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David M. Whitacre *Editor*

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Foreword

International concern in scientific, industrial, and governmental communities over traces of xenobiotics in foods and in both abiotic and biotic environments has justified the present triumvirate of specialized publications in this field: comprehensive reviews, rapidly published research papers and progress reports, and archival documentations. These three international publications are integrated and scheduled to provide the coherency essential for nonduplicative and current progress in a field as dynamic and complex as environmental contamination and toxicology. This series is reserved exclusively for the diversified literature on "toxic" chemicals in our food, our feeds, our homes, recreational and working surroundings, our domestic animals, our wildlife, and ourselves. Tremendous efforts worldwide have been mobilized to evaluate the nature, presence, magnitude, fate, and toxicology of the chemicals loosed upon the Earth. Among the sequelae of this broad new emphasis is an undeniable need for an articulated set of authoritative publications, where one can find the latest important world literature produced by these emerging areas of science together with documentation of pertinent ancillary legislation.

Research directors and legislative or administrative advisers do not have the time to scan the escalating number of technical publications that may contain articles important to current responsibility. Rather, these individuals need the background provided by detailed reviews and the assurance that the latest information is made available to them, all with minimal literature searching. Similarly, the scientist assigned or attracted to a new problem is required to glean all literature pertinent to the task, to publish new developments or important new experimental details quickly, to inform others of findings that might alter their own efforts, and eventually to publish all his/her supporting data and conclusions for archival purposes.

In the fields of environmental contamination and toxicology, the sum of these concerns and responsibilities is decisively addressed by the uniform, encompassing, and timely publication format of the Springer triumvirate:

> *Reviews of Environmental Contamination and Toxicology* [Vol. 1 through 97 (1962–1986) as Residue Reviews] for detailed review articles concerned with any aspects of chemical contaminants, including pesticides, in the total environment with toxicological considerations and consequences.

> *Bulletin of Environmental Contamination and Toxicology* (Vol. 1 in 1966) for rapid publication of short reports of significant advances and discoveries in the fields of air, soil, water, and food contamination and pollution as well as methodology and other disciplines concerned with the introduction, presence, and effects of toxicants in the total environment.
>
> *Archives of Environmental Contamination and Toxicology* (Vol. 1 in 1973) for important complete articles emphasizing and describing original experimental or theoretical research work pertaining to the scientific aspects of chemical contaminants in the environment.

Manuscripts for Reviews and the Archives are in identical formats and are peer reviewed by scientists in the field for adequacy and value; manuscripts for the *Bulletin* are also reviewed, but are published by photo-offset from camera-ready copy to provide the latest results with minimum delay. The individual editors of these three publications comprise the joint Coordinating Board of Editors with referral within the board of manuscripts submitted to one publication but deemed by major emphasis or length more suitable for one of the others.

Coordinating Board of Editors

Preface

The role of *Reviews* is to publish detailed scientific review articles on all aspects ofenvironmental contamination and associated toxicological consequences. Such articlesfacilitate the often complex task of accessing and interpreting cogent scientificdata within the confines of one or more closely related research fields.

In the nearly 50 years since *Reviews of Environmental Contamination andToxicology* (formerly *Residue Reviews*) was first published, the number, scope, andcomplexity of environmental pollution incidents have grown unabated. During thisentire period, the emphasis has been on publishing articles that address the presenceand toxicity of environmental contaminants. New research is published each yearon a myriad of environmental pollution issues facing people worldwide. This fact,and the routine discovery and reporting of new environmental contamination cases,creates an increasingly important function for *Reviews*.

The staggering volume of scientific literature demands remedy by which data canbe synthesized and made available to readers in an abridged form. *Reviews* addressesthis need and provides detailed reviews worldwide to key scientists and science orpolicy administrators, whether employed by government, universities, or the privatesector.

There is a panoply of environmental issues and concerns on which many scientistshave focused their research in past years. The scope of this list is quitebroad, encompassing environmental events globally that affect marine and terrestrialecosystems; biotic and abiotic environments; impacts on plants, humans, andwildlife; and pollutants, both chemical and radioactive; as well as the ravages ofenvironmental disease in virtually all environmental media (soil, water, air). Newor enhanced safety and environmental concerns have emerged in the last decade tobe added to incidents covered by the media, studied by scientists, and addressedby governmental and private institutions. Among these are events so striking thatthey are creating a paradigm shift. Two in particular are at the center of everincreasingmedia as well as scientific attention: bioterrorism and global warming.Unfortunately, these very worrisome issues are now superimposed on the alreadyextensive list of ongoing environmental challenges.

The ultimate role of publishing scientific research is to enhance understandingof the environment in ways that allow the public to be better informed. Theterm “informed public” as used by Thomas Jefferson in the age of enlightenmentconveyed the thought of soundness and good judgment. In the modern sense, being“well informed” has the narrower meaning of having access to sufficient information. Because the public still gets most of its information on science and technologyfrom TV news and reports, the role for scientists as interpreters and brokers of scientificinformation to the public will grow rather than diminish. Environmentalismis the newest global political force, resulting in the emergence of multinational consortiato control pollution and the evolution of the environmental ethic.Will the newpolitics of the twenty-first century involve a consortium of technologists and environmentalists,or a progressive confrontation? These matters are of genuine concernto governmental agencies and legislative bodies around the world.

For those who make the decisions about how our planet is managed, there is anongoing need for continual surveillance and intelligent controls to avoid endangeringthe environment, public health, and wildlife. Ensuring safety-in-use of the manychemicals involved in our highly industrialized culture is a dynamic challenge, forthe old, established materials are continually being displaced by newly developedmolecules more acceptable to federal and state regulatory agencies, public healthofficials, and environmentalists.

Reviews publishes synoptic articles designed to treat the presence, fate, and, ifpossible, the safety of xenobiotics in any segment of the environment. These reviewscan be either general or specific, but properly lie in the domains of analytical chemistryand its methodology, biochemistry, human and animal medicine, legislation,pharmacology, physiology, toxicology, and regulation. Certain affairs in food technologyconcerned specifically with pesticide and other food-additive problems mayalso be appropriate.

Because manuscripts are published in the order in which they are received infinal form, it may seem that some important aspects have been neglected at times. However, these apparent omissions are recognized, and pertinent manuscripts arelikely in preparation or planned. The field is so very large and the interests in itare so varied that the editor and the editorial board earnestly solicit authors andsuggestions of underrepresented topics to make this international book series yetmore useful and worthwhile.

Justification for the preparation of any review for this book series is that it dealswith some aspect of the many real problems arising from the presence of foreignchemicals in our surroundings. Thus, manuscripts may encompass case studies fromany country. Food additives, including pesticides, or their metabolites that may persistinto human food and animal feeds are within this scope. Additionally, chemicalcontamination in any manner of air, water, soil, or plant or animal life is within theseobjectives and their purview.

Manuscripts are often contributed by invitation. However, nominations for newtopics or topics in areas that are rapidly advancing are welcome. Preliminary communicationwith the editor is recommended before volunteered review manuscriptsare submitted.

Summerfield, NC, USA David M. Whitacre

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Soil Column Leaching of Pesticides

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Contents

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1 Introduction

Groundwater (GW) constitutes the most important source of drinking water, and despite the benefit of pesticides in food production, the contamination of GW by biologically active pesticides at unacceptable levels should be avoided. A number of pesticides and their degradation products have frequently been detected in field GW monitoring programs (Cohen et al. 1984; Hancock et al. 2008; Kolpin et al. 2000). Regulatory agencies in each country are responsible for preventing contamination of GW by pesticides or their degradates. Regulators have developed methods to assess both existing and newly developed pesticides for any tendency to leach in soil. The US EPA has performed monitoring studies to determine if pesticides contaminate GW (Wells et al. 1995) and has recently introduced a conceptual environmental model to better evaluate GW contamination (USEPA 2008b). In Europe, a stepwise evaluation procedure for regulating GW contamination by pesticides and their degradates is used, and this has recently been updated; the revision not only utilizes computer simulations of predicted environmental concentrations to determine if the 0.1 ppb trigger level is exceeded, but also relies on data from higher-tier field experiments (Boesten et al. 2009). To estimate the leaching behavior of a pesticide in soil or to compare its relative mobility with other pesticides, the sophisticated simulation approaches used generally require considerable data on the environmental fate of the pesticide. Because the cost of conducting field experiments over extended time periods can be extremely high, it is useful to collect relevant information on pesticide soil mobility by first using experimental laboratory approaches. For soil mobility, such approaches include batch adsorption studies, soil thin-layer chromatography, and soil column leaching (Häfner 1994; Helling and Dragun 1981; USEPA 2008a). Although laboratory soil column leaching and batch adsorption/desorption studies have been performed on many pesticides, the results of these studies do not always reflect what actually occurs in the field. Nevertheless, such studies normally provide valuable information on the potential mobility of pesticides in soil if they are well-controlled and focused, and the results are mathematically analyzed using an appropriate model.

Pesticide transport processes in soil have been addressed in many excellent reviews, primarily from the viewpoints of pesticide properties (Bewick 1994; Russell 1995), soil science—hydrology (Brown et al. 1995; Jarvis 2007), and large-scale outdoor lysimeter and field studies (Flury 1996; Führ et al. 1990, 2003; Kördel et al. 2008). The agricultural practices that control soil transport such as tillage and addition of soil amendments, have been discussed in these reviews, but the discussions have often produced little that is conclusive, because the reviewed studies were of different scales and used different methodology. However, many reliable small-column laboratory leaching studies have been performed for various chemical classes of pesticides, and these have been used to estimate the potential soil mobility of pesticides. Since the same processes and factors operate in controlled lab conditions as under field conditions, the latter type of studies are important, because they provide a more integrated picture of how pesticides move under natural conditions.

In this review, I first address soil pesticide mobility in the context of soil characteristics and structure, and then address the typical methodology used to evaluate pesticide mobility. I also address the inherent merits and demerits of the various methods used in defining pesticide mobility. Another key goal herein is to address the value of soil column leaching studies, by reviewing both pesticide properties and soil factors that control the behavior of pesticides in soil. In addition, I address both the theory behind and the models available on solute transport in soils for the purpose of better explaining the results collected from soil column leaching studies. Finally, I provide an overview summary of the existing column leaching data that has been published in the literature. The structures of pesticides that appear in this review are presented in the attached Appendix.

2 Characteristics and Structure of Soil

The mobility of any pesticide in agricultural land is principally governed by the movement of water through soil, since most pesticides possess a low vapor pressure and the contribution from vapor transport is negligible. Rainfall and irrigation constitute the main sources by which water reaches agricultural fields (Bewick 1994; Brown et al. 1995; Russell 1995). A portion of water that reaches soil is lost by either evaporation from the surface or via run-off when the water content of the soil exceeds its water-holding capacity. The residual water is then available for vertical and lateral infiltration into the soil profile. The infiltration rate is determined by factors such as soil permeability and structural composition (with tilth at the soil surface), antecedent moisture content, the presence of cracks, fissures and macropores, and the level of the water table. Among these factors, the presence of macropores in soil is known to drastically modify pesticide mobility. Water also moves upwards in soils at a rate dependent on the drying rate of soil and the nature of the vegetation present (evapotranspiration).

Soil is a very heterogeneous system that is composed of sand, silt, clay, and organic materials. Soil is also known to contain pores that are occupied by water and air. Soil aggregates variously produce a complex structure that results in a range of porosity and density that is specific to each soil type. Novak et al. (2001a) examined the size effect of clay soil aggregates in packed column leaching experiments with atrazine (74; number refers to structure shown in Appendix) and trifluralin (98). Much less leaching of these herbicides was observed in soil columns prepared with smaller-size aggregates (1–5 mm) than with larger ones (>5 mm). This is possibly due to the higher adsorption properties of the smaller aggregates, which have a larger surface area. Not only does soil texture and organic matter content influence the soil adsorption/desorption processes of pesticides, but biological properties such as microbial activity can also drastically affect pesticide degradation rates, and hence mobility behavior (Aharonson et al. 1987; Bewick 1994; Helling and Gish 1986). Among the various properties that affect pesticide distribution and mobility in soil, water retention, and hydraulic conductivity are most important.

Climate is also an important factor that can affect pesticide mobility, by modulating soil conditions (Bewick 1994; Russell 1995). Soil temperatures vary, both diurnally and seasonally, and affect the activity of soil-dwelling microbes. Moreover, soil temperatures are affected by rainfall, which in turn, affects the extent of leaching when pesticides are applied, e.g., in the spring vs. the fall. Both rainfall and wind influence the water content of surface soils, which conversely affects the rate of evapotranspiration.

2.1 Macropores

The definition of a soil macropore is ambiguous, because the term has no generally accepted definition; however, macropores are generally characterized as having or displaying a high water flow-through rate (Beven and Germann 1982; Kördel et al. 2008). The fraction of macropores in soil is small, as compared with the total soil volume. However, the saturated hydraulic conductivity in macropores is extremely high and exceeds the saturated hydraulic conductivity of a matrix of sand, silt, and clay by 2–6 orders of magnitude (Kördel et al. 2008). The flow rate through a macropore is thought to be controlled primarily by its diameter, the topology of its network and wall conditions. The diameter of a macropore is considered to be in the range of 50 μm to 10 mm. Many studies have been performed on nonequilibrium macropore flow (or preferential flow) in soils, and excellent reviews on this topic have been written (Jarvis 2007; Kördel et al. 2008; White 1985).

Macropores are primarily classified by their shapes. The existence of open-ended macropores that are located in permeable subsoils, or in the vicinity of a field drain pipe, accentuate water flow; in contrast, dead-ended macropores that terminate in homogeneous subsoils initially exhibit fast flow, shortly followed by a slower matrix flow (Kördel and Klein 2006). The three-dimensional structure of macropores is important when a non-chromatographic flow of water along macropores predominates. The distribution of soil space voids has been examined by staining soil with fluorescent dye, such as Rhodamine B, during the conduct of leaching studies (Flury et al. 1994; Kung 1990). Natural soil fissures in the field were shown to enhance the downward movement of Cl^- in structured clay soils, and these could be visualized well using fluorescein dye (Kissel et al. 1973). Seyfried and Rao (1987) have reported that convective flow is confined to small regions of the cross section of a soil column; different dye staining patterns occurred between saturated and unsaturated flow conditions in undisturbed soil columns. Ghodrati and Jury (1990) applied the anionic dye Acid-Red 1 to undisturbed and surface-disturbed field plots, then irrigated the plots and examined the horizontal and vertical distribution of the dye. The water in the soil profiles moved by preferential flow in a heterogeneous pattern, which displayed a vertical fingering 5–20 cm wide. However, when the leaching patterns in the six soil cores extracted from this field were averaged, the leaching pattern was similar to that which would be expected under chromatographic flow conditions. A similar trend was confirmed in 14 Swiss fields, where water was transported more deeply by percolating through cracks and fissures in the well-structured loamy and clayey soils than in unstructured soils (Flury et al. 1994).

One problem associated with the dye staining technique is that it is necessary to destroy the stained soil core if further visual observations are made. As an alternative method, a nondestructive X-ray computed tomographic (CT) scan was developed to study macropores (Reinken et al. 1995). Vanderborght et al. (2002) showed that the larger pores in the soil profile could be identified by either dye staining or X-ray CT scan methods; however, the latter method gave more information on the three-dimensional structure of smaller pores. Furthermore, a reduced network of larger pores without lateral mixing was observed for deeper field-collected soil layers. Significant differences in the distribution of void spaces were observed for paddy, upland, and forest soils using soft X-ray CT to evaluate soil columns eluted with CH_2I_2 (Mori et al. 1999). Contrasting with the developed network of fine pores that existed in forest soil, many macropores originating from decayed rice roots were observed in paddy soil.

Recently, a new method has been used to evaluate macropore networks. This method is based on single photon emission computed tomography (SPECT), and has been successfully applied to examine the geometry of macropore networks in soil (Perret et al. 1999). Topological analysis of an undisturbed sandy loam soil column showed that the average length of a major network is about 4 cm. More than 60% of the networks are made up of four branches, and each path therein is inclined to approximately 0–55° from the vertical. The authors have also used SPECT to monitor the real-time movement of solutes in undisturbed soil columns by employing $Na^{99m}TcO_4$ as a tracer (Perret et al. 2000). The comparison of the SPECT results obtained on macropore distribution with those visualized using the X-ray CT method clearly showed that macropore continuity played a significant role in the preferential transport of solutes through soils.

Macropores are also classified by the process of their formation (Beven and Germann 1982; Jarvis 2007; Kördel et al. 2008). One type of macropore is formed via an abiotic process (e.g., from seasonal freeze/thaw cycles) in soil (cracks and fissures) and the erosive action of subsurface water flow (natural soil pipes). Such macropores have a tortuosity of 1.2–2.0 and are usually more frequently observed in structured clayey soils that have a clay content of more than 15–20%. The complex networks of fractures in such soils develop horizontally and vertically in clay-rich till and can be visualized by dye staining (Jørgensen et al. 2002).

