physiological systems that are exposed to W, and are substantially different from their monomeric constituents. Therefore it is reasonable to expect that these compounds also have different biological and toxicological properties [21]. Corrosion and dissolution of metallic W and W alloys, accompanied by a decrease of pH, facilitate W polymerization/condensation reactions. Developed polytungstates, much more toxic than monotungstates, persist in environmental systems and are therefore important for W ecotoxicology [21].

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Chapter 26
Uranium

Brian J. Alloway

Abstract Uranium (U) is a naturally radioactive element and one of its radioisotopes (^{235}U) is the basis for nuclear fission reactions in electricity generation and nuclear weapons. Uranium has both chemotoxic and radiotoxic properties and is a potential hazard to ecosystems and human health. Concentrations in rocks vary with relatively high concentrations occuring in black shales, coal, phosphorites, certain sandstones and some limestone formations and in the soils derived from them. Groundwaters associated with U-rich rocks can contain elevated concentrations of U. Soil contamination can arise from phosphate fertilisers, U mining, nuclear waste processing, nuclear explosions, coal combustion, disposal of coal ash and civil and military uses of depleted uranium (DU). Unlike iron and manganese which also have cations with more than one valency state, the highest valency U(VI) is most mobile and plant-available. High carbonate concentrations can produce soluble complexes, but reducing conditions cause the formation of insoluble ions, and U is strongly adsorbed in soils and sediments rich in iron oxides and organic matter. Plant availability is generally higher in acid conditions.

Keywords Uranium • Radioactivity • ^{235}U • ^{238}U • Depleted uranium • Munitions • Nuclear fission • Half-life • Chemotoxocity • Coal ash • Drinking water

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26.1 Introduction

Uranium (U) is a very important heavy metal because it is naturally radioactive and one of its isotopes is the basis of nuclear fission reactions used for both the generation of electricity and nuclear weapons. Its atomic number is 92, atomic mass 238 and its density is around 19.1 g cm^{-3}. It is found in significant (mg kg^{-1}) quantities in rocks and soils and occurs in economically exploitable deposits in many parts of the world. Uranium has no stable (non-radioactive) isotopes, but has two primordial isotopes (^{235}U and ^{238}U) which undergo radioactive decay to give rise to two different series of lighter elements [30, 33]. The isotope ^{235}U is particularly important because it is the only naturally occurring fissile isotope, which means that it is capable of supporting a neutron-mediated chain reaction releasing large amounts of energy. Because of this, ^{235}U is the basis of nuclear fission electricity generation (nuclear power) and of nuclear weapons and hence is the reason for U being a very valuable mineral resource. However, U has no known essential functions in plants or animals and its radioactive and chemical toxicity are potential hazards to human health and ecosystems when it occurs in soils, vegetation and waters at elevated concentrations. The ^{238}U isotope is the most abundant, comprising 99.28% of the total U in the earth's crust and has a long half life ($T_{1/2}$) of 4.51×10^9 years. Uranium-235 is much less abundant (0.72%), but has a $T_{1/2}$ of 7.13×10^8 years. Uranium-234, a decay product of ^{238}U, has a much lower abundance (0.0055%) and a $T_{1/2}$ of 2.48×10^5 years. Uranium is continually undergoing transformation as the nuclei of the atoms of its isotopes spontaneously disintegrate, or 'decay' to form more stable atoms of lighter elements [16, 31]. The radioactivity of U enables concentrations to be determined by measuring its activity concentration in Bequerels (Bq kg^{-1}) as well as by chemical analysis through dissolution and measurement by inductively coupled plasma-mass spectrometry (ICP-MS) (see Chap. 4). However, concentrations (mg kg^{-1} and μg L^{-1}) will be used in this section to allow comparison with the other (non-radioactive) heavy metal(loid)s.

Uranium-238 is primarily an α particle emitter which decays through an 18 member 'uranium' (or 'radium') series of elements ending in stable ^{206}Pb. This series also includes radium-226 (^{226}Ra) and radon-222 (^{222}Rn) which is a radioactive gas. Uranium-235 decays through 14 radioactive metals of the 'actinide' series of elements in Group 3 of the periodic table, ending with stable ^{207}Pb. The content of ^{235}U in naturally occurring U is too low for its 'nuclear' applications, so the ^{235}U content of U is normally enriched from 0.0058% to 3% for nuclear power generation and to 93% for use in nuclear weapons [16]. The process of enriching the content of ^{235}U leaves a residue with nearly three times less ^{235}U and lower radioactivity than natural U. This residue is referred to as 'depleted uranium' (DU). Both natural U and DU have a very high density (19.1 g cm^3) which is 60% greater than the density of Pb, but not as high as those of tungsten (W), gold (Au), platinum (Pt), iridium (Ir) or osmium (Os). This high density and reduced radioactivity has led to DU having several important civilian and military uses [6, 31].

Mean concentrations of U in soils in different countries are in the range 0.79–11.9 mg kg^{-1}. The mean U in the upper layers (25–40 cm) of Polish soils is

1.36 mg U kg^{-1}, but concentrations of <13.3 mg U kg^{-1} have been found in the Sudeten Mountains and Piedmont areas in Poland. In Finland, surface sediments sampled in the C-horizon of soils contained <8.5 mg U kg^{-1}, but most were in the range 1–5.5 mg kg^{-1} [12]. In Japan, agricultural soils contain 1.4–2.4 mg U kg^{-1}. Swedish agricultural soils contain 1.3–16 mg U kg^{-1} with an average of 4.4 mg U kg^{-1} [13]. It is generally considered that <10 mg U kg^{-1} is background, although this may also include some soils with slight contamination [16].

26.2 Lithogenic Occurrence and Geochemistry

The average concentration of U in the earth's crust is 2.8 mg kg^{-1}, with most rocks typically containing 1–4 mg kg^{-1}. Concentrations of <54 mg kg^{-1} have been reported for granites, but are commonly 2.2–15 mg kg^{-1} [22]. It occurs in a range of minerals including: uranium dioxide (uraninite, UO_2), pitchblende ($U_2O_5{\cdot}UO_3$) or (U_3O_8), carnotite ($K_2(UO_2)_2(VO_4)_2{\cdot}2H_2O$), tyuyamunite ($Ca(UO_2)_2(VO_4)_2{\cdot}5\text{-}8H_2O$), coffinite ($(USiO_4)_{1-x}OH_{4x}$), uranophane ($Ca(UO_2)_2Si_2O_7{\cdot}6H_2O$) and brannerite ($(U,Ca,Ce)(Ti,Fe)_2O_6$) [16]. In magmatic rocks U does not tend to replace other ions in rock forming minerals and is generally present in only low concentrations in basic igneous rocks, such as basalts often with contents of 1 mg U kg^{-1}. Instead, it accumulates in the cooling magma and occurs as discrete grains or veins of U minerals in silica-rich rocks, such as granites (>8 mg U kg^{-1}) and pegmatites which crystallise towards the end of the cooling sequence of magmas [3].

Sedimentary rocks are estimated to have an average U content of 4 mg kg^{-1}, but several different types of sedimentary rocks can be relatively enriched in U. These include black shales, phosphorites, clays, limestones and some sandstones (see Chap. 2 and Table 2.2). Uranium deposits can form in sandy sediments (which eventually form sandstones) from ions in groundwater when there is a change from oxic to reducing conditions. The highly soluble U^{6+} uranyl ions ($UO_2{}^{2+}$) are reduced to U^{4+} typically (UO_2) which precipitates between the sand grains and forms 'roll-type' deposits. Complexation by organic matter and precipitation in reducing conditions result in U accumulations in P- and organic-rich sediments such as black shales, peats and coals (Chap. 2, Sect. 2.3.1.1). Some coal strata in the Yunnan province of China have very high U contents (20–315 mg kg^{-1}) with an average of 65 mg kg^{-1} [24]. Coals in the USA generally have relatively low U contents (<20 mg kg^{-1}) with most in the range 1–4 mg kg^{-1} [28]. The ash yield of coal burnt in the USA is around 10% of the mass of the original coal. Therefore the concentration of the radioactive elements in this ash that are not lost as particles to the atmosphere during combustion will be around ten times the concentration in the original coal [10, 28]. Uranium concentrations typically range between 85 and 254 mg kg^{-1} (or 100–300 mg kg^{-1} U_3O_8) in European coal ash which is a potentially valuable secondary source of U for the future (and a possible hazard in the environment).