The other process by which macropores are formed is via a biotic one, which is frequently observed to occur in silty soils resulting from the formation of pores by soil fauna (moles and earthworms) and from growing or decayed plant roots. The typical diameter of a macropore in the former (fauna-derived) process is <1 to >50 mm, whereas macropores formed by decaying roots are smaller and are plant species-dependent. Edwards et al. (1988) probed the nature of the soil profile at three depths down to 30 cm in a no-till field of silt loam soil. By using photography with an image analyzer, they found macropores that appeared to derive from plant roots. Macropores having a diameter of >0.4 mm were abundant ($>3{,}000$ pores per m^2), and the total macropore area was about 1.4% of their cross-section at each depth. The density of burrow macropores was two-fold higher in a no-till corn field than in a grass-legume meadow (Edwards et al. 1992b). Moreover, a lower macropore density was observed in a conventionally tilled field than in an apple orchard up to a depth of 20 cm (Siczek et al. 2008). It was confirmed that earthworm burrowing participated in the creation of macropores in the no-till corn field, and this was considered to have affected water flow. The water flow was measured directly by collecting percolated water samples from earthworm holes at a depth of 30–50 cm; about 13-fold more water moved through these holes than was expected from their area distribution (Edwards et al. 1989). Using soil blocks that had a well-developed network of earthworm burrows, it was demonstrated in a series of laboratory studies that the presence of macropores caused a heterogeneous water flow (Edwards et al. 1992a, 1993; Shipitalo et al. 1990). After $SrBr_2$ was applied to the soil surface, percolates were collected from each of 64 grids at the bottom of the blocks. In this way, it was demonstrated that specific grids were connected to macropores that gave a markedly larger volume of percolate. It was also shown that antecedent water added by pre-irrigation enhanced the diffusion of Sr^{2+} and Br^{-} into the soil matrix and reduced leaching through macropores.

The inner wall of a macropore has differing characteristics in terms of both physicochemical properties and organic composition, compared to the soil matrix. The inner wall of macropores, created by decaying roots that occur in deeper layers of paddy soil, become coated with alluvial clay particles, and are physically strong enough to sustain a preferential flow, even in soils that have a low bulk density (Mori et al. 1999). Ellerbrock and Gerke (2004) isolated organic matter for analysis, either from the coatings and interior of aggregates in a structured loamy arable soil or from the walls of decayed root channels or material found in earthworm burrows in an unstructured forest sandy soil. The differences they found, in terms of the amounts of total C and N observed for wall, coatings and the matrix of arable soil, were insignificant. However, the soil matrix had a slightly higher cation exchange capacity (CEC). In contrast, higher amounts of total C and N, as well as CEC, were detected in the burrow-filling material, than in the decayed-root walls. Infra-red (IR) analysis of the organic material extracted from each portion by hot water or pyrophosphate showed that the hydrophobicity of the coatings increased with depth and was higher than in the matrix, as judged from the higher IR absorption intensities resulting from C–H, C=O and C=C bonds. Although the two extraction methods gave different IR patterns, comparable or higher C=O and C=C absorption was observed in decayed root walls and burrow fillings than in surface soil. These differences are reasonably accounted for by organic waste that results from plants and earthworms. In one experiment, burrow-lining material collected from soil columns in the presence of two individual earthworms, contained 1.5–2 times more organic carbon, when decomposed corn or soybean leaves were fed (Farenhorst et al. 2001). Furthermore, a higher amount of nitrate-N was eluted from burrow macropores than from artificially man-made holes that had similar diameters (Edwards et al. 1992b). More organic carbon was detected in the dye-stained walls of decayed root macropores than the neighboring soil matrix, by using the fumigation–extraction method (Bundt et al. 2001). A higher microbial population was reported to exist in macropores than in the soil matrix, based on monitoring data from 44 field sites in Denmark (Vinther et al. 1999). Stehouwer et al. (1993) examined the depth-dependence of total organic carbon content and alkaline phosphatase activity in 50-cm depth soil profiles and reported that these values were at least 2–3 times higher in the earthworm burrow linings than in the corresponding soil matrix.

2.2 Colloids and Dissolved Organic Matter

A pesticide dissolved in pore water either diffuses or is transported with the movement of water and is simultaneously partitioned into the soil matrix. However, there are many kinds of materials that exist in pore water. Among these are humic substances, metal oxides and clay particles, any of which may be partly dissolved and present as colloids or suspensions (De Jonge et al. 2004; Katagi 2006; McCarthy and Zachara 1989; Ouyang et al. 1996). Water-dispersible colloids (WDC) include layer silicates, Fe- and Al-oxyhydroxides, humic substances, and bacteria and display particle sizes between 1 nm and 10 μm in diameter. Abiotic colloids naturally disperse from soil aggregates by infiltration of water. Most WDCs are negatively charged, and their stability is sensitive to certain parameters such as the electrolyte concentration that affects the electric double layer around them. WDCs are stable at pH values greater than $\mathrm{pH_{zpc}}$, which is defined as the pH value giving the zero point of charge (ZPC) at which the total charge from cations and anions at the surface is equal to zero. WDCs become unstable at $\mathrm{pHs} < \mathrm{pH_{zpc}}$ due to reduced electrostatic repulsion as a result of having a thinner electrical double layer (Barton and Karathanasis 2003; Seta and Karathanasis 1997a). Dissolved organic materials (DOM), such as fulvic and humic acids in pore water, are considered to be coagulated as a result of having divalent or trivalent metal cation bridges that lead to their precipitation on the surface of clay minerals (Reemtsma et al. 1999). These materials generally have reactive surfaces onto which cationic species or hydrophobic chemicals may adsorb (Grolimund et al. 1996). The concentration of soil colloids is highly dependent on the physical properties and structure of the soils in which they exist; when they are measured as dissolved organic carbon (DOC), their concentration ranges from 10 to 1,000 mg $\mathrm{kg^{-1}}$ (Laegdsmand et al. 2005; Reemtsma et al. 1999; Williams et al. 2002; Worrall et al. 2001). Therefore, when assessing the leaching rate of pesticides, one must consider not only how the pesticide interacts with WDCs but also the mobility of WDCs in macropores.

The partitioning of pesticide molecules to WDCs and DOM is considered to proceed via van der Waals forces, complexation and electrostatic attraction (Katagi 2002); as a result, the soil adsorption coefficient [K_d, Eq. (3)] of a pesticide may change with its changing partition coefficient (K_WDC or $K_\mathrm{DOM(C)}$) between water and WDC or DOM(C) (Dunnivant et al. 1992a; Magee et al. 1991). The following equation describes this phenomenon

$$K_d^{app} = K_d / (1 + [C] \times K_{WDC\,or\,DOM(C)}) \tag{1}$$

where, K_d^{app} is the apparent soil adsorption coefficient (L kg^{-1} in a linear isotherm; ≥0) of a pesticide in the presence of WDC or DOM(C) at a given concentration [C]. The retardation factors (R, Eq. (7); dimensionless, ≥1) for phenanthrene and polychlorinated biphenyls in packed soil columns decreased with the increasing DOC concentration in the mobile phase; under this condition, the log K_{DOC} was estimated to be 4–5 by Eq. (1) from the K_d^{app} values.

Khan and Thomson (1990) examined the effect of DOM on the transport of DDT (101) using Triton X-100 as a humic substance model. The retardation of DDT (101) was greatly reduced by three orders of magnitude at a surfactant concentration of 1,000 ppm, and the effect of DOM was considered to be significant for a hydrophobic chemical having a log K_{ow} (*n*-octanol-water partition coefficient) of >5. Interactions with DOM have been thoroughly investigated for the herbicide napropamide (114). More elution of (114) from soil columns occurred in the presence of DOM, strongly suggesting that the transport of (114) occurred by association with DOM (Nelson et al. 2000). Such an association was also indicated by the decreased K_d values that were observed in the presence of DOM. Dialysis of the leachates showed that more than 80% of (114) was associated with DOM having a molecular weight of 500–1,000 Da (Williams et al. 2002). An analysis using size exclusion chromatography showed a similar association for simazine (75) and its hydroxyl derivative with DOM, and this association was increased by aging (Ertung et al. 2002). When derivatized by silylation, the aqueous extracts of the compost treated with (75) resulted in reduced molecular weights of DOM and an increased release of (75); this indicated that the DOM was structurally integrated via hydrogen bonding and was involved in the association with (75). The dialysis of leachates from soil columns treated with diuron (35) indicated the contribution of DOM (molecular weight of <1,000 Da) to the association with pesticide molecules (Thevenot et al. 2009). Weak interactions for (35) were observed in a batch adsorption study performed with polar DOM that had lower humidification (Cox et al. 2007). Chen et al. (2010) reported a higher association of prometryn (79) with DOM that had a molecular weight of >14,000 Da than that having a lower molecular weight. Thus, higher mobility, both in soil column leaching and soil TLC (thin layer chromatographic) studies, was observed when DOM had a higher molecular weight. Analysis of the DOM-pesticide associated complex by infra-red (IR) and excitation–emission matrix fluorescence spectroscopies showed that DOM has a higher fraction of aromatic moieties and carbohydrate structures and was involved in the association. However, much less DOM of a higher molecular weight was detected in the leachate of (114), and this may indicate the importance of the duration of contact and soil texture to the interactions.

The WDC species such as clay minerals and metal oxides show strong adsorptive capacities towards metal cations, inorganic acid anions, and organic functional groups (Ouyang et al. 1996). Hence, similar interactions with ionizable pesticides are likely to occur. Glyphosate (15), strongly adsorbed to Al- and Fe-oxides, was transported by association with WDCs in an intact soil column packed with a surface tillage (Gjettermann et al. 2009). Its adsorption to slightly alkaline soils was enhanced by the formation of a ternary complex with Cu^{2+} at the soil surface (Dousset et al. 2007). The strong association of cationic paraquat (133) with Li-montmorillonite increased (133) leaching in a soil column, while the presence of Ca^{2+} in the eluent caused flocculation of the clay and resulted in reduced leaching (Vinten et al. 1983). Ionized picloram (84) ($pK_a = 2.3$) showed very little adsorption to soils at neutral pHs, while the strong interactions of salicylic acid ($pK_a = 2.9$) with iron oxides resulted in much higher adsorption to the same soils (Celis et al. 2005). Therefore, components of WDC, dissolved metal cations and pesticide structure interact to influence the adsorption of an ionizable pesticide.

The mobility of WDCs is primarily affected by their stability and by physical factors such as particle size, pore-size distribution, and the presence of soil macropore networks. Seta and Karathanasis (1997a) reported that the transport of WDCs through undisturbed soil columns increased as pH and the content of total exchangeable bases increased, and decreased as the content of Fe/Al-flocculants and kaolinite of a higher particle size increased. This clearly indicated the importance of the stability and the particle size of the WDCs to their mobility. WDCs eluted faster than a Cl^- tracer, as demonstrated by their breakthrough curves (BTC). Results indicated that a size exclusion mechanism was involved in the mobility of the WDCs; their mobility was influenced when their larger mean diameters were 0.2–1 μm. By monitoring effluents with block-type lysimeters fitted with laser dynamic light scattering devices, the particle size of WDCs was discovered to increase as water flow rate increased (Kaplan et al. 1993). The increased water flow rate resulted in a higher shear stress that produced an increase in the release of larger particles such as kaolinite and vermiculite, which was concomitant with the increased content of total organic carbon in the eluates. Since the DOC concentration was kept at a low level and was independent of a flow rate, most organic carbon was considered to be associated with the WDCs consisting of these particles. In many soil column leaching studies, the concentration of WDCs in effluent reached an early maximum, followed by a decrease over time. Grolimund and Borkovec (1999) proposed a multiple particle population model to explain such behavior, wherein the activation energy of a WDC release rate follows an exponential distribution. This model successfully explained the time-dependent release of WDCs. More detailed investigation on the movement of WDCs through macropores was conducted by Laegdsmand et al. (1999, 2005). They found that loosely bound WDCs that had high organic content were released first, followed by WDCs that diffused from macropore walls. The authors confirmed that high ionic strength in percolating water limited the mobilization of WDCs, and the rate of colloid leaching was positively correlated with flow velocity during prolonged leaching. Recently, Poulsen et al. (2006) successfully applied a two-region model, described in Sect. 6.1, that utilized mobile and immobile water phases in the soil profile to explain the elution patterns of WDCs from 33 undisturbed soil columns. The WDCs were predominantly transported through macropores that had diameters of >150 μm. There was no relationship between the spatial distribution of WDCs in soil and the extent of leaching.

Different elution patterns have been reported for WDCs and DOC in field leaching studies with prochloraz (126) (Villholth et al. 2000). WDCs were primarily leached with the very water that rapidly drained through macropores after rainfall or irrigation events. In contrast, the leaching peaks of DOC in the BTC became flatter, which suggested different mechanisms of release and transport. Dunnivant et al. (1992b) examined the leaching behavior of DOC in packed columns of aquifer sandy soil. Elution of DOC always followed the Br^- tracer, which suggested that a size exclusion mechanism was unlikely for movement of DOC. Hydrophobic DOC was more highly retained in soil and less desorbed than hydrophilic DOC. Reemtsma et al. (1999) characterized DOC that was released from soil by elution with various salt solutions, and then isolated by ultrafiltration and solid-phase extraction. When the salt solution contained calcium chloride, soluble fractions with lower molecular weights of an aliphatic character were rapidly released. Another salt NaH_2PO_4 had strong affinity for Fe/Al-oxyhydroxides and an ability to replace Ca^{2+} from organic complexes. Higher DOC release after elution by NaH_2PO_4 indicated aggregation of DOC by Ca^{2+} and divalent bridging of the DOC to clay minerals. There was an increase in UV absorption of eluent containing DOC at 254 nm as elution proceeded, and this indicated a gradual release of fractions with an aromatic character. Similar elution profiles were reported for leachates from soil columns to which DOM originating from spent and weathered mushroom substrate was applied (Guo and Chorover 2003). More acidic DOCs, having COOH and phenolic OH functional groups, were released more quickly from the columns. By using dialysis membranes with a different molecular weight cut-off, Williams et al. (2002) found that DOC with a molecular weight of 500–1,000 Da was dominant (>80%) in the eluates, with a much smaller contribution from higher molecular weight fractions.

3 Leaching Methodology

The adsorption–desorption processes that occur when pesticides leach can be conveniently evaluated by using the batch equilibrium method. However, the measured soil dispersion in an excess of water is often very different to that which occurs under actual field conditions. Soil thin-layer chromatography (TLC) and thick-layer chromatography, where plates are developed by using aqueous $CaCl_{2,}$ were introduced to obtain an R_f value as a simple index of soil mobility (Helling and Dragun 1981; Lynch 1995; Russell 1995). However, neither the water flux nor the soil water content can be controlled when soil TLC is used to determine mobility and natural soil aggregation is missing. When using these methods, the extraction and quantification steps are the most time-consuming, especially when nonradiolabeled pesticides are used.

Alternatively, the direct detection of a chemical in eluates by UV and/or radioactivity has led to the development of a reverse-phase chromatographic method that utilizes a column packed with fine sand. The use of a chemical retardation factor (R) in the column chromatography has been proposed by Nkedl-Kizza et al. (1987), as a mobility index described by the following equation.

$$\log(R_{\mathrm{m}} - 1) = \log(R_{\mathrm{W}} - 1) - \alpha_{\mathrm{c}} \times \sigma_{\mathrm{c}} \times f_{\mathrm{c}} \qquad (2)$$

R_{m} and R_{w} refer to retardation factors in water–cosolvent mixture and water, respectively, α_{c} and σ_{c} refer to cosolvency power and an empirical constant that account for water–cosolvent–sorbent interactions, and f_{c} refers to a volumetric fraction of any organic cosolvent. The asymmetry in the BTCs of atrazine (74) and diuron (35) decreased with an increasing f_{c} in the methanol–water mixture used as an eluent. Since the symmetric BTC was observed at lower f_{c} values for (74), which had a similar hydrocarbonaceous surface area to (35), a higher contribution of non-equilibrium soil sorption was expected for (35). By applying Eq. (2) to the methanol–10 mM $CaCl_2$ mixture at various f_{c}, Wood et al. (1990) obtained the R_{w} value of (35) close to what was calculated from the adsorption coefficient in the batch equilibrium method. The application of soil-column liquid chromatography provided a good estimate of the K_{d} values for (74) and tebuconazole (127) (Ni et al. 2004), and this estimate was more accurate than the one using a C_{18} reverse-phase column (Xu et al. 1999). Less change in enthalpy for partition of a chemical from solvent to soil than to the C_{18} surface was determined by linear free-energy relationship analysis of the retardation factor at various temperatures, which accounted for this difference (Liang et al. 2002). Bi et al. (2006, 2007, 2010) observed that cation exchange and surface complexation take place in soil for interactions involving *S*-, *O*- and *N*-heterocycles. Therefore, the absence of such interactions when using the C_{18} reversed-phase may produce a poor estimate of adsorption coefficients for pesticides.

3.1 Column Leaching

Different from soil TLC and reverse-phase liquid chromatography techniques, the soil column leaching technique (Fig. 1a) can be employed to better simulate water flux in a soil profile. These packed soil columns are utilized not only to compare mobility between pesticides but also to mechanistically analyze pesticide movement in soil (Helling and Dragun 1981; Lynch 1995; Russell 1995; Weber et al. 1986). The methodology of soil column leaching has been thoroughly tested and standardized (Lynch 1995; OECD 2004; USEPA 2008a). To facilitate the analysis of polycyclic aromatic hydrocarbons at very low concentrations, Reemtsma and Mehrtens (1997), utilized an on-line solid-phase extraction of eluates, which was linked with GC-MS. The distribution of herbicides leached from a soil column can also be conveniently bioassayed by using a sensitive plant species (Günther et al. 1993; Mersie and Foy 1986; Nelson and Penner 2007; Weber et al. 1986). Furthermore, when a radiolabeled pesticide is used, both the BTC and distribution in the column can be easily evaluated for the pesticide and its metabolites. Fortunately, data have shown that the relative mobility of pesticides test similarly, when either column leaching or soil thin- and thick-layer chromatographic methods are used (Wu and Santelmann 1975).

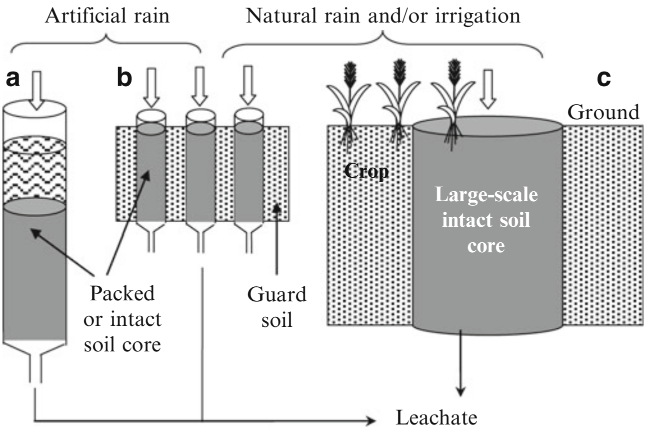


Fig. 1 Various soil column leaching apparatus (a) Typical soil column used in laboratory. (b) Semi-outdoor soil columns. (c) Outdoor lysimeter

A disturbed soil column, uniformly packed with sieved soil, is generally used for pesticide leaching studies. Such columns are generally more reproducible than using other techniques to evaluate pesticide transport. Isensee and Sadeghi (1992) reported statistically insignificant differences in the leaching of two dyes that were applied to the center or to the edge of a 10-cm diameter soil column. However, an edge-flow effect along the column wall may exist and should be checked by using a tracer such as Cl^-. To prevent edge effects, beads or silicone sealer can be applied to the inside wall of a column at appropriate intervals (Weber and Whitacre 1982). Smaller-scale studies usually utilize glass columns, but columns made of stainless steel, Teflon® or polyvinyl chloride (PVC), are used in larger-scale studies. With regard to column-surface effects on pesticides, Koskinen et al. (1999) reported only slight adsorption of five ^{14}C-labeled pesticides to a PVC column. The typical size of a soil column is 4 cm in diameter and 30 cm in length. Undisturbed intact soil cores, extracted from the field, can be utilized to investigate preferential flow and the effects of soil amendment and tillage, as described in Sect. 5 (Brown et al. 1995; Helling and Dragun 1981; Weber et al. 1986). Large-diameter undisturbed soil cores can be collected using a hydraulic pressure system (El Hadiri et al. 2003). When performing studies with undisturbed soil columns, the boundary edge flow effect can generally be prevented by applying a sealant, such as paraffin wax and epoxy cement to the inner walls of the column (Arthur et al. 1998; Isensee and Sadeghi 1992).

In column leaching studies, pesticides are applied to the column as a pulse in a minimal volume of either a solution or treated soil (Elrick and French 1966; Nielsen and Biggar 1961). The miscible displacement method, which involves percolation with pesticide solution, followed by percolation with a pesticide-free solution, is frequently used to estimate mobility parameters for pesticides. Such column studies, when augmented by mathematical modeling, have been extensively used for determining several key parameters of mobility for pesticides and organic chemicals, including the effect of soil disturbance (McMahon and Thomas 1974), soil amendments (Graber et al. 1997; Socías-Viciana et al. 1999), nonequilibrium adsorption (Angley et al. 1992; Baskaran et al. 1996; Brusseau et al. 1991; Chiang et al. 2001; Mao and Ren 2004; Selim and Zhu 2002; Spurlock et al. 1995; Suárez et al. 2007), preferential transport (Seyfried and Rao 1987; Singh and Kanwar 1991), macromolecule effects (Enfield et al. 1989), colloids (Seta and Karathanasis 1996, 1997b), and aging and biodegradation effects (Estrella et al. 1993; Guo and Wagenet 1999; Langner et al. 1998).

Soil columns are eluted with distilled or deionized water, and preferably with electrolytes such as 5–10 mM $CaCl_2$ or $CaSO_4$ to minimize colloidal dispersion (Helling and Dragun 1981). Water is typically administered through a funnel, but may be more uniformly added to a larger soil surface area using a rainfall simulator to control the velocity of water flux (Laegdsmand et al. 2005; Mersie et al. 1999; Münch et al. 2002; Wietersen et al. 1993). In the field, the upper soil profile is unsaturated and contains air-filled voids, whereas the pores below the water-logged part of the soil are filled with water. This latter situation is simulated in soil columns by maintaining a constant water flow, in which water-saturated conditions persist (i.e., constant water head). If unsaturated conditions near the soil surface are to be tested, a transient/interrupted flow utilizing suction can be used to emulate the normal flows of field water, but it is more difficult to control the water flux under these conditions. Therefore, a computerized system capable of real-time measurement of soil water content by tensiometers has been developed to control water flux (Düring and Hummel 1999; El Ouaghlidi et al. 1999; Fermanich et al. 1991; Krahe et al. 1997).

Material balance is an important index to measure and may serve to help establish the validity of a column leaching study, especially when ^{14}C-labeled pesticides are used. Quantitation of volatiles, including carbon dioxide from volatilization and microbial mineralization, is indispensable to achieving a good measure of material balance. The ability of pesticides to undergo mineralization has been examined in closed column systems equipped with various traps under static (Kruger et al. 1996; Locke et al. 1994) and air-flow (Alhajjar et al. 1990; Griessbach et al. 1998; Irwin et al. 1996; Langenbach et al. 2000) conditions. Both $^{14}CO_2$ and organic volatiles were recovered in unaged soil columns, and no clear advantage between the trapping methods was found (Arthur et al. 1998). However, upon soil aging, up to 20% of the applied ^{14}C was collected as $^{14}CO_2$ as a result of the leaching of fenpropathrin (28) and cypermethrin (29) (Sakata et al. 1986, 1990). ^{14}C recovery fluctuated between 70 and 100%, providing an indication of how difficult it was to successfully trap all volatiles.

The measured mobility of pesticides was variable, especially in undisturbed soil columns, even when conditions were carefully controlled. Such variability originates from several factors that include differences in the spatial distribution of soil voids that may originate from fissures and biopores (Flury et al. 1994; Ghodrati and Jury 1990; Lennartz 1999), variability in soil characteristics, and the nature of the microbial populations that inhabit the soil (Bending et al. 2006; Charnay et al. 2005; Coquet and Barriuso 2002; Shaw and Burns 1998; Stenrød et al. 2006). Larger-scale undisturbed soil cores, with a diameter and length of >0.5 m, were utilized to investigate the relationship between pesticide transport and heterogeneous soil structure under laboratory conditions (Beck et al. 1995; Jørgensen et al. 1998; Takamatsu et al. 2007). Differences in the spatial distribution of soil voids was found to cause the variable water flow in soil matrix and through macropores, depending on the flow rate of water, and resulted in variable leaching patterns of the tested pesticides. Moreover, the effects of diurnal and seasonal changes in temperature and rainfall may also produce patterns of pesticide transport under natural conditions that are different to those observed in the laboratory. To bridge the potential gaps between laboratory-column leaching and field studies, a technique depicted in Fig. 1b can be used. In this system, a number of soil cores are installed in a chamber and the spaces between them are filled with soil or sand. This system can be conveniently used outdoors or in a greenhouse to simulate outdoor climate conditions (Beulke et al. 2001; Cherrier et al. 2005; Jones et al. 1998; Leake 1991; Walker et al. 1996; Weber et al. 2007).

3.2 Outdoor Lysimeters

Outdoor lysimeter techniques have been developed to bridge the gaps that may exist between data obtained under laboratory vs. field mobility study conditions and several test guidelines are available (BBA 1990; Dutch Commission 1987; EFSA 2007a; OECD 2000) that address the conduct of lysimeter studies. However, in general, lysimeters are vessels that contain a soil monolith (Fig. 1c) that is useful for studying the several phases of the hydrological cycle. Such phases include infiltration, runoff, evapotranspiration, and the removal of soluble constituents in drainage, under conditions that approximate typical agronomic practices and meteorology. To reflect regional differences in soils and climate, special studies may be required, as performed by Francaviglia et al. (2000), who proposed an experimental design that was specific to the Mediterranean region. Many excellent reviews are available that address pesticide mobility as determined by using lysimeters (Bergström 2000; Führ et al. 1990, 1998, 2003; Hance and Führ 1992; Hassink and Kördel 2000; Kördel and Klein 2006; Kördel et al. 1991; Russell 1995).

Lysimeters that are designed to weigh the water that flows through them are also used. Such lysimeters can directly measure water gain and loss. However, nonweighing lysimeters are generally utilized, because they are easier to handle and are less expensive. It is recommended in lysimeter studies that the soil monolith has a surface area of >0.5 m^2 and a depth of 1–1.3 m. Moreover, it is important to carefully extract the monolith from the field without compacting the soil; this is usually accomplished by using a drilling technique (Leake 1991; Persson and Bergström 1991). Collecting a soil monolith under dry conditions is preferred so as to prevent later shrinkage that can enhance side-wall flow effects (Bergström 1990; Kördel et al. 1991). Soil monoliths are then buried in the ground with gravel and porous ceramic plates at the bottom (Leake 1991; Yon 1992). When a soil monolith is vegetated, the same crops/vegetation should be grown around it to act as a guard crop (Fig. 1c). Lysimeters having a large surface area enabled the planting of grapevines to examine herbicide behavior under simulated natural conditions (Fent et al. 1993).

Soil water is easily collected from the bottom of such free-draining lysimeters. In larger-size lysimeters, the ability to use porous ceramic candles or plates for collecting soil water is limited, because of the potential disturbance to the soil structure (Pütz et al. 1998; Roy et al. 2001; Schoen et al. 1999a). Kördel and Klein (2006) reported that macropores were disrupted when suction plates produced lower pesticide concentrations in soil water; this effect was caused by disruption to the rapid water flux. Crops that have reached the harvest stage and soil samples that represent the entire soil profile should be collected for analysis at the termination of a lysimeter study. Analyses of these samples should show the distribution in samples, not only of the pesticide itself but also any metabolites. When performing lysimeter studies, the use of a radiotracer enables researchers to obtain information on both the transport and the environmental fate of the test pesticide, under natural conditions (Führ et al. 1998). The effects of the formulation on pesticide mobility are also often tested. Formulations, in which the active ingredient is radiolabeled, may be applied to vegetated lysimeters under natural conditions with appropriate irrigation (Führ et al. 1990; Keller and Weber 1997; OECD 2000). The specific protocols and their associated conditions for the conduct of lysimeter studies have evolved over time. OECD (2000) originally requested duplicate studies, and a study duration of 2–3 years, but, more recently, a longer test period and more replicates have been recommended by EFSA (2007a).

Loss of a portion of applied pesticide from outdoor lysimeters is expected to occur. The extent of loss depends on the rate of volatility and biodegradability of the tested pesticide. Führ et al. (1998) reported a significant loss from volatilization and mineralization in lysimeter studies performed on 13 pesticides. The levels of the losses for the corresponding pesticides were 20–85% of the applied dose. To continuously collect volatiles, Schroll et al. (1992) installed a volatilization chamber that was composed of a series of traps at the soil surface of a lysimeter. They found more volatilization for pendimethalin (99), which has a higher vapor pressure, than for terbutylazine (78). However, Schroll et al. (1999) discovered that differences in mineralization for the two herbicides were insignificant between agricultural and forest soils. Recently, Schroll and Kühn (2004) tested a plant chamber that enclosed the upper parts of plants as part of a weighing lysimeter study performed with ^{14}C-labeled isoproturon (38). In this study, it was demonstrated that soil mineralization was higher than that in plants, but volatilization was similar from both surfaces, and high levels of ^{14}C recovery (97–99%) were observed. The extent of mineralization and volatilization was shown to be dependent on soil type (Schroll et al. 2008). Similar trends were observed for glyphosate (15) (Grundmann et al. 2008). In one other approach, a UV-transparent wind tunnel was installed over a lysimeter (Wolters et al. 2003). This approach achieved both satisfactory results and a good material balance.

Rice plants are grown under water management systems that are different than those are used for other arable crops. Hence, specific lysimeter systems are used to track pesticide mobility under flooded rice conditions. By using a flooded paddy-soil monolith, equipped with a volatile trap covering a portion of the soil surface, the behavior of carbofuran (17) and bentazon (93) was examined over a period of 4 years (Lee et al. 1994, 1996). Mineralization reached a plateau within 20 weeks, and ^{14}C was predominantly distributed in the upper soil layers and in the straw of rice plants. A similar ^{14}C distribution was observed for cinosulfuron (53) (Lee et al. 1998), propiconazole (131) (Kim et al. 2002), and molinate (22) (Park et al. 2005), although the leached amounts were different. Lee et al. (2003) also reported that mineralization of azimsulfuron (56) was enhanced by changing the conditions in the lysimeter from one that was flooded to an aerobic non-flooded one. Recently, Nhung et al. (2009) designed a disturbed paddy-soil lysimeter to simulate a field (measured) water balance and reported that the degradation profiles of benthiocarb (21) and simetryn (2-SCH_3 derivative of simazine) (75)) in water compared well to the measured dissipation profiles of these compounds in the paddy field.

For determining pesticide mobility in soil, an outdoor lysimeter study has many advantages over laboratory column leaching studies. In outdoor studies, one can examine and evaluate the seasonal effect of an application on leaching in ways that include: differences in water flux and degradation (Brown et al. 2000; Kördel et al. 1992), the contribution of preferential flow (Hassink and Kördel 2000), plant uptake with evapotranspiration (Führ et al. 2003; Hellpointer 1998). Such effects cannot be determined by conducting laboratory column leaching studies. However, lysimeter studies do have a few intrinsic disadvantages. Lysimeters represent a natural soil profile, but the variability of profiles, even within a single field may be high, and therefore, may require many replicates to obtain an accurate view of field pesticide transport (OECD 2000; Parsons et al. 1995; Russell 1995). Moreover, neither the presence of a near-surface GW table or aquifer nor the lateral flow resulting from slowly permeable or impermeable soils is addressed in the outdoor lysimeter system (Brown et al. 1995; Hollis and Carter 1990). By sub-irrigating the soil monolith, Jebellie et al. (2000) discovered that the depth of a water table caused a statistically insignificant effect on residues of metolachlor (67) in soil and pore water. Fent et al. (1999) used an outdoor lysimeter, and compared results with a field plot of the same dimension. They demonstrated that the ^{14}C-pesticide, its main metabolite and two tracers were similarly distributed in the soil profiles of both systems, with almost identical average amounts of each pesticide leached. Therefore, the presence of a shallow GW table or aquifer seems not to significantly affect the transport of pesticide, when a vertical water flow predominates. In contrast, the absence of lateral flow may produce overestimates of the long-term accumulation of pesticides in soil (Klein et al. 1998) or may impart a different character to its vertical transport. The most critical difference from a field study is the presence of a zero-tension bottom boundary in the lysimeter that significantly affects upward and downward movement of water (Bergström 2000; OECD 2000; Hassink and Kördel 2000). Indeed, Fogg et al. (1994) reported much higher leaching in an outdoor lysimeter study that was possibly due to the existence of a zero-tension bottom layer.

3.3 Field Leaching

The simple approach to overcoming the zero-tension boundary issue in outdoor lysimeter studies is to directly drive the leaching cylinder into the field (Copin et al. 2000). The movement of the pesticide and its metabolites can then be conveniently monitored by analyzing the extracted and segmented soil core at each soil depth (Anderson and Dulka 1985; Keller and Weber 1995; Koskinen et al. 1998; Sorenson et al. 1994; Weber et al. 2006). Soil water can be collected by installing suction cups below each core (Carter and Fogg 1995). By using the conservative $^{36}Cl^{-}$ tracer in a field leaching study, Hance et al. (1981) showed that cultivating soil opens channels in the surface that can result in more leaching. However, the transport of pesticides from either lateral flow in the soil profile or surface run-off cannot be estimated using this method. One alternative approach is to utilize a larger field lysimeter under more controlled conditions (Edwards and Glass 1971; Glass and Edwards 1979). In one such study, the leachate and run-off from three pesticides, including dicamba (83), were periodically monitored using a sloped undisturbed soil block that had a surface area of 8 m^2 and a depth of 2.4 m (Glass and Edwards 1979). Malone et al. (2004) more recently examined the loss of several herbicides from such a lysimeter system and found that leaching events occurred shortly after heavy rainfall and resulted from preferential flow.

More realistic methods for performing field leaching studies are represented by two approaches; a small-scale prospective groundwater (PGW) monitoring study that was proposed by the US EPA (Chang and Ying 1998; Russell 1995; USEPA 2008b) and a terrestrial field dissipation study (Alister et al. 2008; Corbin et al. 2006; Peters et al. 2002; USEPA 2008c; Walker and Welch 1989). Newcombe et al. (2005) conducted a PGW monitoring study of acetochlor (66) at eight 1.2-ha US sites and demonstrated that this herbicide was unlikely to contaminate GW in most areas. A sophisticated field leaching study was conducted on glyphosate (15) and its metabolite aminomethylphosphonic acid (AMPA) in Europe by Kjær et al. (2005). Water samples were collected from suction cups, wells, and drainage to monitor the movement of these chemicals. The authors confirmed that the transport of these chemicals in soil was driven mainly by the complicated balance between water flux, adsorption, and microbial degradation.