World production of U totalled 53,663 t U (or 63,285 t U_3O_8) in 2010, having risen from 35,574 t U in 2003 [33]. Uranium is currently mined in 20 countries, but six countries produce 85% of total mine output. Kazakhstan produces the most U (17,803 t in 2010), followed by Canada (9,783 t) and Australia (5,900 t), respectively. The U ore deposits being mined currently contain >0.1% U (1,000 mg U kg^{-1}), but certain mines have ores with <20% U. Some ores of other heavy metal (loid)s and phosphorites contain sufficient U to make its recovery economically worthwhile as a by-product. These include Cu ore at Olympic Dam mine in Australia (with 140 mg U kg^{-1}), Au-bearing ores in South Africa and P deposits in Florida, USA and Morocco. An important secondary source of U is the decommissioning of nuclear weapon warheads by the USA and Russia, which has supplied 13% of global U requirements since 2000 [33].

26.3 Chemical Behaviour in Soils and Availability to Plants

The speciation of U in soil and aqueous systems is highly dependent on the pH and redox status. Uranium (VI) species dominate in oxidising environments and their adsorption under alkaline conditions is poor because of the predominance of neutral or negatively charged species. The hydrated uranyl cation (UO_2^{2+}) is the main soluble form of U in the soil and waters. The metal–oxygen bonds in this linear molecule are very strong, making the ion unreactive. As a result of U (VI) being very soluble in water, and therefore very mobile, the risk to groundwater and potable water supplies is considerable because of both its radio- and chemical toxicity. However, concentrations of U in oxidising conditions can be limited by adsorption onto P minerals, Fe oxides, clay minerals and humic organic matter and this sorption is greatest at around neutral pH. These minerals and organic matter can act as both sinks and sources of U depending on sorption–desorption dynamics [22].

Uranium (IV) species dominate in reducing environments and tend to form strong hydrolytic complexes and sparingly soluble precipitates that control U(IV) concentrations in groundwaters. However, Pulford [16] refers to the work of Suzuki et al. [26] which shows that it might be possible for some of the UO_2 to be precipitated as nanoparticles (<2 nm) which could be transported through soil pores. If these particles reach a more oxidising environment, they could be oxidised to form soluble U (VI) (uranyl) ions which are more likely to migrate or be plant available in freely drained soils. Uranium (IV) also forms strong complexes with naturally occurring organic materials, including more soluble U (IV) organic complexes with dissolved organic compounds (DOC). The environmental factors affecting the migration (and solubility) of U include: redox status, pH, type and concentration of ligand (carbonate, fluoride, sulphate and DOC) and Fe and Al oxide content [3, 27].

In low ionic strength solutions with low U (VI) concentrations, dissolved uranyl concentrations will be controlled by cation exchange and adsorption processes. The high valency of U ions gives them a relatively high replacing power on exchange sites compared to divalent and monovalent ions of other metals. However, as the ionic strength of the solution increases, other ions such as Ca^{2+}, Mg^{2+} and K^+ will displace uranyl ions from soil exchange sites forcing them into solution. Therefore the uranyl ion is highly mobile in high ionic strength solutions. Not only will other cations dominate exchanges sites, but carbonate ions will form soluble complexes with uranyl ions, further lowering the activity of this ion and increasing the total amount of U in solution. Sorption onto Fe and Mn oxides can be a major mechanism by which U is removed from solution. These oxides act as an irreversible sink for U, which is then not fully in isotopic equilibrium with isotopes in solution. Adsorption of U onto Fe oxides and smectite clay is extensive in the absence of dissolved carbonate, but is greatly diminished when carbonate or organic matter are present [27].

Naturally occurring organic (humic) matter is a possible sink for U in soils and sediments. This probably involves ion exchange with carboxylic and other acidic functional groups on the humic material. These groups can coordinate with the uranyl ion, displacing water of hydration to form stable complexes. In sediments, OM may reduce dissolved U (VI) species to soluble U (IV) species.

Soil pH affects U (VI) sorption, firstly because it affects U speciation and secondly because it affects the number of cation exchange sites [27]. It is important to stress that unlike other metal cations with more than one valency state, such as Fe and Mn, the higher valency U (VI) species which forms the oxycation UO_2^{2+}, is the soluble form of U and the lower valency U (IV) species form insoluble compounds. This is the opposite of Fe and Mn where the lower valency ions are the soluble forms. Unlike most other metal cations, liming soils to increase the soil pH does not reduce the concentration of U in solution, nor its bioavailability, but rather increases it due to the formation of highly stable uranyl-carbonate complexes. Under acidic conditions U is present as UO_2^{2+}, under neutral conditions, hydroxide complexes such as UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5^+$ and $(UO_2)_3(OH)_7^-$ or phosphate complexes such as $UO_2HPO_4^0$ and $UO_2(HPO_4)_2^{2-}$ are found and under alkaline conditions carbonate complexes such as $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ predominate [7]. However, Ebbs et al. [7] found that treating U-contaminated soils with citric acid (which reduced the pH to 5.0) increased the mobility and bioavailability of U with accumulation by red beet (*Beta vulgaris*) increasing by a factor of 14 relative to controls at pH 6.8.

Uranium adsorption onto clay minerals is complicated and involves multiple binding sites [27]. Adsorption of U is stronger in soils with FeOx minerals or coatings on quartz grains and/or clay minerals than sandy soils dominated by quartz and feldspar minerals [27]. A higher CEC will retain more U, while carbonate increases mobility. Uranium migrates more rapidly in sandy soils than loams and this can be upwards or downwards depending on the relative balance of precipitation and evaporation [20].

Root uptake of U is via a complex pathway involving a set of redox reactions, organic complexation and microbial activity. In hydroponic experiments with ryegrass, Vandenhove et al. [29] showed that the uranyl cation and uranyl carbonate complexes together with anionic P complexes ($UO_2PO_4^-$) are probably the species most readily taken up by the roots and translocated to the shoots of ryegrass. They found soil-plant transfer coefficients varying by more than 100-fold (0.0003–0.0340), but showed that there was no significant correlation between these coefficients and U in the soil solution, with U in ammonium acetate or ammonium oxalate extracts, or with permanent soil characteristics such as soil granulometry, organic matter content or cation exchange capacity.

Research on the uptake and translocation of U in plants has shown that the activity of U in plants is limited because it tends to adsorb on cell walls. Consequently, concentrations are highest on root surfaces and are lower in shoots. Shahandeh and Hosner [19] grew plants of several species on soil spiked with 100 mg U kg^{-1}. Shoot concentrations varied between 3.2 and 24 mg kg^{-1}, but concentrations in the roots ranged from 89 to 810 mg kg^{-1} (DW). Dicot plant species generally accumulated more U than monocots (grasses and cereals) with sunflower (*Helianthus annus*) and Indian mustard (*Brassica juncea*) accumulating the most U, while wheat (*Triticum aestivum*) and ryegrass (*Lolium perenne*) accumulated the least. When sunflowers were grown on a range of soil types, uptake was greater on calcareous soils compared with acid soils (due to soluble uranyl-carbonate complexes) [3].

Sheppard and Evenden [20] reviewed literature on soil:plant concentration ratios (CRs) for a range of plant species. They found that CRs varied more than 30,000 fold. Root crops had higher CRs than fruit, cereal or leafy vegetable crops. Concentration ratios were also higher for sandy soils, peats and U mine tailings.