The second realistic means for measuring field leaching utilized a field dissipation approach. This approach is more convenient, and the amount of pesticide leached is monitored in this approach by either a drainage system (Felding 1995; Jones et al. 2000; Kladivko et al. 1991; Novak et al. 2001b; Petersen et al. 2002; Traub-Eberhard et al. 1994) or a porous suction sampler (Carter and Fogg 1995; Fogg et al. 1994; Gatzweiler et al. 1999; Guzzella et al. 2003; Peters et al. 2002; Suzuki 2000), which is buried under the ground. However, with such devices any disturbance of soil structure will affect the leaching behavior of tested pesticides (Flury 1996). The dissipation of a ^{14}C-labeled form of a formulated product provides researchers with more information on the distribution and environmental fate of a pesticide under real field conditions than using unlabeled products (Baker et al. 2002). Alternatively, two other methods to monitor the concentration of a pesticide and its metabolites in soil water are to use wells (Isensee et al. 1990; Kim and Feagley 2002; Rosenbom et al. 2010), or pan-lysimeters (Hall et al. 1989; Tindall and Vencill 1995).

Drip irrigation technology has been developed, especially for semi-arid regions, to improve the efficiency of water use and to reduce soil erosion. Garratt et al. (2007)

sprayed imidacloprid (117) and procymidone (115) on green beans grown in the greenhouse and found that their vertical transport in soil occurred in parallel with periodical drip irrigation. Drip irrigation emitters buried at a depth of 45–60 cm in a hop yard resulted in the distribution of (117) residues to remain within a 30-cm radial distance from the emitters (Felsot et al. 2003). Ceasing irrigation reduced the further leaching of (117) to deeper soil layers. Even when a pesticide is uniformly applied to the field, the presence of vegetation produces a heterogeneous water flux, which results in nonuniform leaching. Saison et al. (2008) performed a field study on cadusafos (14) in a banana plantation and found that more (14) is lost at the base of the plant by leaching under a much larger water flux than that around the base. Delphin and Chapot (2006) injected three herbicides into the soil profile and monitored soil water collected below the injection points with suction cups. The retardation factor of each herbicide was calculated from the ratio of the drainage volumes of the peak concentrations of each herbicide vs. Br^-, and the results were comparable to the theoretically estimated values from each soil adsorption coefficient.

The leaching results from an agricultural field can be applied to leaching that occurs in other situations. Putting greens on golf courses consist of a unique type of turf at the surface, which is infiltrated with organic thatch composed of decomposed roots and stems, over a sandy soil and/or coarse gravel. The thatch layer plays a key role in enhancing adsorption and accentuating microbial degradation, thus preventing the occurrence of leaching. Such effects from thatch were reported for iprodione (116) and selected fungicides (Strömqvist and Jarvis 2005; Wu et al. 2002b). Wu et al. (2002a) installed lysimeters fitted with flux chambers on the turf surface of a putting green. Although the sandy and gravel layer of the under-surface of a putting green should be more permeable than an agricultural field, more of the chlorpyrifos (4) and trichlorfon (13) applied to the putting green were lost by volatilization and clipping removal of creeping bentgrass, compared to losses from leaching and degradation. In addition, railway embankments are covered by gravel, thereby reducing the potential for pesticide sorption; leaching under such conditions can therefore occur rapidly. Börjesson et al. (2004) assessed the possibility of GW contamination from application of imazapyr (87) to Swedish railway embankments. The pesticide (87) became localized in the surface soil layers as a result of its persistence in soil water. Moreover, leaching of (87) was reported to more likely occur from the center of the track, which was covered by gravel, than from the sides of the track.

4 Soil Processes Controlling Pesticide Mobility

After application, pesticides that are deposited on plant and soil surfaces undergo volatilization and photodegradation (Katagi 2004). Pesticides entering the unsaturated soil profile undergo adsorption/desorption and degradation, and a proportion of the chemical is transported downwards through the soil profile with the water flux. Surfactants and other reagents in pesticide formulations are known to modify the water solubility and adsorption/desorption properties of pesticides by micelle formation or association; however, their effect on the soil biodegradation of pesticides is ambiguous (Katagi 2008). Sprayable formulations do not generally influence pesticide leaching in the field, because the pesticide and other ingredients in formulation leach separately; in contrast, granular or controlled-release formulations may affect leaching markedly of some pesticides, by changing the amount of free pesticide that is subjected to degradation and transport in the soil (Flury 1996; Katagi 2008).

As mentioned above, sorption and degradation are two of the basic properties of pesticides that control leaching (Aharonson et al. 1987; Bewick 1994; Russell 1995). By using the convection–dispersion model, as described in Sect. 6.1, and by assuming equilibrium sorption, first-order degradation kinetics and passive plant uptake Boesten (1991) demonstrated that soil adsorption and degradation significantly controlled the amount of pesticide leached. Since pesticide molecules that are dissolved in pore water or are associated with organic matter, colloids, and particles move with the water flux, the adsorption/desorption process in the soil matrix determines the leaching behavior of the pesticide. Furthermore, soil microbes play an important role in degrading pesticides, and the increased microbial activity and biomass at the plant root—soil interface enhances the degradation rate in the rhizosphere (Anderson et al. 1993, 1994). Such microbial enhancement has been confirmed by observing a more rapid dissipation of herbicides in small outdoor lysimeters planted with barley than in those containing only bare soil (Rüdel et al. 1993). Such enhancement was also affirmed by the relationship that exists between biomass carbon and the degradation of atrazine (74) in vegetated lysimeters (Lin et al. 2003). Abiotic hydrolysis occurs only minimally, except when soils are rather acidic or alkaline, because slower hydrolysis prevails at neutral pHs for most pesticides (Katagi 2002). In deeper soil layers and in GW, anaerobic biodegradation and/or redox reactions with reduced species such as Fe^{2+} may also contribute to pesticide breakdown (Aharonson et al. 1987; Bewick 1994).

Adsorption and degradation processes are affected by the variability of soil characteristics in the field and by extrinsic agricultural practices. By using the soils collected from 17 to 29 locations at two US sites, Rao et al. (1986) examined how the adsorption coefficient (K_{oc}), normalized for the fraction of organic carbon content (f_{oc}), and the aerobic dissipation half-life (DT_{50}) varied spatially for three pesticides. The spatial variability of K_{oc} corresponded well to that of OC, with a coefficient of variance (CV) of less than 20%. There was no statistically significant spatial variability in DT_{50}, but increased persistence was observed in deeper soils. The variability of pesticide properties, as well as the type of distribution, normal or log-normal, is a very important consideration in a leaching simulation (Dubus et al. 2003a).

4.1 Adsorption and Desorption

Soil sorption processes are governed by physical, electrostatic, and chemical interactions and depend on the properties of the pesticide involved and on the adsorbent. The simple linear and empirically derived Freundlich equations are generally used to describe the adsorption of pesticides and their metabolites (Katagi 2006). These equations are as follows

$$\text{Linear isotherm}: K_{\mathrm{d}} = q_{\mathrm{e}} / C_{\mathrm{e}} \tag{3}$$

$$\text{Freundlich isotherm}: \ln q_{\mathrm{e}} = \ln K_{\mathrm{F}} + \left(\frac{1}{n}\right) \ln C_{\mathrm{e}} \tag{4}$$

Where

K_{d}, linear adsorption coefficient (L kg^{-1});
K_{F}, Freundlich adsorption coefficient (L$^{1/n}$ mg$^{1-1/n}$ kg^{-1});
q_{e}, amount of pesticide per unit weight of soil (mg kg^{-1});
C_{e}, concentration of pesticide in water (mg L^{-1}).

The value $1/n$ is a joint measure of both the relative magnitude and diversity of energies associated with a particular adsorption process. Solute partitioning to soil organic matter is one of the most important mechanisms by which adsorption to soil occurs, and it is the dominant factor in soil adsorption when f_{oc} is $>2\%$ (Arienzo et al. 1994). Adsorption interactions with clay, silt, or metal oxides are more important for soils which have a lower f_{oc} (Celis et al. 2005; Morillo et al. 2004; Sánchez-Camazano et al. 1994; Wauchope et al. 2002). The f_{oc} value tends to decrease with soil depth and hence, lower K_{d} values are usually reported at deeper soil layers (Felding 1997; Walker et al. 1989). In general, the higher the adsorption coefficient of a pesticide, the less it leaches in soil, unless there are effects from facilitated transport by dissolved organic matter, or preferential flow occurs (Baskaran et al. 1996; Fernandes et al. 2003; Grover 1977; McCall et al. 1980). The K_{d} value obtained by the batch equilibrium method does not always correlate with that estimated from the retardation factor in the column leaching study, suggesting that adsorption–desorption processes involved in leaching processes are quite complex (Elabd et al. 1986).

Both soil pH and clay greatly affect soil sorption processes, especially for ionizable pesticides. The sulfonylurea (Abdulla et al. 2001; Walker et al. 1989) and imidazolinone herbicides (Johnson et al. 2000; Regitano et al. 2005; Weber et al. 2003) are ionized at soil pHs greater than their pK_{a} (i.e. ~4), which ionization produces less soil adsorption and a higher degree of leaching from electrostatic repulsion towards the negatively charged soil surface. A similar relationship was reported for 2,4-D (59), but the pH effect was partly masked by its hydrophobic interactions with soil organic matters (Mallawatantri et al. 1996). In contrast, the cationic fentin acetate (124) and protonated carbendazim (24) are tightly bound to soils due to an electrostatic attraction (Aharonson and Kafkafi 1975; Barnes et al. 1973). The interaction of ionizable 2,4-D (59) and simazine (75) with Fe-montmorillonite has been individually examined by using X-ray diffraction and IR measurements (Cox et al. 2000). The acidic clay made a large fraction of (59) undissociated and (75) entered into the basal spacing of the clay, which increased their adsorption.

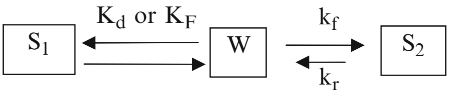
The adsorption coefficient of pesticides sometimes increases with time, indicating the presence of a nonequilibrium slow adsorption process, which follows a rapid one (Pignatello 2000). The slower process is thought to originate from the resistance of the soil matrix to the diffusion of pesticide molecules through pores and organic matter. Furthermore, hysteresis, where adsorption and desorption values deviate from one another also occurs for some pesticides, and results from the interactions of pesticide molecules specifically with organic matter and/or clay. Once these interactions occur, pesticide molecules can become strongly resistant to desorption. Pignatello (2000) has proposed several possible mechanisms for how such interactions occur. These include the formation of metastable states and insufficient time for establishing equilibrium. Hysteresis is usually evaluated by the following equation.

$$H = \frac{(1/n_{\text{des}})}{(1/n_{\text{ads}})} \tag{5}$$

Where H is a hysteresis index, and the subscripts relate to desorption and adsorption.

When adsorption is determined using the batch equilibrium method, the H values in various soils appeared to be dependent on the chemical structure of the pesticide and were reported to be both >1 (Calderón et al. 2004; Cuevas et al. 2008; Fernandes et al. 2003; Morillo et al. 2004) and <1 (Gupta and Gajbhiye 2002a; Khoury et al. 2001).

The slower adsorption process has been examined by conducting either batch adsorption or soil leaching studies for various pesticides. Oi (1999) reported that the K_{d} value of imidacloprid (17) increased by a factor of 3–4, as a result of aging two soils for 100 days; such aging resulted in the reduction of leaching by a factor of 2 in this column study. In a similar experiment, the K_{d} value of imazethapyr (87) increased by a factor of 10, as a result of soil aging for 16 days (O'Dell et al. 1992). After soil aging for up to 30 days, (87) experienced time-dependent adsorption and leaching was progressively reduced, even when the compound existed in a dissociated form (at pH 5–8) (Johnson et al. 2000). Such time-dependent adsorption can be mathematically described by a two-compartment model. One of the compartments is a reversible site (S_1) that is in equilibrium with a pore water phase (W) and is described by either a linear or Freundlich isotherm. In contrast to this rapid process, the transfer of molecules to the other S_2 compartment (slow-desorption site) is a diffusion-limited process that is defined by mass transfer rate constants (k_{f}, k_{r}).



Gaston and Locke (2000) reported that the two-site equilibrium–kinetic model shown above describes the time-dependent adsorption of acifluorfen (70) well. O'Dell et al. (1992) estimated the fraction of S_1 to be 0.3–0.6 for imazethapyr (87) and similar values (0.4 and 0.5) were reported for isoproturon (38) and terbuthylazine (78) in batch equilibrium studies, assuming the two-site model (Köhne et al. 2006). S_2 may consist of sites having different adsorption characteristics, as demonstrated by Baskaran et al. (1996). Plots of the adsorbed concentrations of 2,4-D (59) and phorate (9) vs. (equilibration time)$^{1/2}$ were bimodal straight lines, indicating the presence of at least two types of sorption sites that are controlled by diffusion. By examining the leaching behavior of a pesticide that was used to treat seeds, Sabbagh et al. (2007) introduced the third irreversible site to which pesticide is very tightly bound. The rate constant of this bound formation was found to be less than that of the kinetic desorption from the S_2 site by about one order of magnitude. In mathematical modeling, the concept of this third site was found to be indispensable in more precisely describing the tailing that occurred in the breakthrough curve (BTC) of triticonazole (130) (Beigel and Di Pietro 1999).

It was assumed that nonequilibrium sorption processes were prevalent in leaching studies conducted with chlorsulfuron (46), because of the asymmetric BTCs that were observed (Veeh et al. 1994). Based on the very low K_d value of chlorsulfuron (46), it was assumed that intra-aggregate diffusive mass transfer occurred instead of the expected kinetic adsorption. The effect of soil aggregate size on adsorption and desorption under static conditions has been examined for isoproturon (38) using soil aggregates of <3, 3–6, and 6–10 mm in diameter (Walker et al. 1999). As aggregate size increased adsorption slowed, but desorption occurred more rapidly. It was therefore concluded that the sorption processes were controlled by differences either in the external surfaces of the aggregates exposed to the solution of (38), or the diffusion of (38). However, when the method involved shaking, the effect of aggregate size on the adsorption of atrazine (74) was minimal for aggregates having a radius of 0.5–5 mm (Novak et al. 1994). van Beinum et al. (2005) and Villaverde et al. (2009) examined the influence of soil aggregates on pesticide time-dependent sorption, using aggregates coated with sodium alginate to promote molecular diffusion into pores. Their results indicated that there was less adsorption to the coated soil aggregates than to the dispersed noncoated soil particles. This probably resulted from the reduced accessibility of pesticide molecules to the inside of the aggregates. Sorption of pesticide in the aggregates was regarded to be a diffusion-controlled and reversible process and to have occurred via an intra-aggregation diffusion model. This model was successfully applied to explain the leaching behavior of three pesticides through undisturbed soil columns (van Beinum et al. 2006). The effect of initial moisture content on the diffusion of isoproturon (38) into aggregate pores was also investigated. By comparing the sorption processes of (38) and ^3H_2O in soil aggregates at three moisture levels, Johnson et al. (1999) demonstrated that the diffusion process contributed to adsorption in wet aggregates. In contrast, (38) did not leach differently when compared in wet and dry heavy-clay soils (Beulke et al. 2004a). In addition to the intra-aggregate diffusion mechanism, diffusion in soil organic matter including humic acids can be supposed, especially for neutral organic chemicals. Organic matter may behave as a rubbery gel or glassy matter and may affect the diffusion of chemicals, when partitioned from an aqueous phase (Pignatello 2000). Brusseau et al. (1991) reported that this mechanism plays a central role as a rate-limiting process, in the nonequilibrium sorption of aromatic hydrocarbons and chlorinated benzenes.

The large variability that occurs in K_d values, even within small areas, makes the assessment of pesticide mobility more difficult (Farenhorst 2006). Wood et al. (1987) examined the relationship between the K_d values of metolachlor (67) and the various soil properties that prevailed in a 4-ha field. Soil texture had a CV of 10–30%, while organic matter content showed a CV of 40–50%. Geostatistical analysis provided a good correlation between K_d values and the OM contents in surface soils. Analysis by semivariograms of K_d and OM showed similar anisotropic patterns with a spatial dependence of up to 110 m. A similar variability was reported for the K_d values of atrazine (74) in the same field. However, the spatial distribution between K_d and K_{oc} was different, and the OC content only explained 60% of the variance in K_d. This indicated that soil pH and clay content also played a role in sorption (Novak et al. 1997). Jaynes et al. (1995) reported a field spatial dependence of <80 m in the K_d of (74), with its log-normal distribution as observed for f_{oc}. A large variance in K_d was observed for four herbicides in 21 French soil types, but the variability was greatly reduced by normalizing with the OC content, which resulted in CV values of ~10% (Coquet and Barriuso 2002). Furthermore, Kolmogorov-Smirnov statistics showed the normal distribution of K_{oc} rather than the log-normal one.

4.2 Biodegradation

The microbial degradation of a pesticide is the other important process which controls its residue levels and transport in a soil profile (Führ et al. 2003; Lynch 1995; OECD 2000, 2004; USEPA 2008a). For pesticides that are susceptible to hydrolysis and dissociation, degradation may be pH dependent (Si et al. 2005; van der Linden et al. 2009; Worrall et al. 2001). To simulate the degradation of a pesticide in a soil profile, Boesten (1991) has divided the degradation rate constant (k_d) into three terms, each representing the effects of temperature, soil moisture content, and soil depth, as shown below.

$$k_d = f_t \times f_\theta \times f_z \times k_{ref} \tag{6}$$

Where: k_{ref}, reference first-order degradation rate constant at standard temperature (T_{ref}) and moisture content (θ_{ref}), estimated by a laboratory metabolism study; f_t, temperature term expressed as exp $[E_a \times (T - T_{ref})/(R \times T \times T_{ref})]$; f_θ, soil moisture term expressed by the Walker's relationship as $(\theta/\theta_{ref})^B$; f_z, soil depth factor usually described by a numerical function.