Microorganisms can concentrate U in their tissues up to 300 times the concentration in soils [12]. Microorganisms can also degrade soluble organic complexes of U in soils and rocks which enhances U precipitation and deposition. Fungi (such as *Aspergillus niger* and *Penicillium funiculosum*) were able to take up large amounts of U in their mycelium from rocks and this was enhanced by nutrient deficiency, high U content in the rock and low pH [3].

26.4 Soil Contamination

Soils can be contaminated with U from the mining and processing of U ores, nuclear reactor operations, leakage from wastes, accidents at nuclear sites, manufacture and testing/use of nuclear weapons, aerosol particles and fly ash from coal-burning for electricity generation, and long-term application of P fertilisers [16]. Soils contaminated from U mining and processing works in Canada were found to have <572 mg U kg^{-1} [3]. In the urban area of Port Hope in Ontario, Canada, which has U mines and related processing industry, concentrations of <258 mg U kg^{-1} were found in areas subjected to airborne deposition [3]. In the vicinity of the Blizzard U deposit in British Columbia, Canada, concentrations of <390 mg U kg^{-1} were found, but the typical range is 5–15 mg U kg^{-1} with background levels in soils in the area of 3–7 mg kg^{-1}. Concentrations in the groundwater were 18.8 μg U L^{-1} which is above the World Health Organisation's provisional limit of 15 μg U L^{-1} [3].

The high density and reduced radioactivity (60% of natural U) of DU has resulted in it having many applications. Civilian uses include counterweights in aircraft, fork lift trucks and keels of racing sailboats, radiation shielding in medical radiation therapy and industrial radiography. There are two important military uses of DU, these are in armour-piercing projectiles (used for the first time in the First Gulf War in 1991) and in defensive armour plating on military vehicles (against conventional munitions). In armour-piercing ammunition, the DU is in the form of a rod-like penetrator relying on its kinetic energy and pyrophoricity (burning on impact to create high temperatures of <1,132°C) to penetrate defensive armour. The penetrator sharpens as it melts and pierces heavy armour. These DU munitions have little use against non-armoured targets [1]. The high temperature generated on impact of the DU projectile against armour plating produces an aerosol of fine U oxide particles (10–35% of the total U) which are dispersed both inside and outside the tank. However, no nanoparticles of DU have been found in the vicinity of penetrated (destroyed) vehicles. Penetrator projectiles which fail to impact against a hard surface remain largely intact in the soil. It has been found that DU-containing penetrators buried in topsoil for 7 years had decreased in mass by approximately 25%. Hence, a DU penetrator buried in soil could possibly be completely corroded to oxides in 25–35 years after impact [2].

Investigations by UNEP in Bosnia and Herzgovina in 2002–2003 showed that local ground contamination by oxides of U could be detected <200 m from the point of impact of DU-containing munitions [2]. Concentrations of <376 mg U kg^{-1} (or 5,334 Bq kg^{-1}) were found in Kosovo and <4.5 mg U kg^{-1} (or 116 Bq kg^{-1}) in Bosnia Herzegovina [4]. Investigations in areas of intensive DU ammunition use in Kosovo showed concentrations of <18,000 mg U kg^{-1}, with many thousands of DU particles in a few mg of soil, but the radioactivity in these areas was still low (8.8–100 Bq kg^{-1})[1].

Phosphatic fertilisers are probably the most ubiquitous source of U contamination of agricultural soils. Fertilisers made from phosphorite deposits in Tanzania contain 250–570 mg U kg^{-1} and concentrations of 100–200 mg U kg^{-1} were found in fertilisers made from Moroccan phosphorites. Elevated U concentrations from fertilisers are normally confined to topsoils. Agricultural soils in Mexico had concentrations of <51 mg U kg^{-1} compared with 1 mg U kg^{-1} in non-agricultural soils [16]. The U in P fertilisers has a distinct $^{234}U:^{238}U$ activity ratio (AR) which is inherited from the phosporite rock that the fertiliser was made from. Use of this ratio enables U from P fertiliser to be distinguished from native U in soils, organic matter and waters [34, 35]. In Florida, P fertilisers have been found to contain <182 mg U kg^{-1} and P nutritional supplements derived from phosphorite rock fed to cattle can contain <203 mg U kg^{-1}. Much of this is excreted in the faeces and can be a significant source of U contamination of pastures or arable soils treated with manures [23].

Rothbaum et al. [17] determined the amount of U applied to arable and grassland soils in field experiments at Rothamsted Experimental Station in England and at a site in New Zealand. Application of superphosphate fertiliser gave annual inputs of 33 kg P and 15 g U ha^{-1} $year^{-1}$ in three experiments at Rothamsted and 37 kg P and 16 g U ha^{-1} $year^{-1}$ in one experiment in New Zealand. Most of the U applied annually since 1889 at Rothamsted (total = 1.3 kg U ha^{-1}) was retained in the plough layer of arable soils and in the organic matter in the grassland topsoil and little evidence of movement down the profile to the subsoil was detected [8].

Uptake of U by plants is of interest both from the human and animal health point of view, but also with regard to biogeochemical prospecting for possible new economic deposits of U. Soluble fractions of U appear to be readily taken up by plants. In areas of U mineralisation, plants accumulated 100 times more U than those in other areas [12]. Preliminary studies on vegetation near the site of a proposed new U mine in Jharkhand State, in north east India, showed elevated concentrations of U in several plant species, including *Hydrographis peniculata,* a herbaceous plant in the family *Acanthaceae,* native to India and Sri Lanka; *Cyperus rotundus* (coco-grass, purple nut sedge, red nut sedge), a species of sedge and a member of the family Cyperaceae, and *Nymphea* species (tropical lilies). Uranium concentrations were highest in roots (539–7,972 μg U kg^{-1} FW) with a geometric mean of 1,438 μg U kg^{-1} FW. Uranium was accumulated by roots to a greater extent than other radionuclides, the order was: U (natural) $>$ polonium-210 (^{210}Po) $>$ radium-226 (^{226}Ra) $>$ thorium (Th). The U concentrations in shoots ranged from 8.5 to 78 μg U kg^{-1} FW with a geometric mean of 27.2 μg U kg^{-1}. The pattern of shoot uptake differed from that in the roots with U concentrations being the lowest: ^{210}Po $>$ ^{226}Ra $>$ Th (α) $>$ U(nat) [11].

Phytoremediation of U contaminated soils has been widely investigated. A study by Ebbs et al. [7] showed that treatment of a U-contaminated soil with citric acid reduced the soil pH to 5.0 and increased U accumulation in red beet (*Beta vulgaris*) by a factor of 14 and could provide the basis of an effective phytoremediation strategy for U-contaminated soils. Chang et al. [5] investigated the use of citric acid to enhance the uptake of U by four different plant species. Indian mustard (*Brassica juncea*) was found to have the most enhanced accumulation of U ($<$2,000 mg U kg^{-1}) and the greatest enhanced root accumulation ($<$3,500 mg U kg^{-1}) was found in canola (also called oil seed rape, *Brassica napus* var *napus*). The U was probably taken up into the plants as U-citrate complexes and accumulation followed the order: roots $>$ shoots $=$ leaves. Indian mustard was considered to have the greatest potential for the phytoremediation of U-contaminated soil, but there is a possibility that the citric acid treatment may also accelerate migration of U down the soil profile. However, there are also some research findings which suggest that citric acid may degrade rapidly in soils and not cause serious contamination of groundwater.