E_a, R, and T are activation energy, gas constant, and absolute temperature, respectively. The typical median E_a value of 65.4 kJ mol^{-1} was proposed by EFSA (2007b), based on an evaluation of existing pesticide metabolism data. B is an empirical constant of 0.7 proposed by Walker (1974) and can be optimized for each pesticide based on the moisture dependence of its degradation rate. Faster degradation is generally reported at higher temperatures and moisture contents in soil (Beulke et al. 2005; Roy et al. 2001; Vischetti and Businelli 1992; Vischetti et al. 1997). In addition to temperature dependence, the elapsing time between pesticide application and the first infiltration event has been shown to significantly affect the leaching behavior of pesticides in outdoor lysimeter studies (Brown et al. 2000; Flury 1996; Sakaliene et al. 2009). Because the microbial population present in deeper soil is smaller, a smaller f_z value (<1) is generally assumed to exist with increasing soil depth (Kelsey and Alexander 1995; Shaw and Burns 1998). Mills et al. (2001) recently confirmed that the degradation of acetochlor (66) was slower in deeper soil layers that have a reduced microbial population. Beulke et al. (2000) calibrated the laboratory degradation half-lives of pesticides derived from 178 existing field dissipation studies, taking account of f_t and f_θ on a daily basis. By comparison with the field half-lives, over- and under-estimation was observed for 44% and 17% of the calibrated values, respectively. Many possible reasons were proposed for these deviations, including the contribution of other nonmicrobial degradation pathways, the use of inappropriate values for the E_a and B constants, and variability in the laboratory half-life.

Differences in biodegradation rates between flask incubation and leaching column conditions have been reported by many researchers. Chlortoluron (36) and terbutryn (80) degraded more slowly, by a factor of up to 3–9, when applied to the surface of laboratory soil columns, than when incubated with moistened soil in biometer flasks (Lechón et al. 1997). The tighter packing of soil without percolation resulted in reduced aeration at the soil surface layer where the pesticides were located, resulting in reduced degradation. Topp et al. (1994) reported that the formation of bound residues from ^{14}C-atrazine (74) was similar in both flasks and undisturbed soil columns under the same static conditions, but that bound residue formation was reduced in the repacked soil columns. The authors speculated that disruption to the soil structure in the packed column caused a reduction in aeration, resulting in less degradation of atrazine (74). Interestingly, bentazon (93) which was uniformly applied to the repacked soil columns degraded more rapidly near the soil surface, but no such depth effect was observed for cyanazine (76), which is less persistent in soil. McDonald et al. (2006) have recently shown the opposite effect of aeration on the longer-term mineralization of strobilurin fungicides in a column leaching study. These observations indicate that the effect of aeration on biodegradation is quite ambiguous (Beulke et al. 2005).

More rapid dissipation of herbicides has been reported in column leaching and outdoor lysimeter studies, as compared to static incubation in biometers (Guo and Wagenet 1999; Rüdel et al. 1993). Kelsey and Alexander (1995) have shown the effect of water movement on the biodegradation of *p*-nitrophenol (PNP), by using the miscible displacement technique and by employing various water flow rates in soil columns of different lengths. The number of PNP-degrading microbes, mostly located in the upper soil layer increased with time, and the increased residence time of PNP in the longer soil column enhanced its biodegradation. The repeated application of 2,4-D (59) significantly increased the number of (59) degrading microbes, and its leaching behavior was well described by the Monod equation (Shaw and Burns 1998). A similar mechanism was considered to be contributing to the increased degradation of (59) in the soil column at a slower flow rate (Estrella et al. 1993; Langner et al. 1998).

The high variability of pesticide dissipation half-lives (DT_{50}), with a CV of up to 30–50%, is well documented in the scientific literature. Not only is variation apparent within and among soils but testing methods are also considered to result in high variability. When DT_{50} values in lab soil studies vary too much, researchers should consider that pesticides may be lost by volatilization or codistillation. The log-normal distribution is frequently assumed for DT_{50} values and is justified by constructing a probability distribution function (Dubus et al. 2003a; Wolt et al. 2001); the particular distribution pattern often depends on the soil type (Beulke et al. 2004b). By examining the microbial degradation of isoproturon (38) in soils collected from 30 subsites of a UK field, Walker et al. (2001) classified soils into three categories. Twelve soils exhibited first-order degradation kinetics, nine soils exhibited exponential decay followed by more rapid degradation, and for the remaining soils, microbial adaptation with a time lag was observed. The DT_{50} values were most correlated with soil pH and biomass, indicating that these different degradation mechanisms stem from microbial diversity. Rodríguez-Cruz et al. (2006, 2008) reported a good correlation between DT_{50} values and these soil properties. Principle component analysis on the mineralization of three herbicides including (38) showed that about 70% of the variance was accounted for by soil texture, organic carbon (OC) content and K_d (Charnay et al. 2005). Soil surface layers taken at 20 m intervals from a UK sandy loam field showed 20–30% CV in biomass carbon content and dehydrogenase activity, and the time taken to achieve 25% degradation of azoxystrobin (108) was correlated with soil pH and OC content (Bending et al. 2006).

The involvement of microbes in the variable degradation of 2,4-D (59) was clearly demonstrated by the analysis of fatty acid methyl esters (FAME) extracted from soil (Farenhorst et al. 2008). More than 70% of the variation in cumulative mineralization over 130 days, and the mineralization rate constant can be explained by the levels of FAME *i*17:1 and *a*18, which are associated with soil microbes. Therefore, microbial variability in the field would result in a spatially variable DT_{50}. The % mineralization of glyphosate (15) in soils collected from a field site in Denmark was spatially correlated with the soil OC content and showed a positive relationship with microbial respiration and activity (Vinther et al. 2008). Stenrød et al. (2006) recently reported considerable spatial heterogeneity in the mineralization of (15), even across a small area within a single field. Furthermore, differing pesticide degradation rates have been observed among small soil aggregates. Beulke et al. (2005) reported slower degradation of cyanazine (76) and bentazon (93), by a factor of 1.5–1.7 in larger soil aggregates (3–5 mm), compared with smaller ones (<3 mm). By contrast, increased mineralization of (59) was reported in larger soil aggregates having a particle size of 2–7 mm (Gonod et al. 2003). Bundt et al. (2001) conducted mineralization experiments using soil cubes with a 6 mm edge taken from the same slice of undisturbed soil core. The highest mineralization activity was found to be localized in the soil slices neighboring preferential flow paths at three depths. The existence of a hot spot exhibiting an intense area of microbial activity may be one reason for the observed variability in pesticide biodegradation.

Pesticide molecules are gradually dispersed in soil aggregates with time. Comfort et al. (1992) reported an increased dispersion coefficient with aging by analyzing the BTCs of dicamba (83), using the convection–dispersion model. During aging, pesticide molecules may be partly entrapped at sites that are resistant to desorption. Hence, when kinetic adsorption is involved in aging, biodegradation is not the only factor that can contribute to a reduction in leaching. Renaud et al. (2004) conducted leaching studies with three urea and sulfonylurea herbicides in undisturbed soils that were aged for 3–57 days. The authors found that the dissipation rates of the herbicides detected in the column leachates were much faster than was expected from their measured soil DT_{50} values, and that biodegradation could only account for 30–85% of the observed dissipation. This observation is probably explained by the time-dependent adsorption of these herbicides in soil, as reported by Walker et al. (2005). Pignatello et al. (1993) reported that more than 80% of aged atrazine (74) and metolachlor (67) were located in a slow exchange compartment of the soil, and a two-compartment hysteric mass transfer model described the slower leaching of the aged residues well. The influence of time-dependent adsorption on leaching is also supported by the results of an aged leaching study with terbumeton (81) (Conrad et al. 2006). Following 15 days of aging, the authors reported that an increased amount of (81) was diffused into soil micropores that were resistant to rapid desorption, thus causing a reduction in the amount of (81) available for leaching. Higher microbial activity in aged soil also caused a marked reduction in leaching. Leached amounts of ^{14}C-isoproturon (38), collected from a soil column from a grassed buffer strip and aged for 44 days, were reduced by a factor of 10 compared to the amounts leached through an unaged column, and an increase in the formation of bound residues was also observed in the aged soil column (Benoit et al. 2000). The behavior of bound residues formed by aging has been investigated in larger-scale outdoor lysimeter systems. Based on long-term analysis of soils treated with ^{14}C-pesticides in outdoor lysimeters, Burauel and Führ (2000) reported that >80% of residual ^{14}C remained in the top soil layer (0–30 cm) mainly as bound residues, and the biological availability of this material to plants was highest in the year of the application. A depth-dependent decrease of residual ^{14}C from 8.8% to 0.7% was reported for the lysimeter treated with atrazine (74) and aged for more than 20 years (Jablonowski et al. 2008). The major part of the extractable fraction of soil residues was unknown polar degradates, with a trace amount of 2-OH derivative.

4.3 Mobility Index

Predicting pesticide mobility under real field conditions, even if qualitative, is very useful when evaluating the potential of a pesticide to contaminate GW. A key set of environmental parameters and field conditions that influence GW contamination were extracted from GW monitoring data in the USA, and are known as the Cohen's criteria (Cohen et al. 1984; Wells et al. 1995; Table 1). Based on the first cycle of the National Water Quality Assessment, Kolpin et al. (2000) reported that the frequency of pesticide detection in GW is correlated with DT_{50}, and K_{oc} values and with the use pattern of the pesticide. A similar correlation has been shown for atrazine (74), metolachlor (67), and primisulfuron-methyl (50) in field lysimeter studies conducted at several field sites in the USA (Weber et al. 2006, 2007).

Table 1 Mobility indices used for evaluation of groundwater contamination

Index	Equation or parameter	Mobility class	Reference
Cohen's criteria	Soil DT_{50} (field, lab) >2–3 weeks, Hydrolysis DT_{50} >25 weeks, Aqueous photolysis DT_{50} >1 weeks, Soil K_{oc} <300–500, Soil K_d <5, $K_H < 10^{-2}$, WS > 30 ppm or field leaching at >75–90 cm	High leaching potential when measured E-fate properties: and -clause + Movement in the field soil profile	Cohen et al. (1984)
McCall's criteria	K_{oc} determined by batch equilibrium method	0–50, Very high 50–150, High 150–500, Medium 500–2,000, Low 2,000–5,000, Slight >5,000, Immobile	McCall et al. (1981)
RF(H)	$R_f = \{1 + (K_{oc} \times f_{oc} \times \rho \times (\theta^{-0.67} - 1)\}^{-1}$	Leacher (→1) Non-leacher (→0)	Hamaker (1975)
Tc	$Tc = (\theta \times RF \times L)/q$ $RF = 1 + (\rho \times f_{oc} \times K_{oc})/\theta_{fc} + (AC \times K_H)/\theta_{fc}$	Relative comparison	Jury et al. (1983)
AF	$AF = \exp\{-(0.693 \times L \times RF \times \theta_{fc})/(q \times DT_{50})\}$ $RF = 1 + (\rho \times f_{oc} \times K_{oc})/\theta_{fc} + (AC \times K_H)/\theta_{fc}$	ln AF 0 to −1 High −1 to −2 Medium −2 to −3 Low −3 to −4 Very low <−4 Unlikely	Rao et al. (1985)

(continued)

Table 1 (continued)

Index	Equation or parameter	Mobility class	Reference
LPI	$\mathrm{LPI} = (1{,}000 \times \mathrm{DT}_{50} \times q)/(0.693 \times L \times \mathrm{RF} \times \theta_{\mathrm{fc}})$	>90, Very high	Meeks and Dean (1990)
	$\mathrm{RF} = 1 + (\rho \times f_{\mathrm{oc}} \times K_{\mathrm{oc}})/\theta_{\mathrm{fc}} + (\mathrm{AC} \times K_{\mathrm{H}})/\theta_{\mathrm{fc}}$	75–89, High	
		50–74, Moderate	
		25–49, Low	
		0–24, Very low	
LEACH	$\mathrm{LEACH} = (\mathrm{WS} \times \mathrm{DT}_{50})/(V_{\mathrm{p}} \times K_{\mathrm{oc}})$	Relative comparison	Laskowski et al. (1982)
LIX	$\mathrm{LIX} = \exp(-0.693 \times K_{\mathrm{oc}}/\mathrm{DT}_{50})$	Leacher (→1)	Spadotto (2002)
		Non-leacher (→0)	
GUS	$\mathrm{GUS} = (\log \mathrm{DT}_{50}) \times (4 - \log K_{\mathrm{oc}})$	>2.8, Leacher	Gustafson (1989)
		1.8–2.8, Intermediate	
		<1.8, Non-leacher	

Water solubility (WS), vapor pressure (V_{p}), bulk density (ρ), half-life (DT_{50}), groundwater depth (L), volumetric soil water content (θ: f_{c}, at field capacity), groundwater recharge rate (q), organic carbon (f_{oc}), adsorption coefficient (K_{d}) and its organic carbon-normalized value (K_{oc}), air-filled porosity (AC), Henry's law constant (K_{H})

Many researchers have proposed indices to predict the mobility of pesticides in the field (Bewick 1994; Helling and Dragun 1981; Russell 1995) as listed in Table 1. The K_{oc} value, obtained by using the batch equilibrium method, is the simplest and most useful index (McCall et al. 1981). The HPLC retention time of a pesticide relative to 2,4-D (59) was also reported to be useful for classifying pesticide mobility (McCall et al. 1980). The mobility index (MI), defined as $\Sigma(D_i \times F_i)$, was used as a simple transport parameter in a leaching study (Helling and Dragun 1981). D_i is the mean distance of each soil column segment from the surface and F_i is the normalized fraction of pesticide in each segment. The MI value divided by the length of the soil column is analogous to the R_f value in soil TLC studies. The MI values of pesticides in the field have been shown to correlate well with soil organic matter and clay content and the soil adsorption coefficient (Mora et al. 1997; Ohmes and Mueller 2007; van Leemput et al. 1986; Weber et al. 1993, 2003, 2006, 2007).

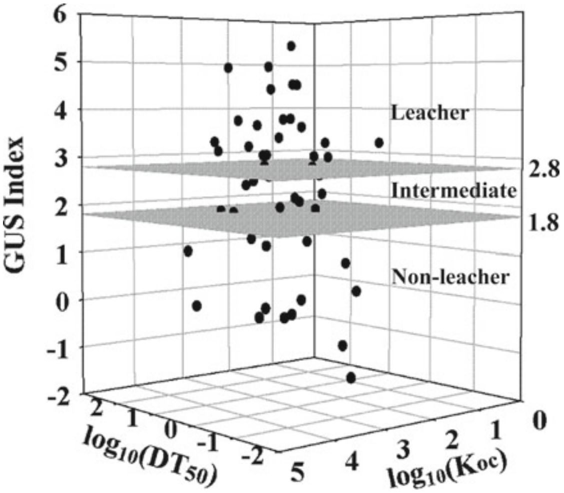
The most useful chromatographic index of mobility is the retardation factor (R), as defined below, when linear adsorption of a pesticide to soil is assumed (Helling and Dragun 1981).

$$R = 1 + (\rho \times K_d) / \theta \tag{7}$$

where ρ, θ, and K_d are soil bulk density, soil water content and the soil adsorption coefficient, respectively. Hamaker (1975) proposed the RF(H) index by introducing the effect of soil moisture content to the retardation factor. By directly considering the convective transport of a solute in soil under steady water flow, several indices were developed. Jury et al. (1983) introduced the travel time (T_c) necessary for the pesticide to reach GW at a depth of L. The RF term represents the retardation of pesticide leaching from soil adsorption and partitioning between vapor and liquid phases in soil; the attenuation factor (AF) was further developed by assuming similar dissipation in the root and vadose zones of the soil profile (Rao et al. 1985). A geographic information system linking the AF index to spatial parameters in soil was successfully applied to a county-level assessment of sites vulnerable to GW contamination from three pesticides (Shukla et al. 2000). Since the AF index gives a wide range of values, Li et al. (1998) proposed a corresponding ln (ln AF) value for mobility assessment. Martins et al. (2007) also reported that the AF index underestimated the field leaching of seven pesticides. To more precisely predict the transport of pesticides, Kookana et al. (2005) introduced both depth-dependent soil adsorption and microbial degradation to the AF index. However, the use of a worst-case assumption for the recharge rate produced an overestimation of leaching for the test pesticides, none of which were detected in field monitoring studies. As an alternative approach, Meeks and Dean (1990) derived the leaching potential index (LPI), which is equal to the reciprocal of ln AF multiplied by –1,000. A positive correlation was demonstrated between the detection of 1,2-dibromochloropropane in 272 wells located in areas vulnerable to GW contamination and LPI values.

The relative leaching potential index (RLPI), defined as $(K_{oc}/DT_{50}) \times 10$, was developed as a simple index and is easily estimated from data on the adsorption and degradation of pesticides in soil. The RLPI showed a good correlation with the leaching depth of pesticides (Futch and Singh 1999). The LEACH index was derived

Fig. 2 The (Groundwater Ubiquity Score (GUS) index of pesticides K_{oc}, arithmetic mean of soil adsorption coefficient; DT_{50}, geometric mean of dissipation half-life in soil metabolism



by Laskowski et al. (1982) by adding a volatilization term to RLPI and Spadotto (2002) modified the RLPI to an exponential formula, which they referred to as the screening leachability index (LIX). However, the most utilized index is the groundwater ubiquity score (GUS), which was developed by Gustafson (1989), and is based on the field DT_{50} value. The GUS index of >2.8 for a leacher and <1.8 for a non-leacher was successfully applied to evaluate pesticide monitoring data from water supplies in England and Wales (Brown et al. 1995). The relative leachability of pesticides and their metabolites in soil column leaching experiments was accurately estimated using GUS (Caracciolo et al. 2005; Fava et al. 2001, 2006, 2007; Fenoll et al. 2010; Khoury et al. 2001). Furthermore, correlation of GUS with GW and drainage monitoring data identified pesticides that had values for DT_{50} >3 days, K_{oc} <7,000 and GUS >0.4 as possible leachers from golf courses (Suzuki et al. 1998). Recently, it has been reported that the GUS index is useful for evaluating the loss of pesticides through macropore flow (Kördel et al. 2008) and in lysimeter studies (Vischetti et al. 2002). To determine the applicability of GUS to a lysimeter study, GUS values were conveniently calculated and plotted (Fig. 2), using the geometric mean laboratory DT_{50} and arithmetic mean K_{oc} values of 53 pesticides for which outdoor lysimeter studies are available (EFSA 2011; EU 2011). The index was used to classify 21 pesticides as leachers (GUS >2.8) and 14 as having intermediate mobility (2.8 > GUS > 1.8). However, only 4 of the pesticides investigated were detected at maximum concentrations of >0.1 ppb in the lysimeter studies, which is the EU criterion for a leacher. Since the pesticides with GUS <1.8 exhibited insignificant leaching in the lysimeter studies (at <0.1 ppb), GUS can be used as a reasonably conservative index.

When used to predict pesticide leaching in the field, the indices listed in Table 1 should be confirmed. The AF and LEACH indices gave a similar ranking of potential GW contamination for 41 pesticides (Rao et al. 1985). Kogan et al. (2007) recently applied six leaching indices to the vertical distribution of five pesticides that were applied to a field and found good correlation with Hamaker's RF(H), GUS, and LPI. Since these indices assume depth- and time-independent degradation and sorption, and uniform soil structure with a steady-state water flow without the consideration of meteorological conditions, their ability to provide an accurate prediction of pesticide mobility in the field is limited. Nevertheless, these indices can be used as indicators of potential GW contamination and can provide a reasonable estimate of the relative mobility of pesticides.

5 Soil Factors Controlling Pesticide Mobility

5.1 Soil Moisture

By using dye-staining techniques, the initial moisture content of soils was found to have little or no impact on the water flow pattern in most soils, unless macropores existed (Flury et al. 1994). Lower initial soil moisture content resulted in deeper penetration of water through the interfaces of soil aggregates and through decayed root channels, as evidenced by using dye-staining techniques (Schwartz et al. 1999). Surface tillage did not change the mean penetration and spreading rates of dyes in the soil profile, but produced more uniform staining near the soil surface. Soil tillage is thought to destroy the macropore networks of decayed root channels and earthworm burrows, resulting in the distribution of dye tracers around shallower root zones (Steenhuis et al. 1990). By staining a paddy field plot with Brilliant Blue dye, followed by visual analysis of both the horizontal and vertical soil profiles, it was shown that the lateral spreading of dye dominates the plough layer, whereas most of the soil matrix below the plough layer was unstained, except in the vicinity of the macropores (Sander and Gerke 2007).

The extent of WDC leaching was greatly affected by soil moisture and clay content (Kjaergaard et al. 2004). Colloid leaching from dry soils was low and independent of clay content, whereas higher leaching rates were observed in wet soils with higher clay content. As occurs with the leaching of colloids, organic carbon that exists predominantly in dissolved form was eluted more rapidly from wetter undisturbed soil columns. Kluitenberg and Horton (1990) showed that the initial water content of macropores controlled the dispersion of a solute in undisturbed soil columns. After the pulse application of $CaCl_2$, the soil column was percolated with aqueous $CaSO_4$ continuously under ponding or intermittently, and the BTC of Cl^- was monitored. An increase in the dispersion of Cl^- from the macropores to the surrounding soil matrix, before the resumption of elution, reduced the leaching of Cl^- by discontinuous percolation. Soil moisture also affects the extent of pesticide leaching. Higher amounts of bentazon (93) leached through small columns containing air-dried soil that had been aged for 6 days than through wetter soil columns (50 and 100% of water-holding capacity). This difference was attributed to the higher diffusion of (93) into the immobilized water of the meso- and micropores in dry soil

(Guimont et al. 2005). However, the effect of soil moisture on leaching appeared ambiguous in an outdoor lysimeter study performed with isoproturon (38) (Brown et al. 2001). Kazemi et al. (2008, 2009) investigated the effect of antecedent water content on the field leaching of four pesticides by using rainout shelters. The pesticides with a higher pore water velocity leached more rapidly in dry plots and also displayed lower rates of biodegradation than was the case in wet plots.

5.2 Preferential Flow

A preferential flow pathway can be defined as a space in the soil profile that has a lower bulk density and a higher hydraulic conductivity than that of the surrounding soil matrix. A solute is transported by preferential flow much earlier than would be expected for chromatographic flow, irrespective of its adsorption and degradation properties. Preferential flow can occur through macropores (macropore flow) generally observed to exist in structured soil and can also sometimes occur in unstructured soil as a fingered flow of water (Brown et al. 1995; Larsson et al. 1999; Tindall and Vencill 1995; White 1985). Brown et al. (1995) proposed that an air pressure build-up ahead of a wetting front, water repellency, and spatial variation in soil texture are factors that operate to produce fingered preferential flow.

Preferential flow through macropores has been characterized by the rapid breakthrough of pesticides from undisturbed columns of well-structured soils (Doran et al. 2008; Kamra et al. 2001; Kruger et al. 1996; Matocha and Hossner 1999; Morgan et al. 1995; O'Dell et al. 1992; Riise et al. 1992, 1994; Singh et al. 2002; van Beinum et al. 2006), and it is generally enhanced by high irrigation intensity (Düring and Hummel 1999; Starrett et al. 1996). In large undisturbed clay columns that have many fractures, Jørgensen et al. (1998) demonstrated that the diffusion of two herbicides and Cl^- from the fractures to the soil matrix was a key process and simulated their BTCs well. Czapar et al. (1992) demonstrated the rapid leaching of three herbicides through an artificial macropore, which was prepared using a copper tube in the center of a packed soil column, without causing any changes to soil properties such as saturated hydraulic conductivity, bulk density, and porosity. The breakthrough of some antibiotics not previously detected in leachates from standard column leaching studies has recently been reported in artificial macropore columns, indicating extremely rapid transport without any soil matrix interaction (Kay et al. 2005). Therefore, either the tortuosity or the surface properties of macropores are considered to control solute transport during preferential flow.

Having the highest pesticide concentration detected in the first drainage event usually indicates preferential flow in the field (Scorza Júnior et al. 2004). Tindall and Vencill (1995) observed the rapid breakthrough of 2,4-D (59) and dicamba (83) in a silty loam field after irrigation. Pearson et al. (1996) reported an increased contribution from preferential flow to the field leaching of (83) with increasing irrigation. Preferential flow was clearly observed when heavy rainfall or irrigation occurred shortly after pesticide application (Brown et al. 1999; Brumhard et al. 1991;

Dörfler et al. 2006; Malone et al. 2004). Although the elapsed time from a pesticide application to the first rainfall or irrigation event masks the distinct contribution of preferential flow through macropores, the earlier breakthrough of a pesticide or its degradates than expected from chromatographic flow has been reported in some outdoor lysimeter studies (Bergström and Jarvis 1993; Pütz et al. 1998; Roy et al. 2001; Schiavon 1988). Furthermore, the contribution of preferential flow can be confirmed in the field by the similar distribution of non-adsorbing conservative tracers and adsorbing solutes such as herbicides and dyes in the soil profile (Flury et al. 1995; Kung et al. 2000). In excavated undisturbed columns from the field, a positive correlation was observed between the percentage of stained area by depth and the breakthrough of Br^-, indicating the involvement of preferential flow. Steenhuis et al. (1990), detected alachlor (65) and atrazine (74) in well water from no-till corn plots, most probably as a result of preferential flow along earthworm burrows and corn root channels, as shown by dye staining. However, not all of the fractures in clay soil profiles may always become stained with dye (Jørgensen et al. 2002), and hence the results of dye staining should be cautiously interpreted.

The differences in adsorption and microbial degradation in macropores, compared to the soil matrix affects the leaching of pesticides. Mallawatantri et al. (1996) examined the adsorption and mineralization of three ^{14}C-labeled pesticides using soils collected from three horizons at depths of 0–0.65, 1.05–1.35, and 1.4–3.5 m, and from the macropore linings of the deepest soil horizon. Both K_F values and mineralization decreased in the order of the surface horizon soil, linings and the soils of the two deeper horizons, and adsorption and mineralization were positively correlated with organic carbon content and microbial population. Gaston and Locke (2002) reported more biomass carbon in the dye-stained macropore region of undisturbed soil cores, where more air and dissolved organic matter are supplied from the soil surface by the downward movement of water. However, based on the analysis of data from existing outdoor lysimeter and field leaching studies, Kördel et al. (2008) found that pesticide loss via macropore flow did not correlate with any specific environmental or pesticide parameter; many of these parameters affect each other in unpredictable ways.

The walls of earthworm burrows were reported to have a high adsorptive capacity for alachlor (65) and atrazine (74) (Edwards et al. 1992b). By directly introducing aqueous herbicide solutions to open-ended burrows in the field, the breakthrough of these herbicides was reduced by 80–90%, when compared to breakthrough in adjacent man-made holes. Furthermore, Stehouwer et al. (1993) measured the K_F values of (74) by the batch equilibrium method, using both the burrow linings and soil matrix collected at seven depths up to 50 cm. A significant correlation ($r^2 = 0.97$) between K_F and total organic carbon (TOC) was observed in the test soils, and the measured K_F values for the burrow linings that had the highest TOC content were more than 1.5 times higher than those for the soil matrix. Increased adsorption to burrow linings was also reported for metolachlor (67), but the effect was insignificant for weakly sorbed herbicides such as dicamba (83) and primisulfuron (acid of (53)) (Stehouwer et al. 1994). The effect of living earthworms on pesticide leaching has also been examined. An increase in the number of individual earthworms introduced to soil cores resulted in increased elution of (74), indicating the involvement of preferential flow through the burrows (Sigua et al. 1995). However, in contrast, although preferential flow occurred, Farenhorst et al. (2000) reported a reduction in the leaching of (74) in the presence of living earthworms, possibly due to their ingestion of surface residues of the compound.

5.3 Soil Tillage, Amendment, and Vegetation

Normal agricultural practices such as tillage and amendment with organic materials directly affect soil texture and structure, and greatly modify water movement in soil. Furthermore, crop cultivation and weed growth also affect water movement from root expansion and changes in the microbial population in the rhizosphere. The effects of agricultural practices and vegetation on pesticide mobility are summarized in Tables 2 and 3.

Soil Tillage: The effect of tillage on pesticide mobility was quantitatively examined using available experimental data. Ratios of the leached amount (L), adsorption coefficient (K) and retardation factor (R) of pesticides between no-till (NT) or reduced tillage (RT) soil systems, and conventional tillage (CT) systems were used as indices (Table 2). In approximately 40% of the listed studies, the higher mobility of pesticides in NT or RT soil systems, compared to CT systems, is indicated by $L > 1$, $K < 1$, and $R < 1$. The tillage effect depends not only on the soil texture but also on its method and depth and is sometimes masked by preferential flow, even in CT soil systems (Gaston and Locke 1996; Wilson et al. 1998); therefore, it is difficult to reach solid conclusions from the available information. Preferential flow in column leaching studies, characterized by the asymmetrical BTC of conservative tracers, was more frequently observed to occur for undisturbed NT soil, whereas chromatographic flow was generally observed for disturbed CT soil (Cox et al. 1999; Singh and Kanwar 1991; Singh et al. 2002). Even under the NT conditions, a reduction in the contribution of preferential flow to the leaching of atrazine (74) was observed in less structured sandy loam soil cores, when compared to structured silt loam soil cores (Sadeghi et al. 2000); these observations indicate the importance to mobility of soil texture. However, the destruction of macropores by earthworm burrows can reduce the contribution of preferential flow, irrespective of tillage practice (Sigua et al. 1995). Higher levels of organic matter in the top layer of NT soil reduce the effect of preferential flow from increased microbial degradation, and therefore, the relative proportion of pesticide leaching in CT soil is higher (Düring and Hummel 1999; Krahe et al. 1997; Levanon et al. 1993, 1994). By analyzing the soil water retention curve of a silt loam soil, Lipiec et al. (2006) reported that the pore throat radius in the NT soil was estimated to be around 1 μm, which is much smaller than that in the matrix domain of the CT soil (110 μm). Therefore, in the absence of preferential flow, it can be concluded that the higher infiltration rate in the CT soil is caused by higher aerial porosity, resulting in increased pesticide mobility. Brown et al. (1990, 1999) reported that finer and deeper tilth had an insignificant effect on

Table 2 Effect of tillage on mobility of pesticide

No.	Pesticide	Species[a]	Type[b]	Effect (NT or RT/CT)[c]	Reference
15	Glyphosate	^{14}C	OL	*L^d*, 0.7	Fomsgaard et al. (2003b)
17	Carbofuran	f	CI	*L*, 0.2–0.5	Levanon et al. (1993)
		f	F	0.1 ppb (NT), ND (CT)	Steenhuis et al. (1990)
37	Fluometuron	ai	CI	*K*, 0.7–2.4	Wilson et al. (1998)
38	Isoproturon	ai	CI	*R*, 1.2–4.0; *K*, 1.3–3.4	Vincent et al. (2007)
		^{14}C	L	*L^d*, 0.03	Fomsgaard et al. (2003a)
62	Mecoprop	f	F	*L*, 9.1	Elliott et al. (2000)
65	Alachlor	^{14}C	CI	*L*, 1.4–2.1; *D*(5), 0.9–1.0; *K*, 0.9–1.7	Clay et al. (1991)
		f	F	0.1–0.3 ppb (NT), ND (CT)	Steenhuis et al. (1990)
67	Metolachlor	ai	CI,CP	*L*, 1.4; *L**, 1.7–2.4	Singh et al. (2002)
		f	F	*L*, 3.5–31	Hall et al. (1991)
		f	CI	*L*, 0.7–0.8	Levanon et al. (1993)
		f	CI	*L*, 0.5	Düring and Hummel (1999)
		f	F	*L*, 0.6–4.0	Fortin et al. (2002)
70	Acifluorfen	ai	CI	*L*, 0.9; *K*, 0.96–1.04	Gaston and Locke (2000)
74	Atrazine	f	F	0.1–0.4 ppb (NT), mostly ND (CT)	Steenhuis et al. (1990)
		f	F	*L*, 6.4–104	Hall et al. (1991)
		f	CI	*L*, 0.6–0.8	Levanon et al. (1993)
		f	F	*L*, 0.7–3.7	Fortin et al. (2002)
		^{14}C	CI	*L*, 2.3–9.4	Sigua et al. (1995)
78	Terbuthylazine	ai	CI,CP	*L*, 1.8; *L**, 1.6–3.7	Singh et al. (2002)
		f	CI	*L*, 0.7–0.8	Düring and Hummel (1999)
82	Bromoxynil	f	F	*L*, 1.3	Elliott et al. (2000)
83	Dicamba	f	F	*L*, 1.9–456	Hall and Mumma (1994)
		f	F	*L*, 5.1	Elliott et al. (2000)
85	Clopyralid	ai	CI	*L^d*, 1.9–5.0; *D^d*(4), 0.8–0.9	Cox et al. (1999)
93	Bentazon	^{14}C	CI	*L*, 1.1	Gaston and Locke (1996)
94	Metribuzin	ai	CI	*R*, 1.2–1.8	Dao (1995)
		ai	CI	*R*, 1.6–3.4	Vincent et al. (2007)
95	Metamitron	ai	CI	*L^d*, 0.3–0.4; *D^d*(4), 0.2–0.5	Cox et al. (1999)
		f	CI	*L*, 0.6–0.8	Düring and Hummel (1999)

[a] Applied with ai (non-labeled), f (formulation), or ^{14}C (radiolabel). [b] CP and CI, column leaching using packed (disturbed) and intact (undisturbed) soil cores, respectively; OL, outdoor lysimeter; F, field lysimeter. [c] NT, no-tilled soil; RT, reduced tillage soil; CT, conventionally tilled soil. Effect, ratio of each parameter in NT (^{d}, RT) versus CT; *L*, leached amount (% of the applied dose, ppm or ppb); *D*(*x*), distribution at top *x*-cm soil core (%); *K*, adsorption coefficient (L kg^{-1}); *R*, retardation factor ((7), dimensionless). *means the ratio for intact soils versus packed ones. ND, not detected

the distribution of a radiotracer and patterns of dye staining in the top soil layer, when compared to normal tillage using a mole plough. However, the finer tilth resulted in an increased water-holding capacity at the soil surface, thereby reducing the contribution of preferential flow and reducing the leaching of isoproturon (38).