26.5 Risk Assessment

Uranium compounds can cause both chemical toxicity (chemotoxicity) and radiation toxicity (radiotoxicity). Radiotoxicity is due to the radiation emitted by U incorporated into an organism's body (internal dose) together with that emitted by U adjacent to the organism (external dose). Due to the long half lives of U isotopes and their slow rate of decay, their radiotoxicity is expected to be relatively low and it is probably chemotoxicity which is the greater hazard to human health caused by U [3]. It is considered that the major health risks from U are kidney disease from drinking water and lung disease from inhaled fine particles. Radon-222, a radioactive gas and decay product of ^{238}U, is often found in areas underlain with rocks containing significant concentrations of U, such as granites and shales. It is an additional possible health hazard affecting the lungs and is closely associated with aerosols of U isotopes [3].

For plants and other soil organisms, it is widely considered that the chemical toxicity of U is a greater risk than radiotoxicity. Pulford [16] refers to work by Sheppard et al. [21] who reviewed the literature on the ecotoxicity of U and put forward predicted no effect concentrations (PNECs) of 250 mg U kg^{-1} (dry soil) for terrestrial plants, 100 mg U kg^{-1} for other soil organisms and 0.1 mg U kg^{-1} body weight day^{-1} for soil mammals. Soil quality guidelines for the protection of both human health and ecosystems published by the Canadian Council of Ministers of the Environment [3] in 2007 are: 23 mg U kg^{-1} for agricultural land, 23 mg U kg^{-1} for residential and parkland, 33 mg U kg^{-1} for commercial use and 300 mg kg^{-1} for industrial uses. The UK Environment Agency [9] gives a soil guideline (radioactivity) value of 4 Bq kg^{-1} for natural U in residential land with home-grown produce.

26.5.1 Depleted Uranium

In humans, DU is not a significant health hazard unless it is taken into the body by inhalation, ingested in food or drink or as fragments of DU munitions in wounds. American forces used more than 300 t of DU in the First Gulf War (1991). Some experts attribute ‘Gulf War Syndrome’, the unexplained illness amongst soldiers reported after this war, at least in part to exposure to DU. There have been calls for more rigorous testing of Gulf War veterans to determine whether they were exposed to DU [6]. A large part (50–96%) of the aerosol generated on impact of a DU penetrator comprises respirable particles that could enter the lower respiratory tract and would not be expelled [6]. A larger proportion of the aerosol is dispersed inside the target vehicle than in the external environment [1]. Inhalation of fine particles of U or DU and/or drinking water containing soluble forms of U are probably the highest risks to human health from either radiotoxicity or chemotoxicity of U. Anybody entering military vehicles which have been attacked with DU-containing munitions is at highest risk of adverse health effects. With regard to effects on terrestrial ecosystems, DU was found to have an inhibitory effect on soil microbial processes in experiments in which relatively insoluble schoepite ($UO_2(OH)_2 \cdot H_2O$) from deployed DU-containing munitions was finely ground and mixed with soil. Uranium concentrations of 500 mg kg^{-1} caused a decrease in soil respiration rates. At 25,000 mg U kg^{-1}, decomposition processes were inhibited. Uranyl sulphate inhibited the action of *Thiobacillus ferrooxidans* in aqueous culture at concentrations as low as 0.4 mM (95 mg L^{-1}) [3].

The EU Scientific Committee on Health and Environmental Risks [18] concluded that except in areas very close to destroyed vehicles and penetrators, DU contamination in the war zones is not widespread and is generally low. Possible risks for terrestrial and aquatic ecosystems were considered to be very low.

26.5.2 Uranium in Groundwater and Drinking Water

The range of concentrations of U in groundwaters reported from around the world is <8,000 μg U L^{-1} with higher concentrations generally occurring in areas with significant U mineralization and/or U-rich granitic terrains such as western USA and Scandinavia [22]. A survey of 101 groundwater samples from all over England and Wales showed a range of U concentrations from <0.02 to 48 μg L^{-1} (median 0.39 μg L^{-1}). The majority of these were below the WHO provisional guideline value of 15 μg U L^{-1} [22]. A larger database of 1,556 groundwater samples surveyed earlier from the whole of Great Britain showed a slightly wider range of <0.01–67 μg U L^{-1}, but a lower median value (0.29 μg U L^{-1}). Eleven samples (0.71%) exceeded the WHO provisional guideline value (15 μg U L^{-1}) and seven samples (0.45%) exceeded the Canadian standard of 20 μg U L^{-1} and just three samples exceeded the US EPA maximum tolerable contaminant level of 30 μg U L^{-1}. The highest U concentrations were in groundwater samples from red sandstone beds where the U is desorbed from Fe oxide cements and coatings on sand grains [22]. A survey of U in groundwater in the Kolar district of South India found <1,443 μg U L^{-1} with nearly 22% exceeding the previous WHO standard of 30 μg U L^{-1} [25]. Groundwaters often have higher concentrations of U than surface waters because of the large solid:solution ratios in aquifers and the greater influence of water- rock reactions.

Clinical studies of 324 people in Nova Scotia, Canada, who were exposed to varying amounts of U in drinking water (<700 μg U L^{-1}) from private wells did not find any relationship between renal disease and exposure to U. However, there was a trend towards increasing excretion of urinary β-2-microglobulin with increasing U concentration in well water which could be an indicator of subclinical toxicity. The study concluded that a guideline value of 15 μg U L^{-1} was supported by the epidemiological data. In the case of chemical toxicity from U, nephritis is the primary chemically induced effect on the health of humans [32].

A study in Finland of 95 men and 98 women who had consumed drinking water with high concentrations of U from wells for an average of 16 years showed no evidence of renal damage. The median U concentration in drinking water was 25 μg L^{-1}(<1,500 μg L^{-1}) [14]. Some bottled spring waters can contain significant concentrations of U. Smedley et al. [22] reported concentrations of <0.01–13 μg U L^{-1} in bottled waters, but these are still below the provisional standard of 15 μg L^{-1} [22].

Finally, with regard to human risk assessment, it is important to recognise that coal combustion, mainly in coal-fired electricity generating stations, is a significant source of naturally radioactive elements, such as U and Th. The particles emitted in the exhausts from this combustion are more efficiently trapped in filters nowadays, but in the past large quantities were dispersed far and wide into the environment and will have accumulated in topsoils (especially organic-rich soils and peats) and sediments. Even more significant are the large tonnages of fly ash from coal combustion that have to be disposed of. The radioactive materials in this ash (as well as the exhaust particles captured by filters) contain fissionable materials which are both a potential resource for the future, if the technology can be developed to separate them, and also a growing possible health and environmental hazard. Thirty three years ago many people were shocked to read an article in the journal ‘Science’ (December 8, 1978) by McBride et al. of the Oak Ridge National Laboratory, which stated that “Americans living near coal-fired electricity generating plants are exposed to higher doses of radiation than those living near to nuclear power plants that meet government regulations.”[15].

26.5.3 Thorium

Apart from U, the only other naturally occurring radioactive heavy metallic element which is relatively abundant in the environment is thorium (Th). Its atomic number is 90, its atomic mass 232 and density is 11.72 g cm^{-3}. Both U and Th are similar in that they exist in (IV) and (VI) valency forms. Hydrated uranyl cations (UO_2^{2+}) and Th^{4+} are responsible for the solubility of these metals in soils over a wide range of pH. However, uranyl cations are more soluble than Th^{4+} and therefore U tends to be leached out of soils to a greater extent [12]. Thorium is around three times more abundant in rocks and soils than U. Natural Th is not fissile and so cannot be used as a nuclear fuel for power generation. However, it could be transformed in a breeder reactor to ^{233}U which is fissile [34]. Regrettably, space does not permit a discussion of Th or other radioactive elements in soils and the environment.

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Chapter 27
Vanadium

Paula Madejón

Abstract Vanadium (V) is widely distributed in nature, and has oxidation states of II, III, IV or V. The content of this element in soil depends upon the parent material. Combustion of coals and oils represents the major source of V enrichment of the biosphere. The most important minerals of V are Vanadite and Roscoelite. Trace concentrations of V have been reported to benefit plant growth, while higher concentrations are toxic. Pentavalent compounds are the most toxic and the toxicity of V compounds usually increases as the valence increases.