The large variability observed in field leaching rates is known to be dependent on the distribution of macropores in the soil profile (Hall et al. 1989). Dye-staining experiments in field soil profiles have highlighted the presence of vertical macropores in NT soils, indicating the existence of preferential flow (Steenhuis et al. 1990). Reduced leaching of pesticides caused by tillage at the soil surface has been reported in many field studies, and examples are presented in Table 2. Four pesticides were subject to increased leaching to GW from NT corn plots than from CT plots; their concentrations in GW increased rapidly as a result of preferential flow, after the first major precipitation event (Isensee and Sadeghi 1995; Isensee et al. 1990). Elliott et al. (2000) reported that increased leaching from NT plots as compared to CT plots is more clearly observed for less adsorptive pesticides. Furthermore, differences in the contribution of leaching and surface runoff are considered to be responsible for the loss of pesticides in NT and CT fields. By analyzing runoff water and percolates in pan lysimeters, Hall et al. (1991) reported that losses of four herbicides via preferential flow were 3–8 times higher from the NT corn field compared to the CT field. A similar result was reported for dicamba (83) (Hall and Mumma 1994). An insignificant difference in leached amounts of atrazine (74) and metolachlor (67) was observed in RT and CT fields, where preferential flow occurred irrespective of tillage (Fortin et al. 2002). Fomsgaard et al. (2003a, b) also reported that the effect of soil tillage was insignificant on the leaching of glyphosate (15), isoproturon (38), and their metabolites in outdoor lysimeters made up of NT and CT soils.

Soil Amendment: Organic materials, such as cattle manure, plant residues, peat, sewage sludge, and fertilizers, are generally used to amend the soil surface in agricultural fields. These organic amendments are known to modify soil structure. By using mercury intrusion porosimetry and a scanning electron microscope, Cox et al. (1997) examined the effect of sprinkling olive oil mill wastewater, consisting mainly of soft tissues from olive pulp, mucilage and oil, over a field for 3 years. The fraction of larger pores in the soil having a radius of >10 μm was found to greatly decrease through the cementing and aggregating of soil particles caused by the applied organic materials. This structural change markedly reduced the leaching of clopyralid (85). However, leaching was not consistently correlated with the change in soil porosity and the influence of organic amendments on adsorption and biodegradation appeared to be having more of an effect on the extent of pesticide leaching (Cox et al. 2001; Fernandes et al. 2006). The effect of soil amendments on pesticide mobility can be evaluated by examining how chemical parameters change from the tillage effect. In most cases, a higher organic matter content from amendments increased the adsorption (K) of a pesticide to soil, resulting in a reduction in leaching ($L < 1$) and more retardation ($R > 1$), (Table 3). Soil amendment with urea did not increase DOC, but it was shown to increase the K_F of metolachlor (67), thus reducing leaching. Hence it was concluded that urea was likely to create more active adsorption sites in soil (Singh 2003). Urea also affected the soil adsorption of

Table 3 Effects of soil amendment, vegetation and elution medium on mobility of pesticides

No.	Pesticide	Species[a]	Type[b]	Soil amendment, vegetation or elution medium[c]	Effect[d]	Reference
Soil amendment						
3	Diazinon	^{14}C	CP	Raw organic materials, unaged & 2-month aging	*L*: 0.9–1.0, 0.6	Sánchez-Martín et al. (1997)
				Humic acids, solid and liquid at 12–25 mg $C\,g^{-1}$soil	*L*: 1.1, 0.01–0.08	
6	Methidathion	ai	CP	2.5-cm incorporation of dewatered sewage at 4 %	*L*: 0.6	Sánchez et al. (2003)
35	Diuron	ai	BA	+ 4 and 12 % peat	*K*: 6–16	González-Pradas et al. (1998)
		^{14}C	L	+ Plant- or plant/animal-origin organics at 10 $t\,ha^{-1}$	*L*: 0.6–1.8	Thevenot et al. (2008)
36	Chlortoluron	ai	CI	+ Liquid cattle manure 12-h pre-leaching	*L*: 0	Kördel et al. (1992)
38	Isoproturon	ai	CI	15-cm incorporation with cattle manure and buried straw	*L*: ~0.5	Johnson et al. (1997)
		f	CP	Mixed with compost and barley straw to soil (1:2:1, v/v/v)	*L*: 0.07	Fogg et al. (2004a)
39	Linuron	ai	CP	Surface incorporation of compost, peat or HA at 15 $t\,ha^{-1}$	*L*: 0.07–1.0	Sánchez-Camazano et al. (2000)
44	Tebuthiuron	^{14}C	CI	Incorporated with ground litter humus or hardwood stand	*L*: 0.03–0.4	Stone et al. (1993)
52	Ethametsulfuron-Me	ai	CP	+ Humic acids or peat at 0.5–5 %	*L*: 0.3/0.5–0.7	Si et al. (2006)
62	Mecoprop	ai	CP	+ 4 and 10 % peat	*L*: 0.7–0.9, 0.4–0.7	Matallo et al. (1999)
65	Alachlor	ai	CP	+ Sewage or corn sweetener filtrates at 0.5–8.4 $t\,C\,ha^{-1}$	*L*: 0.4–0.8/0–0.4	Guo et al. (1993)
		ai	CM	+ Digested sludge, dairy manure or cut alfalfa at 0.29 % OM	*L*: 0.6–0.9	Guo and Wagenet (1999)
67	Metolachlor	ai	CP	+ Cow manure at 2.5 and 5 % or urea at 0.6 and 1.2 mg $N\,cm^{-2}$	*L*: 0.01–0.3/0.2–0.7	Singh (2003)
		ai	BA	Incubated with cut plants at 1.7 % for 40 days	*K*: 1.1–1.5	Yen et al. (2008)
69	Metalaxyl	ai	CP	+ Humic amendments or olive oil residues at 10 %	*L*: 0.7–1.0	Fernandes et al. (2006)
		f	L	30-cm incorporation peat at 20 %	*L*: 1.6	Petrovic et al. (1996)
72	Fomesafen	^{14}C	CP	Limed soil	*L*: 1.1	Weber et al. (1993)
74	Atrazine	ai	CP	15-cm incorporation of sewage, manure or waste activated C	*L*: 0.004–0.9	Guo et al. (1991)
		ai	CP	+ Sewage sludge at 0.5 %	*R*: 1.2–1.3	Graber et al. (1997)
		ai	CP	+ 4 and 12 % peat	*L*: 0.7–0.9	Socías-Viciana et al. (1999)
75	Simazine	ai	BA	+ Liquid, solid humates or solid urban wastes at 5 %	*K*: 1.0–2.6	Cox et al. (2001)
87	Imazethapyr	^{14}C	BA	Adjustment of soil pH by addition of sulfur or $Ca(OH)_2$	*K*: 0.04 (pH 8 vs. 4)	Johnson et al. (2000)
88	Imazaquin	ai	CP	+ Olive mill wastewater or solid urban wastes at 6.25 %	*L*: 0.6–1.1/1.0–1.2	Undabeytia et al. (2004)

(continued)

Table 3 (continued)

No.	Pesticide	Species[a]	Type[b]	Soil amendment, vegetation or elution medium[c]	Effect[d]	Reference
94	Metribuzin	ai	CP	+ Urea at 0.6 and 1.2 mg $\mathrm{N\,cm^{-2}}$	*D*(10): 2.3–5.4	Singh (2006)
		ai	CP	+ Organic manure or fly ash at 2.5 and 5 %	*L*: 0.5–0.7/0–0.2	Majumdar and Singh (2007)
99	Pendimethalin	ai	BA	Incubated with cut plants at 1.7 % for 40 days	*K*: 0.7–2.6	Yen et al. (2008)
101	DDT	^{14}C	CP	Equilibrated with divalent metal cation solutions	*L*: 0.1–0.9	Lalah et al. (2009)
107	Benazolin-ethyl	^{14}C	CI	5-cm incorporation of maize straw at 10 $\mathrm{t\,ha^{-1}}$	*L*: 0.2	Schnitzler et al. (2007)
129	Triadimenol	^{14}C	L	+ Sewage sludge at 5 and 10 $\mathrm{t\,ha^{-1}}$	*L*: 1.3–1.8	Smetnik and Frost (1999)
Vegetation						
15	Glyphosate	ai	L	Rye grass coverage	*L*: 0.3	Landry et al. (2005)
35	Diuron	f	CI	Grass coverage	*L*: 0.2–0.3	Dousett et al. (2007)
67	Metolachlor	f	F	+ Pig or cow manure to CT- and RT fields	*L*: 0.3–0.7, 1.5–2.0	Fortin et al. (2002)
		^{14}C	CI	Coverage of five kinds of grasses[d]	*L*: ~0.6	Belden and Coats (2004)
69	Metalaxyl	f	L	Creeping bentgrass density at 0, 33, 66 and 100 %	*L*: 0.5–0.7	Petrovic et al. (1996)
74	Atrazine	ai	CI	Existence of corn plant residues after harvest	*L*: 0.9–5.6	Green et al. (1995)
		ai	L	Coverage of five kinds of grasses	*L*: 0.45–1.1	Lin et al. (2003)
		ai	CP	Existence of decomposed switchgrass roots	*D*(10): 1.2–1.6	Tsegaye et al. (2007)
		^{14}C	CP	Existence of decomposed alfalfa roots	*L*: 0.3–0.5	Zins et al. (1991)
		^{14}C	CP	Existence of decomposed switchgrass roots	*L*: 0.8–1.1	Mersie et al. (1999)
94	Metribuzin	ai	CP	Covered with mixtures of sand and ground fresh straw	*R*: 1.1–1.3	Dao (1995)
115	Procymidone	ai	L	Grass coverage	*L*: 0.2	Dousset et al. (2010)

4	Chlorpyrifos	^{14}C	CP	DOM extracted from organic fertilizers at 60 and 120 mg L^{-1}	*L*: 1.1	Li et al. (2005)
35	Diuron	ai	CP	Liquid and solid DOM at 5 % (w/v)	*L*: 1.4–1.6	Cox et al. (2007)
36	Chlortoluron	ai	CP	DOM extracted from sludge and straw at 50 and 150 mg L^{-1}	*L*: 1.9–2.6	Song et al. (2008)
61	MCPA	^{14}C	CP	Humic or fulvic acids at 20–40 mg OC L^{-1}	L: 0.94–1.0	Haberhauer et al. (2002)
64	Cyhalofo*p*-butyl	ai	BA	DOM extracted from composts	*K*: 0.2–0.3	Blasioli et al. (2008)
74	Atrazine	ai	CM	Fraction of methanol increasing to 50 %	*R*: 0.3	Nkedl-Kizza et al. (1987)
		ai	CI	Soil colloids at 300 mg L^{-1}	*L*:1.0–1.9	Barton and Karathanasis (2003)
		^{14}C	CI	14.8 M NH_4OH at 40 mg N cm^{-2}	*L*: 1.3–1.6	Liu et al. (1995)
74	Atrazine	^{14}C	CI	Soil fulvic acids at 50 mg L^{-1}	*L*: 1.0	Spark and Swift (1998)
		^{14}C	CP	Anionic (0.1 and 0.3 %) or cationic (0.02 and 0.3 %) surfactants	*L*: 0.2–0.7, 0.9–1.1	Abu-Zreig et al. (2000)
75	Simazine	ai	CP	Soil DOM (FA) at 60 and 80 mg OC L^{-1}	*R*: 0.96–1.3	Spurlock and Biggar (1990)
79	Prometryn	ai	CP	DOM extracted from lake sludge and rice straw at 160 mg C L^{-1}	*L*: 1.7–2.3	Jiang et al. (2008)
121	Metazoxolon	f	F	1 % Renex 30® surfactant	*D*(5): 0.9	Morrod (1982)

[a]Applied with ai (non-labeled), f (formulation) or ^{14}C (radio-label). [b]BA, batch adsorption; CP and CI, column leaching using packed (disturbed) and intact (undisturbed) soil cores, respectively; CM, miscible displacement; *L*, outdoor lysimeter; *F*, field lysimeter. [c]% of amendment on the weight basis toward soil. OC, organic carbon. OM, organic matters. DOM, dissolved organic matters. CT, conventional tillage; RT, reduced tillage. [d]Ratio of elution by amendment, vegetation or modified eluent versus control. *L*, leached amount (% of the applied dose, ppm or ppb); *D*(*x*), distribution at top *x*-cm soil core (%); *K*, adsorption coefficient (L kg^{-1}); *R*, retardation factor [(7), dimensionless]

metribuzin (94) (Singh 2006). The increased adsorption and biodegradation resulting from soil amendments reduces the leaching of pesticides in proportion to the loading rate of each material (Cox et al. 2001; Guo et al. 1991, 1993). Stone et al. (1993) reported a reduction in the amounts of hexazinone (92) and tebuthiuron (44) leached from outdoor lysimeters containing a surface layer of coarsely-ground litter humus. The authors concluded that this effect was caused by the increased retention and biodegradation of these pesticides in the lysimeters. Graber et al. (1997) demonstrated a reduction in the leaching of four triazine herbicides from an increased application of compost or sludge. When increased soil adsorption is the main contributory factor in reducing pesticide leaching, the BTC generally becomes flatter with its peak shifting to larger pore volumes (Fernandes et al. 2003; Matallo et al. 1999; Singh 2003).

Hydrophobic pesticides adsorb to organic matter mainly via van der Waals interactions, while hydrogen-bond networks towards carboxyl and phenolic-OH groups in organic matter are formed with hydrophilic pesticides. Soil amendment with potassium humates extracted from oxidized coal and lignite, rich in aliphatic and aromatic carbons as evidenced by ^{13}C-NMR, was found to be effective in reducing the leaching of diazinon (3) (Sánchez-Martín et al. 1997). Si et al. (2006) reported increased retention of ethametsulfuron-methyl (methyl ester of (52)) in soil columns amended with humic acids and peat. As a result of organic amendment, the C = O absorption in the IR spectrum of the herbicide shifted to a lower wavenumber, with the highest shifts observed for C = N and N–H, thus strongly suggesting the formation of hydrogen bonds. Inorganic materials such as fly ash can also be effective adsorbents for pesticides. Majumdar and Singh (2007) observed a marked increase in the K_F of metribuzin (94) following the addition of fly ash consisting of clay and silt particles to soil columns. The addition of flyash retarded the movement of metribuzin more than did the manure amendment.

Organic amendment does not always reduce pesticide leaching. Undabeytia et al. (2004) reported a reduction in K_F values for imazaquin (88) in soils amended with urban waste compost and olive mill waste, with an insignificant retardation in leaching. These waste materials may have acted to block the adsorption sites in soil and/or cause protonation of (88) by an increase in pH. The facilitated transport of pesticides by association with WDC and dissolved organic matter (DOM) sometimes occurs in amended soils. Socías-Viciana et al. (1999) observed reduced leaching of MCPA (61) following peat amendment as a result of its increased adsorption to soil, while atrazine (74) was observed to break though earlier in the soil columns following peat amendment at a higher loading rate and also showed a concomitant increase in the concentration of DOM in the eluates. Increased elution of diuron (35) from undisturbed soil columns amended with plant- and animal-origin composts was also observed in the outdoor study of Thevenot et al. (2008, 2009). Such results can be accounted for by the facilitated transport of (35) and (74) that was associated with DOM. A similar mechanism was also proposed for the increased downward movement of two triazine herbicides and bromacil (89) in a sludge-amended field leaching study (Graber et al. 2001). However, the higher affinity of soil organic matter towards pesticides decreased the contribution of pesticide association with DOM.

Using cow manure as a soil amendment greatly increased the DOC content of soils, but the increased K_F value of metolachlor (67), combined with reduced leaching in the amended soil indicates higher adsorption of (67) to the bulk organic matter in soil, as compared to its association with DOM (Singh 2003). Furthermore, the contribution of preferential flow sometimes makes the effect of organic amendment ambiguous, as was demonstrated in a lysimeter study with triadimenol (129); in this study, leaching was enhanced and was unaffected by the application of organic materials (Smetnik and Frost 1999).

Plant materials are also utilized as soil amendments. The soil incorporation of cut alfalfa with dairy manure was shown to increase the biodegradation rate of alachlor (65) by a factor of 1.5–2, compared with non-amended soil (Guo and Wagenet 1999). Amendment with cut maize straws markedly accelerated the degradation of benazolin (acid of (107)) in a column leaching study (Schnitzler et al. 2007). However, a limited effect on biodegradation was reported for six hydrophilic pesticides in outdoor lysimeters amended with unchopped barley straw (Fogg et al. 2004a, b) and for dinitroaniline and acetoanilide herbicides following incorporation of cut plant materials (Yen et al. 2008). The effect of organic amendment in these cases may be masked by the high humic content of the soil, as reported by Suzuki (2000). Johnson et al. (1997) utilized a dye-staining technique to visualize preferential flow pathways produced by the incorporation of straw to soil. The authors also reported increased adsorption and biodegradation of isoproturon (38) in the soil columns. The combined application of crop residues and cattle manure greatly reduced the contribution of preferential flow in the leaching of metribuzin (94) from enhanced adsorption (Dao 1995). Interestingly, adding plant materials to the soil surface without incorporation resulted in a bimodal BTC for atrazine (74), especially in soil columns containing macropores (Green et al. 1995). The fraction of (74) intercepted by plant residues during application was washed off by later percolation and was rapidly transported via macropores, while (74) reached the soil surface directly and was considered to move more slowly in the soil matrix.

Vegetation: Crops and weeds increase the organic matter content in soil. Either higher adsorption to soil or higher microbial activity in the rhizosphere can increase biodegradation, resulting in the reduction of pesticide leaching (Table 3). Less downward movement of water from increased vegetative evapotranspiration may also reduce leaching. The contribution of adsorption was confirmed by the results of a column leaching study, using undisturbed soils excavated from bare, buffer zone and grass-covered field plots (Dousset et al. 2010). The adsorption of diuron (35) and tebuconazole (127) increased in the grass-covered soil and reduced leaching. However, vegetation appeared to have less of an effect on the leaching of procymidone (115) in this study, which may be from its increased soil persistence, even in the presence of a large microbial population, and from its facilitated transport by DOM. With regard to the effects of increased microbial activity under vegetation, Hassink et al. (1994) reported a more rapid degradation of three herbicides in the surface soil of cores that were collected from a meadow planted with grasses, than in those collected from bare field soil and gravel track. In grass-covered outdoor lysimeters treated with (35), increased amounts of hydrophilic metabolites were detected in leachates, as compared with bare soil lysimeters (Jacobson et al. 2005). When outdoor lysimeters were planted with five grasses, more metabolites formed by *N*-dealkylation of atrazine (74) were observed in soil and leachates, and the volume of leachate was reduced (Lin et al. 2003). A similar effect was observed in vegetated undisturbed soil columns, but individual differences among the five grasses tested were not as marked (Belden and Coats 2004).