Keywords Vanadium • Air pollution • Catalyst • Coal • Fossil fuel • Vanadinite • Phosphate • Steel

27.1 Introduction

Vanadium (V) is a lithophilic element, widely distributed in nature with a mean content in the earth's crust of 110 mg kg^{-1} (ranking 20th in abundance) [38], although other authors report an average of 150 mg kg^{-1} [60] and some reported an abundance of 98–230 mg kg^{-1} [42].

Vanadium compounds in nature have oxidation states of II, III, IV, or V. Its oxidation state is variable, but under weathering conditions it is mainly V^{5+}. In the oxidized state, V^{5+} shows isomorphic relation to other cations such as As^{5+} and Mo^{5+} [26] whereas V^{3+} has similar ionic radius to Fe^{3+}, and may replace it in Fe minerals.

The V content of a soil depends upon the parent material and the pedogenic processes associated with its development. Bowen [9] indicated a range of 3–500 mg kg^{-1} (mean 90 mg kg^{-1}). Mitchell [32] reported V levels of 20–250 from

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a range of Scottish soils. Studies in Poland indicate a mean value of 18.4 mg kg^{-1}, with higher levels in silt and loamy soils and lower levels in sandy soils [16]. The reference soils of the USA contain V in the range of 36–150 mg kg^{-1} [21]. The median V content in agricultural soils of Japan is 180 mg kg^{-1} [48]. In China, the geometric mean value for V is 77 mg kg^{-1} [11]. Medians for background values for German soils on different parent materials are between 10 and 70 mg kg^{-1} [51].

Vanadium is ubiquitous in the lithosphere and is widely distributed in nature and the prevalence of V exceeds that of metals as Cu and Pb [36], and equals that of Zn and Sn [10]. Therefore its potential to enter the food chain is significant.

Combustion of coals and oils represents the major source of V enrichment of the biosphere. Vanadium is the major trace metal in petroleum products, especially in the heavier fractions. This is enhanced because many fossil fuels contain V, particularly coal (at concentrations of between 19 and 126 mg kg^{-1} in ash) and crude oil (at concentrations of between 3 and 257 mg kg^{-1}) [36]. It causes undesirable side effects in the refining process and corrosion in oil-fired power plants. Consequently, it is the most widely determined metal in petroleum and its derivatives [1]. Another input of V into the environment is its use in steel production. Vanadium steel which contains from 0.1% V to 3% V is tough, strong and heat resistant [2]. Another important use of V is a catalyst in a variety of reactions. Vanadium pentoxide put on an inert support material is the principal catalyst used in the oxidation of SO_2 to SO_3 in the production of sulphuric acid. The disposal of spent catalysts could also be a point source for contamination of the biosphere and food with V [2].

Vanadium is considered as the marker element of air pollution emitted from the combustion of fossil fuels, particularly residual fuel oils, which constitute the single largest overall release of V to the atmosphere [17, 55]. Because of industrial activities and anthropogenic emissions, V concentrations in soil have increased significantly in recent years, and the number of people affected by V pollution has also increased [33]. According to Hope [25] current V emissions from industrial activities were estimated to comprise ~30% of total atmospheric loading, ~3% of total ocean loading, and ~ 6% of total land loading. These loadings were always considerably less than those resulting from non-anthropogenic sources or events. However, differences between the pre-industrial and current mass and fluxes were not sufficiently great to suggest that injection of anthropogenic V constitutes a significant environmental threat on a global scale.

27.2 Lithogenic Occurrence and Geochemistry

Vanadium exists as a sulphide or in the oxidized form. In igneous rocks, V is largely associated with basic magmas, especially titaniferous magnetites, and may be present in elevated concentrations. In acidic and silicic igneous rocks, the V content is much lower [3].

Of the 60 known V minerals, the most important are: vanadinite, $Pb_5Cl(VO_4)_3$; roscoelite; $KV_2(OH)_2(AlSi_3O_{10})$; mottramite, $Pb(Cu,Zn)(VO_4)(OH)$; and patronite, of variable composition: V_2, V_2S_5. Vanadium can form variable compounds (V oxysalts) of which $(VO_4)^{3-}$ plays a significant role due to adsorptive properties. These minerals have complex compositions, like e.g., carnolite, $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$ [26].

27.3 Chemical Behaviour in Soil and Availability to Plants

The proportion of "extractable" V in a soil is linked to extractant, soil type and drainage. Berrow and Mitchell [7] found the "extractable" V content of a range of Scottish soils to be 0.03–26.0 mg kg^{-1} depending on the degree of drainage of the soil, and the type of the extractant used. EDTA was a more efficient extractant (removing more) than acetic acid, indicative of an organic bound V fraction. Gäbler et al. [20] quantified V adsorption by German soils. The *aqua regia*-extractable (or pseudototal) contents were between 1.7 and 143 mg kg^{-1} (median 32 mg kg^{-1}). The EDTA-extractable V of these soils was between 0.06 and 9 mg kg^{-1}, this is between 0.2% and 35.0% of the *aqua regia* soluble V.

The distribution of V in younger soils, such as Mollisols, closely follows the distribution of Fe, and more importantly, secondary Fe oxides [50]. It is not clear whether V, when in the presence of Fe oxides, is removed from the aqueous phase as a precipitate, such as $Fe(VO_3)_2$, or absorbed onto the surfaces of Fe oxides [40]. Vanadium can be mobilized by soluble soil organic matter under both aerobic and anaerobic conditions [8]. Martin and Kaplan [30] examined the movement of V through the soil profile, in a field experiment using dissolved salts, during 30 months. The main results showed that extractable V concentrations decreased during the first 18 months of treatment. These authors conclude that the presence of Al and Fe oxides and small amounts of clay minerals and organic matter in this highly weathered, low cation exchange soil were probably responsible for the V retention. Cheshire et al. [12] showed an association of V with humic and fulvic acid fractions of a soil, and compared this with other metals. This percentage of total metals in a soil extracted by alkali (i.e. humic and fulvic acid fractions) decreased in the order: $Cu > Al > V > Ni = Co > Mn > Cr > Fe > Sr > Ba$. These authors also showed an uneven distribution of V between humic and fulvic acid fractions, more associated with the later.

Połedniok and Buhl [39] studied the speciation of V in two different soils in Poland. The V content in the individual fractions of both soils depended on the region (except exchangeable and carbonate fractions) and the total V concentration. The highest V contents were found in the soil with higher organic matter, above 40% of the total concentration of V. These authors concluded that the organic fraction constitutes an important source of the potentially available V and it does not form compounds with carbonates. The content of V found in the exchangeable fraction was similar in all studied soils, indicating a constant amount of V accessible for plants, which does not depend on the total concentration of this element in soil [39].

Yanguo et al. [59], studied the chemical speciation of V in a mining-polluted soil and found that it followed the order of: acid soluble $<$ reducible ~ oxidisable $<$ residual. Acid-soluble V accounted for 0.30–1.85%; reducible vanadium, 3.46–8.18%; oxidisable V, 3.36–8.32%; and residual V, 83.37–92.78%, being the dominant fraction. These authors also studied the V adsorption in different types of soils. They found that the amount of absorption of this element followed the increasing order of: loam $>$ light loam $>$ silt loam $>$ sandy soil. Pentavalent V was dominant in these soils. Contents of V in food plants vary widely, from 10 to 700 μg kg^{-1} and do not show a clear regularity in their distribution among plant species and plant organs[26]. Anke [2] found the maximum content of V in several winter species, especially in heather and oak twigs ($<$3,000 μg kg^{-1}). Mosses collected in Norway contained V in a range of $<$0.01–16 mg kg^{-1}, with an average value of 2.8 mg kg^{-1} [6].

The evidence that V is essential for the growth of higher plants is, however, not yet conclusively demonstrated. Trace concentrations of V have been reported to benefit plant growth, while higher concentrations are toxic [43]. Positive evidence has been obtained that if V is essential for lettuce and tomato plants, an adequate tissue level would be $<$2 μg kg^{-1} in dry matter [57]. Other biological effects of V have been observed. Vanadium caused drastic inhibition of chlorophyll biosynthesis, soluble protein and net photosynthesis of seedlings of rice (*Oryza sativa* L.) [47] and decreased Ca absorption by sorghum root tips [58].

There is evidence that V deposited from the atmosphere, or from industrial waste-water appears to be a powerful inhibitor to soil-enzyme activities, even if it is in only trace amounts. This inhibition eventually reduces the mineralization processes that release plant nutrients [5]. Pentavalent compounds are the most toxic and the toxicity of V compounds usually increases as the valency increases [4, 49, 53]. Vanadate, bearing a structural similarity to phosphate, may be taken up by phosphate uptake systems and is a known inhibitor of ATPases [28, 41]. In addition to toxicity, there are a few examples of the physiological role of vanadate like vanadate-dependent nitrogenase in *Azotobacter chroococcum* for nitrogen fixation in absence of molybdate in the environment [15, 45].

Vanadium tends to be accumulated in roots and causes a decrease in the capacity for phosphate uptake by maize roots [44] and inhibited the growth of onion roots [23]. Welch [56] studied the uptake of V by excised barley roots from labelled V solution, and concluded that V is passively absorbed by barley roots. Welch [57] found that the uptake was a linear function of V concentration and highly pH-dependent. At pH 4, the uptake of V was highest, but dropped to a very low level at pH 10. It was relatively constant between the pH levels of 5 and 8. There was no large inhibition of V uptake by roots by the other anions, such as MoO_4^{2-}, BO_3^-; Cl^-, SeO_3^{2-}, $CrO_3^{2-}$and NO_3^-. Wallace et al. [54] found that bush beans absorbed V from culture solution by as much as 13, 8, and 88 mg V kg^{-1} (dry weight) in leaf, stem and root, respectively, and that this resulted in reduced growth, but not chlorosis.

Studies on V toxicity in whole plants [27] showed that soil type exerts a considerable influence over plant response. These different responses could be attributed to reduce plant-available V, as a result of interactions with soil constituents.

Similar results were found by Wang and Liu [55] who studied the effects of V on the growth of soybean seedlings and they were dependent on the soil type. In a fluvo-aquic soil, the concentration of V added in soil was more than 30 mg V kg^{-1} soil, and the dry matter yields of shoots and roots were significantly decreased. However, no marked stunting was observed in an Oxisol; even when V added to the soil was 75 mg V kg^{-1}. These results are related with the fact that at pH 5–9 the Oxisol had a higher adsorption capacity than the fluvo-aquic soil. Furukawa et al. [19] suggested that the inhibition of water uptake is mainly caused by the V already moved to the above-ground part of the plant.

27.4 Soil Contamination

Data relating to field episodes of V pollution are not common. Vaccarino et al. [52] reported instances of leaf and fruit necrosis associated with V-rich ash from an oil-burning plant. Panichev et al. [37] studied the distribution of V (V) species between soil and plants around a V mine in South Africa. The concentration of V (V) species were found in the range 620–1,680 mg kg^{-1} in soil and 4–6 mg kg^{-1} in grass samples. Total amounts of V in soils ranged from 1,570–3,600 mg kg^{-1} and from 8–13 mg kg^{-1} in grasses. These results indicate that a considerable amount of V (about 50%) in soils and plants is present as V (V) species.

27.5 Risk Assessment

Vanadium is an essential trace element for living organisms, but it is harmful to human beings, animals and plants in excessive doses [14, 33]. Its toxicity depends on the physicochemical state of the metal, in particular the valence state and solubility; where an increase in valence state corresponds with an increase in toxicity [13]. The United States of America's Environmental Protection Agency (EPA) has not listed V as a pollutant requiring urgent research and legislation, because "there is no evidence that the general population is at risk, either through deficiency of, or overexposure to vanadium" [18]. However, there are few countries, where standards and regulations for environmental pollution in soil with V are accepted, for example, Russia, where the maximum of 150 mg kg^{-1} is allowed in agricultural soil [37].

Hindy et al. [24] studied levels of V in air, water, soil and plants resulting from the operation of a cement factory in south Cairo. Results were compared with the level of V in a relatively non-polluted residential area. It was concluded that the cement factory was the main source of the element to the adjacent environment. Soldi et al. [46] studied the distribution of V in soil and groundwaters to evaluate the environmental pollution to fossil combustion and oil refinery. The superficial values of V in soils were 65–70 mg kg^{-1} and they found a regular V decrease with depth. These studies concluded with there was no significant contribution from the fallout emitted by the refinery. Mandiwana and Panichev [29] have studied that the presence of atmospheric CO_2 and ammonia (NH_3) enhances the leaching of V from soil thereby making it bioavailable to both plants and animals.

A case of acute cattle poisoning which had happened around a V mine in South Africa some time ago [31] could be connected with ingestion of V from the surface of grass, although as the amount of V (V) in grass itself (about 11 mg kg^{-1}) was not enough to poison the cattle in 48 h.

Nadal et al. [34] studied the levels of V found in soil and vegetation samples collected near a chemical/petrochemical industrial zone of an area in Catalonia, Spain. Vanadium was the only element showing a similar tendency in soil and plants, increases of 54.4% and 100% in soils and herbage (1998–2003). Nadal et al. [35] in another study in the same area found that concentration of V in the petrochemical area was notably higher (34 mg kg^{-1}) than those observed in other areas under study (15.4 mg kg^{-1}). As for soils, higher levels of V were found in vegetation of the industrial areas, being statistically significant near the oil refinery (0.75 mg kg^{-1}) with respect to the blank site levels.

Gummow et al. [22] studied the effect of cattle exposed to V. The mean exposure was 0.55–2.33 mg V /kg body weight/day. These authors also studied V concentration in the milk of cattle over 5 years (mean was 0.23 mg V kg^{-1}) and concluded from current knowledge of toxicity in humans that the tissue and milk residues from cattle should pose no health risk to the consumer.

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Glossary of Specialized Terms

Absorption Movement of metal ions and complexes into voids in soil solid phases and into plant roots

Actinomycetes Rod-shaped or filamentous bacteria of the order Actinomycetales, which are found in soil and are often pathogenic

Adipogenesis Development of fat cells

Adsorption Retention of ions on solid surfaces in the soil by a combination of mechanisms of ion exchange, specific adsorption, precipitation and organic complexation (also referred to as ‘sorption’). Desorption is the release of ions from the various retention mechanisms

Aeolian deposits Particles of fine sand transported by the wind and deposited at distance from the source (also called loess)

Agroforestry An integrated approach of using the interactive benefits from combining trees and shrubs with crops and/or livestock

Alkali disease Selenium poisoning disease in grazing livestock following ingestion of selenium accumulator plants

Allophane An amorphous clay mineral formed by weathering of volcanic glass

Aluminol group Al-OH on mineral surfaces

Ambient background Natural background concentration plus diffuse anthropogenic inputs

Andesite Volcanic rock with intermediate SiO_2 concentration and containing abundant plagioclase feldspar

Anti-ischemic protection Protection against permanent tissue damage caused by ischaemia, especially inside the ‘grey zone’ surrounding more severely affected areas, e.g., during brain stroke or myocardial infarction

Anti-knocking agents Octane boosting compounds (e.g., tetraethyl and tetramethyl Pb) in petrol which prevent pre-ignition which causes damaging engine knocking or ‘pinking’

Antinutrients Compounds which reduce the bioavailability of nutrients (e.g. phytates) in animals/humans

B.J. Alloway (ed.), *Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability*, Environmental Pollution 22, DOI 10.1007/978-94-007-4470-7,

Aqua regia Mixture of concentrated nitric and hydrochloric acids used for the digestion of soil samples to provide “pseudo-total” concentrations of elements (c.f. “true” total analysis with HNO_3, $HClO_4$ and HF acids – Chap. 4)

Arable land Land which is cultivated for crops

Archaea One of the three domains in which all cellular life forms can be grouped, the other being bacteria and eukaryotes. Similar to bacteria in having no nucleus, but biochemically different from them with different ribosomal RNA and different lipids in their plasma membrane

Arrhythmia Pathological changes in the electric activity of the heart causing abnormal disturbance of the heart rhythm

Articular cartilage Cartilage found in joints, which helps to reduce friction

Atherogenic Causing atheroma, *i.e.* cholesterol deposition in vascular walls

β-2-Microglobulin Is a protein which shows an increase in concentration in the blood when there is an increase in either the production or destruction of white blood cells increases. This increase is seen in people with cancers involving white blood cells

Basalt A common extrusive volcanic rock, dark in colour, which contains a high proportion of ferromagnesian minerals, such as olivine and augite which tend to weather relatively rapidly and release a wide range of trace elements as well as Fe and Mg

Bi-nuclear Bonded through two separate ligand sites

Bioaccessibility The potential for a substance to be absorbed by an organism

Biofortification Enhancing the concentration of a nutrient element in crops to increase their nutritional value

Biosolids Solid and semi-solid material in the residue from wastewater treatment, also called ‘sewage sludge’

Biselenite $HSeO_3^-$

Blind staggers A selenium poisoning disease in grazing livestock following ingestion of selenium accumulator plants

Brownfield sites Abandoned industrial or commercially used land which is vacant for redevelopment (which can be hindered by the presence of potentially hazardous materials)

Boulder clay An unstratified mixture of sand, clay, gravel and boulders deposited by a glacier (also called ‘till’)

C3 plants Plants with a basic photosynthesis mechanism which fixes CO_2 in only one stage e.g., wheat, rice, and soya beans

C4 plants Plants which fix CO_2 in two stages and increase its concentrations in their leaves above ambient concentrations, e.g., maize, sugar cane and sorghum

Calcareous soils Soils containing $>30\%$ $CaCO_3$ from either parent material or precipitation from groundwater

Cardiomyocytes Muscle cells in the heart

Case control studies A type of epidemiological study design in which people with a disease are matched with people who don’t have the disease (the ‘controls’) for variables (*e.g.* age, sex) other than those under investigation

Catecholamines Term used in a physiological or pharmacological context as a common designation only for adrenaline and noradrenaline because of their similar physiological actions

Chalcophile Term used by Goldschmidt for sulphur-seeking (literally copper-seeking) elements

Chalcophile metals Metals such as Pb, Hg, Cd, Ag that form sulphide minerals

Chelate Complex containing two or more separate bonds between a polydentate ligand and a single central atom

Chlorosis Pale green or yellow areas on plant leaves caused by a failure to produce chlorophyll

Chondrocytes The only cell type found in cartilage

Codon A sequence of three nucleotides that specifies one particular amino acid to be inserted into the growing polypeptide chain during translation

Cohort studies A form of longitudinal observational study, where age cohorts (groups of people with the same age) are followed over an extended period of time to study how various factors affects their survival or risk of getting particular diseases

Contamination Used interchangeably with ‘pollution’ but convention to use contamination in relation to land and soil (See pollution definition)

Clay loam Soil composed of sand, silt, and clay in relatively even concentration (about 40-40-20% concentration respectively)

Cretaceous The final period of the Mesozoic era when angiosperm (plants) appeared and ended after 65 Ma with dinosaurs becoming extinct

Critical load (CL) “The highest total input rate of a potential pollutant below which significant harmful effects on defined receptors (e.g. human health, ecosystem structure and function) will not occur in a long-term perspective (at steady state), according to current knowledge” (Chap. 8)

Cultivar (cv) Cultivated variety of a crop plant

Cut-off grade The metal(loid) content of an ore below which it is not commercially worthwhile mining

Cytotoxic Term used about drugs that can kill tumour cells and therefore are used for treatment of cancer

Diapir Non-igneous intrusion where a solid, but plastically deformable rock (*e.g.* rock salt) because of buoyancy forces rises into and displaces overlying rocks of higher density

Dimethylselenide $Se(CH_3)_2$, volatile compound formed by various types of living organisms

e-Value Radiolabile metal in soil, i.e., amount of metal in soil that has the same fate as a soluble metal salt after 24 h equilibration in the soil

Epicontinental sea A shallow sea that extends over an area with continental crust, *e.g.* the North Sea

Epidemiological studies Study of health-event patterns in a society – helps to identify risk factors for disease, its prophylaxis and treatment of established cases

Epiphyseal cartilage Cartilage in thin plates forming growth zones in the bones of children

Eukaryotes Organisms with a cell nucleus

Evaporite Sedimentary rock composed mainly of evaporite minerals (e.g., halite NaCl) formed either from seawater or saline inland lakes

Felsic Rocks with a high content of silica and feldspar minerals (acid igneous rocks)

Ferralsols (oxisols) Heavily weathered tropical soils in which primary minerals have all been weathered and Fe and Al oxides predominate

Ferredoxin Iron-sulphur protein in plants that mediates electron transfer during photosynthesis; term is also used for similar proteins in animals

Flavoprotein Proteins that contain a nucleotide derivative of riboflavin: the flavin adenine dinucleotide (FAD) or flavin mononucleotide (FMN)

Fulvic acid (FA) A yellow to yellow-brown humic substance that is soluble in water under all pH conditions

Galvanising Adding a zinc coating to iron or steel to reduce corrosion (rusting)

Gangue minerals Commercially worthless minerals that accompany valuable ore minerals, but may become economic to exploit if the prices of metal(loid) s contained in them rise)

Genotoxicity Damage to DNA, possibly leading to the development of a tumour

Gleying/gleyed soils Imperfectly drained soils that have reducing conditions for part of the year (variable valency elements such as Fe and Mn are in lower valency state, e.g., Fe^{2+} and Mn^{2+})

Global anoxia Lack of oxygen in the entire organism

Gossan Rust-coloured Fe and Mn hydroxide minerals found capping some ore deposits, formed from the weathering of sulphide minerals. Can be useful indicators of the presence of an ore body in mineral prospecting

Granite The most abundant type of deep-seated igneous rock in the Earth's continental crust. SiO_2-rich; contains plagioclase feldspar, potash feldspar and quartz plus small quantities of dark minerals e.g., biotite

Guano Sea bird excreta

Gypsum Mineral with composition $CaSO_4 \cdot 2H_2O$, moderately soluble

Half life ($T_{1/2}$) The half life of an isotope is the length of time it takes for one half of the atoms to disintegrate and is characteristic of each radioactive isotope (e.g., ^{238}U half life is 4.51×10^9 year)

HIV proviral gene DNA copy of the HIV viral genome (composed of RNA) that has been inserted into one of the chromosomes of a virally infected cell

Humic substances Major organic constituents of soil (humic and fulvic acids) formed by bacterial degradation of plant tissues, especially lignin

Hydroperoxides Organic compounds with formula ROOH

Hypoxia A condition in which the body as a whole (generalized hypoxia) or a part of it (tissue hypoxia) is deprived of adequate oxygen supply

Igneous rock Rocks formed from the cooling and crystallization of magma (molten rock)

Immunosuppression Inhibition of immunological functions

Inner-sphere Metal-ligand linkage with no intervening water molecules

Ischemia Severe restriction in blood supply resulting in oxygen deficiency in affected downstream tissue area. Will often lead to cell death by necrosis

Ischemic heart disease Disease characterized by severely reduced blood supply to the heart muscle, leading to lack of oxygen-called angina pectoris (if reversible) and myocardial infarction and causes permanent tissue damage

Isomorphous substitution Replacement of an ion in a crystal without altering the structure, depends on ionic radius and charge

Itai-itai disease Bone deformations in humans due to cadmium-induced decalcification

Kashin-Beck disease Disease partly caused by selenium deficiency that affects children, causes degeneration of articular and epiphyseal cartilage and leads to severe and crippling growth disturbances

Keshan disease A congestive cardiomyopathy caused by dietary deficiency of selenium, named after Keshan County of Heilongjiang province, China, where symptoms were first noted. Affects mainly children and women of child-bearing age

Labile Chemically reactive ions or complexes

Laterite Subsoil layer rich in Fe and Al oxides and kaolinite formed under extreme tropical weathering conditions causing desilication of parent material. Occur at the surface when the overlying soil has been eroded

Lipophilic Having an affinity for lipids (fats)

Lithophile elements Associated with silicon (cf. siderophile – associated with iron; chalcophile – associated with sulphur) (Goldschmidt classification)

Mafic Rocks with a high content of ferromagnesian minerals (basic igneous rocks rich in Fe and Mg)

Marine transgression Rise of sea level relative to the continents, resulting in partial flooding of the latter and expansion of shallow epicontinental seas, like the North Sea today

Meta-analysis A study (often a statistical one) that compares and combines the results of several earlier studies that address a set of related research hypotheses

Michaelis constant Parameter describing the affinity of an enzyme to the substrate, i.e. substrate concentration at which uptake rate is half of the value at saturation

Mono-dentate Bonded through one linkage to a single ligand group

Mono-nuclear Bonded to a single ligand site

Mycorrhizae Fungi which colonize the outer layers of plant roots and whose external mycelium increases the effective absorptive volume of the roots. A symbiotic relationship between fungus and plant

Mycotoxin Toxic substance found in fungi

Natrixeralf Sodium-rich soil type found in areas with semiarid or arid climate

Organometallic Organic compounds containing metal ions

Ombrotrophic bogs Areas of wetland dominated by Sphagnum mosses that derive all their water and nutrients from rainfall (cf. minerotrophic bogs which derive their water and nutrients from springs and drainage water)

Osteoarthropathy Disease affecting joint and bone tissue

Outer-sphere Metal-ligand linkage with intervening water molecules

Oxidative stress Imbalance between the production of reactive oxygen species and a biological system's ability to scavenge them; leads to various forms of chemical injury i.e., on DNA molecules and can strongly affect biochemical and physiological regulatory processes

Peroxynitrite The anion $ONOO^-$. Is an unstable structural isomer of nitrate, NO_3^-

Phosphorites Sedimentary phosphate rock

Phyllosilicates Alumina-silcate clay minerals with sheet-like structures

Phytate Phosphorus-containing compound (inositol hexaphosphate) found in cereal grains which can bind Zn etc. and reduce its bioavailability

Phytoremediation The treatment of environmental problems (bioremediation) through the use of plants that mitigate the environmental problem enough to make it unnecessary to excavate the contaminant material and dispose of it elsewhere

Phytotoxicity When plants suffer from a toxic dose of a substance

Placer deposits Natural concentrations of heavy minerals deposited by gravity in stream and river sediments

Pollution The introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and damage to structures. Used interchangeably with 'contamination' but convention is to use the term 'contamination' in relation to land or soil

Polyphenol Plant water soluble compounds containing several phenol groups which are powerful antioxidants in animals/humans (e.g., in tea, soy beans, olive oil etc.)

Prebiotic Non-digestible food ingredients used as food by intestinal bacteria

Primary minerals Minerals which crystallized from magma and formed igneous rocks

Pyrometallurgical Metal production by processes involving heating to high temperature

Pyrophoric A material which may ignite spontaneously in contact with air or emit sparks when struck (e.g., depleted uranium DU)

Randomized trial Experimental clinical study where participants are assigned randomly to the study group (receiving the active drug or other therapy to be tested) or a control group (not receiving the active drug)

Redox Reduction-oxidation reactions (chemical reactions in which certain atoms have their oxidation number changed)

Regolith Deposit of physically and chemically-weathered rock, differing from soil in being formed abiotically and not containing any organic matter

Reperfusion Return of blood supply after a period of ischemia

Rhizosphere Thin layer (approximately 2 mm thick) around plant roots which is a zone of intense microbial activity due to root secretions

Rhizobia N-fixing symbiotic bacteria found in nodules on the roots of leguminous plants (also referred to as biological N fixation) (fast growing *Rhizobium* species and slow growing *Bradyrhizobium* species)

Ruminants Animals with a four-compartment stomach which enables them to chew the cud, which is the regurgitation of partially chewed herbage from the rumen for more thorough chewing when not grazing. It includes: cattle, sheep, antelopes, deer, giraffes and related species

Secondary minerals Minerals formed from the products of weathering of primary minerals and precipitates (clay minerals, hydrous oxides of Fe, Mn and Al and carbonates)

Selenate The anion SeO_4^{2-} or salts containing this anion

Selenide The anion Se^{2-} or salts containing this anion

Seleniferous Term used about selenium-rich soils allowing growth of toxic selenium accumulator plants

Selenite The anion SeO_3^{2-} or salts containing this anion

Selenol group –SeH group. Has lower pK_a value than the thiol group (−SH) and is therefore dissociated at physiological pH

Selenoprotein P The most abundant selenoprotein in blood plasma, accounting for about 50% of plasma selenium. Contains up to 10 Se atoms per molecule

Selenoproteins Any protein that includes a selenocysteyl (Se-Cys) group Selenocysteine is normally incorporated during translation and uses the codon TGA in the DNA molecule

Se oxyanions Anions that contain selenium and oxygen atoms

Sesquioxides Hydrous oxides of Fe (e.g., $Fe_2O_3.nH_2O$), Mn and Al in soils which are have important adsorptive properties and are abundant in tropical soils

Sewage sludge The residual, semi-solid material left from sewage treatment processes (also called biosolids)

Shale Fine-grained non-carbonaceous sedimentary rock with clay minerals or other clay-size mineral grains as the major component

Siderophile Metallic iron-seeking elements (*e.g.* platinum metals) (Goldschmidt classification)

Silanol group Si-OH on mineral surfaces

Stoichiometry The relationship between the relative quantities of substances taking part in a reaction or forming a compound

Supergene zone Zone of concentration of metals resulting from the deposition of metals released by weathering (oxidation) of overlying sulphide ore minerals

Tert-uni ping pong The rate of consumption of one substrate is proportional to the first kinetics power of the enzyme concentration and the second power of the concentration of the other substrate

Thiocyanate The anion SCN^-

Thioredoxin reductase Se-dependent enzyme that reduces oxidized thioredoxin and several other substrates

Tricarboxylic acid cycle Also known as the citric acid or Kreb's cycle, is a cyclic series of enzyme-catalysed reactions taking place in the mitochondria. It is required for energy release from carbohydrate through ATP in aerobic respiration

Villous atrophy Atrophic degeneration of intestinal mucosa where the intestinal villi are lost

Vitamin B_{12} Vitamin (also called cobalamin) containing cobalt which can only be synthesized by microorganisms, such as in the gut of ruminants. Vitamin B_{12} has many important functions, including red blood cell formation and in the nervous system

Waterlogging Saturation of the soil with water, leading to development of reducing conditions (see gleying)

Xylem One of the two types of transport tissue in plants. Forms tubes that contain water at lower than atmospheric pressure, often negative, and must therefore have strong, stiff walls in order not to collapse. These walls are formed by composite materials containing cellulose to provide tensile strength and lignin to provide stiffness and hardness

Zeolites Tecto-silicates with a 'cage and channel' morphology

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