In contrast, pesticide leaching increased by preferential flow along root channels, where pesticide adsorption to roots was much lower than to soil (Tames and Hance 1969). Caron et al. (1996) reported that annual planting of alfalfa in a field increased the hydraulic conductivity in the subsurface soil. Following spray application of KBr to this field, a bimodal distribution of Br^- in the soil profile was observed, and higher levels of Br^- were found in the deeper soil layers. Preferential flow along decayed root macropores is also an important factor. Increased leaching of ^{14}C-alachlor (65) and ^{14}C-atrazine (74) was reported in soil cores collected from fields planted with alfalfa or switchgrass (Mersie et al. 1999; Tsegaye et al. 2007; Zins et al. 1991), and the faster transport of dicamba (83) and 2,6-difluorobenzoic acid in barley-planted soil columns that had a higher evapotranspiration rate than bare soil columns indicated a contribution from preferential flow (Pearson et al. 1996).

Turf cover and an underlying thatch or mat layer affects the leaching of herbicides. Petrovic et al. (1996) examined the leaching of metalaxyl (69) in sand lysimeters planted with creeping bentgrass at a turf density of 0–100% that had been adjusted by using a turf core aerator. The organic matter content of surface soil increased with increasing turf density and contributed to a decrease in both the peak concentration of (69) in the BTC and the total amount in the leachate. The surface verdure and thatch layers in a field lysimeter planted with creeping bentgrass trapped most of the applied ethofumesate (119) and propiconazole (131) (Gardner and Branham 2001a, b). Halofenozide (122) was similarly trapped in the thatch/mat layer of undisturbed soil columns, but a heavy irrigation event caused significant leaching from preferential flow (Starrett et al. 1996). Influence from preferential flow was also reported by Raturi et al. (2003), in a column leaching study with carbaryl (18) and triclopyr (63) that used soil cores in which 5–8-year-old thatch layers existed. The peaks in the asymmetrical BTCs of the tested pesticides were observed to occur at less than one pore volume, indicating preferential flow.

5.4 Facilitated Transport

Hydrophobic pesticides tend to be tightly adsorbed to the soil matrix, but being association with WDC and DOM sometimes facilitates their transport in soil as described in Sect. 2.2. Ballard (1971) reported that increased amounts of DDT (101) applied to a short forest soil column were released by co-application of urea. Furthermore, the application of anhydrous ammonia to soil columns increased the vertical transport of pyrethroids, atrazine (74), and toxaphene (104), with a concomitant increase of DOC content in the eluates (Liu et al. 1995; Smith and Willis 1985).

Humic substances solubilized by urea and ammonia were associated with these pesticides, which resulted in their enhanced transport. More rapid breakthrough of hydrophobic chemicals has also been observed following the addition of DOM or humic acids to the eluent in column leaching studies (Dunnivant et al. 1992a; Enfield et al. 1989; Magee et al. 1991) (Table 3). The introduction of organic fertilizers to the aqueous phase decreased the batch K_F value of chlorpyrifos (4) and resulted in its faster elution from the soil column (Li et al. 2005). Since enhanced leaching sometimes occurs for less hydrophobic pesticides that have log K_{ow} values < 3, other mechanisms such as hydrogen bonding and hydrophobic interactions may also be operable.

The effect of DOM on the leaching behavior of napropamide (114) has been thoroughly investigated by applying sewage sludge (Letey et al. 2000; Nelson et al. 1998, 2000; Williams et al. 2000, 2006). Napropamide (114) was predominantly retained in the upper soil layers of the amended soil columns, but more (114) was detected in earlier fractions of the eluates, even without any increase of eluted DOM as compared to the non-amended soil columns. These findings can be attributed to the facilitated transport of (114) and its association with DOM; a similar trend was reported in a column leaching study with metolachlor (67) (Singh 2003; Singh et al. 2002). Graber et al. (1995) reported enhanced leaching of atrazine (74) in the field, following irrigation with secondary effluent from a sewage treatment plant that contained a high content of organic matter and suspended solids. The reduced adsorption of (74) to soil in the presence of this effluent indicated the possible association of (74) with DOM. Similar behavior was reported in field leaching studies conducted with bromacil (89) and terbuthylazine (78) (Graber et al. 2001). The probability and degree of association of a pesticide with DOM is highly dependent on the origin of DOM. DOM originating from rice straw decreased the K_F value of prometryne (79) from association and increased its leaching (Jiang et al. 2008). The herbicide 2,4-D (59), which is hydrophilic, demonstrated a decreased adsorption and enhanced leaching when associated with DOM prepared from rice straw (Jiang et al. 2008), fertilizers (Li et al. 2005), and liquid olive mill wastes (Cox et al. 2001). Baskaran et al. (1994) reported that humic substances released from soil play a role in the association with (59). However, DOM displayed conflicting dual actions for diuron (35). Peat incorporation into soil retarded the transport of (35) in an amended soil column as a result of increased soil adsorption (González-Pradas et al. 1998). In contrast, elution with DOM facilitated the transport of (35), and the highest peaks in its BTC were observed at lower pore volumes (Cox et al. 2007). Another urea herbicide, chlortoluron (36), showed a higher mobility in soil TLC when developed with distilled water containing aqueous extracts of sludge and straw (Song et al. 2008). Although more (36) was eluted from the soil columns using these extracts, no peak shift was observed in the corresponding BTCs. The transport of urea herbicides may be more sensitive to the structure and properties of DOM because of their weaker interactions with DOM, as compared to the amide moiety in napropamide (114).

In batch equilibrium and column leaching studies, the effect of soil DOM on the K_d value and BTCs for simazine (75) was not existent or insignificant (Spurlock and

Biggar 1990). The UV–vis absorption of the DOM was characteristic of that of fulvic acids, which may account for the weaker interactions of DOM with (75). Haberhauer et al. (2002) investigated the different effects of humic and fulvic acids on the column leaching of MCPA (61). Humic acids increased leaching via association with MCPA (61), but fulvic acids had less of an effect. The lesser effect of fulvic acids was similarly reported in column leaching studies with five structurally different pesticides having a wide range of log K_{ow} (Spark and Swift 1998). It is important to point out that DOM can change pesticide leaching behavior from mechanisms other than association. The presence of tannic acid and peat extracts reduced soil adsorption and increased leaching for imidacloprid (117), without any (117)-DOM complexes being formed (Flores-Céspedes et al. 2002). Competition for adsorption to soil between (117) and DOM or the enhanced desorption of (117) by DOM may have played a role here. DOM was observed to have no effect on the leaching of cyhalofop (64), while the presence of potassium ion was shown to reduce leaching (Blasioli et al. 2008). The authors speculated that this may have resulted from increased soil adsorption of the inner-sphere complex, with a potassium ion formed at the carboxyl group of (64) via cation bridges.

WDC may also act as carriers for pesticides during leaching. WDC-facilitated transport in the field was reported for prochloraz (126) (Villholth et al. 2000) and pendimethalin (99) (Petersen et al. 2002). De Jonge et al. (1998) detected (126) in eluates from undisturbed sandy loam soil columns at higher concentrations than would be expected based on its soil adsorption properties. Either a lower ionic strength or a higher pH in the eluent increased the leaching of both (126) and WDC, indicating an association of (126) with WDC. However, the fraction of the associated complex was 3–13% of the total amount of (126) in the leachate and hence, the contribution of WDC-facilitated transport through macropores was not significant. Similarly, Worrall et al. (1999) reported the association of isoproturon (38) with WDC in a lysimeter study. The rapid breakthrough of (38) following rainfall coincided with the appearance of WDC in the leachates, in which approximately 12% of (38) was associated with WDC. The association of atrazine (74) with WDC was reported in the field leaching study of Sprague et al. (2000). Concentrations of both WDC and (74) at a depth of 25-cm were highest after the first leaching event and slowly decreased thereafter. Fractionation of the eluates showed 4.9–30% of (74) associated with WDC. A batch adsorption experiment, using isolated WDC and the soil matrix in the above study, showed much higher K_d values for (74) when associated with WDC (71–832 $\mathrm{L\,kg^{-1}}$) than for the soil matrix (0.5–2.5 $\mathrm{L\,kg^{-1}}$).

The contribution of WDC in facilitated transport depends on the structural properties of the pesticide. In a column leaching study, Gjettermann et al. (2009) observed that ploughing the soil surface increased the particle concentration in the leachates by a factor of 2–6, based on turbidity measurement. A higher level of association of glyphosate (15) with WDC was observed for the ploughed soil columns (68%) than for the minimally disturbed ones (17%). In contrast, the association with WDC in the ploughed columns was only 5–13% for pendimethalin (99), while DOM-facilitated transport of (99) was predominant. Interestingly, Seta and Karathanasis (1996, 1997b) reported an absence of association with WDC in the enhanced leaching of atrazine (74) and metolachlor (67) in undisturbed soil columns. The K_F values of the herbicides indicated the low extent of association with WDC (<1–5%). This may contribute to the enhanced leaching either from exclusion of the herbicides from soil adsorption sites by WDC or from reduced ion-exchange interaction of the herbicides with mineral surfaces, caused by adsorption of WDC-associated cations.

6 Modeling and Simulation

Various mathematical models have been developed to predict the potential mobility of pesticides. These models factor in several key parameters, such as water flow, soil structure, and pesticide properties; these parameters are also the ones that affect the behavior of pesticides in laboratory or field studies (i.e., laboratory column leaching studies or large-scale field lysimeter studies). The following models are rather sophisticated and are designed to assess the probability that a pesticide or its metabolites will cause GW contamination under field conditions: PRZM, PEARL, PELMO, and MACRO; these models are also used for regulatory purposes (FOCUS 2011; Klier et al. 2008; USEPA 2011). The application of MACRO, which is known to be better able to simulate macropore flow processes than the other models (FOCUS 2011; Jene et al. 1999), has indicated that leaching of moderately to strongly adsorbed pesticides that have relatively short half-lives, is increased by more than four orders of magnitude as a result of macropore flow (Larsson and Jarvis 2000). The LEACHP(M) and HYDRUS models have also been used to analyze the leaching of pesticides (Cox et al. 1996; Klier et al. 2008; Krzyszowska et al. 1994; Pearson et al. 1996; Pot et al. 2005; Walker et al. 1996). In contrast to the models listed above, which require many input parameters, the meta-models EuroPEARL (Tiktak et al. 2006) and SCI-GROW (Cohen 1998; USEPA 2011), which are based on a limited number of input parameters, can more easily be utilized to estimate pesticide levels in GW. For paddy fields, which have their own characteristic water management systems, the vadose zone fate and transport model (VADOFT) has been developed, in combination with RICEWQ to simulate water movement, and predict not only the concentration of pesticides in the water and sediment phases but also their leaching behavior (Capri and Miao 2002; Karpouzas et al. 2005; Miao et al. 2003). The DT_{50} and K_{oc} values of a pesticide are the key parameters that control leaching behavior in these simulations, but these parameters exhibit a large variability (Boesten and van der Linden 1991; Dubus et al. 2003b). Therefore, Beulke et al. (2004b) applied a probabilistic modeling approach to simulate the leaching of isoproturon (38), using DT_{50} and K_{oc} values as variables. Recently, inverse modeling approaches have been used to estimate optimal DT_{50} and K_{oc} values to emulate pesticide behavior in outdoor lysimeter studies (Dubus et al. 2004; Roulier and Jarvis 2003).

With the exception of screening models, the number of input parameters required for these mathematical models makes it very difficult, in practice, to apply them to

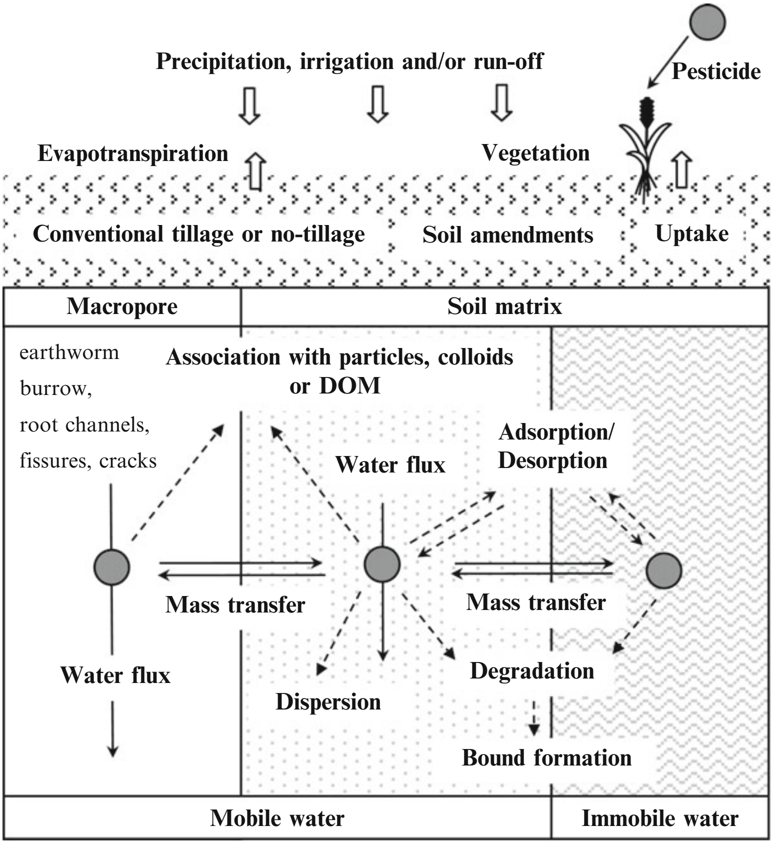


Fig. 3 Conceptual model of pesticide mobility in soil

new pesticides at early stages of development. To gain an understanding of the leaching potential of a pesticide and its metabolites, use of a laboratory soil column leaching study is convenient and effective, and its usefulness increases when it is accompanied by mathematical analyses.

6.1 Equilibrium and Nonequilibrium Transport

Water supplied by precipitation and irrigation moves horizontally and vertically in the field, as shown in Fig. 3. Pesticides are transported in soil by water movement and/or by molecular diffusion, and undergo adsorption/desorption or chemical/microbial degradation during their transport. The behavior of a pesticide molecule during leaching has been mathematically described, by generally assuming that several laws apply to them, i.e., the laws of mass conservation, flux and inter-phase mass transfer, together with the degradation terms in the liquid and solid phases (Aharonson et al. 1987; Jury and Flühler 1992; Helling and Dragun 1981; Helling and Gish 1986; van Genuchten and Wagenet 1989). In any model used, the goodness of fit should be evaluated, for example by following two indicators (Karpouzas et al. 2005) as described immediately below.

$$\text{RMSE}\ (\text{Root mean square error}) = \frac{(100/O_{\mathrm{a}})}{\left\{\sum (P_{\mathrm{i}} - O_{\mathrm{i}})^2 / n\right\}^{1/2}} \tag{8}$$

$$\text{EF (Modeling efficiency)} = 1 - \left\{\sum (P_{\mathrm{i}} - O_{\mathrm{i}})^2 / \sum (O_{\mathrm{i}} - O_{\mathrm{a}})^2\right\} \tag{9}$$

P_i and O_i are the *i*th predicted and observed values, respectively. O_a is an average of O_i and '*n*' is a sample number. Individually, the smaller the RMSE value is, and the closer the value of EF is to 1, the better the fit of the model.

The model basically describes solute transport in a homogeneous medium under steady-state flow, assuming a local equilibrium, and is represented by the classical convection–dispersion equation (CDE) below.

$$\left(1 + K_{\mathrm{d}} \times \rho / \theta\right) \partial C / \partial t + \left(q / \theta\right) \partial C / \partial x - \left(D / \theta\right) \partial^2 C / \partial x^2 + \delta = 0 \tag{10}$$

Where

C, pesticide concentration in the aqueous phase; x, distance; q, water flux; θ, volumetric water content in soil; ρ, soil bulk density; K_d, linear soil adsorption coefficient; D, dispersion coefficient; δ, apparent total first-order degradation rate in water and soil phases.

In Eq. (10), $(1 + K_d \times \rho/\theta)$ and q/θ are the retardation factor (R) and pore water velocity (v), respectively. When the adsorption of a pesticide follows the Freundlich isotherm Eq. (4), the first term should be modified to $[1 + \{(K_F \times \rho)/(\theta \times n)\} \times C^{1/(n-1)}]\ \partial C/\partial t$. Equation (10) can be analytically solved by assuming the boundary and initial conditions given below (Kluitenberg and Horton 1990; Singh and Kanwar 1991).

$$\begin{aligned} \{C(x,t) - \mathrm{Ci}\} / (C_0 - \mathrm{Ci}) &= (1/2)[\mathrm{erfc}\{(R \times x - \nu \times t) / 2(D \times R \times t)^{1/2}\} \\ &\quad + \exp(\nu \times x / D) \times \mathrm{erfc}\{(R \times x + \nu \times t) / 2(D \times R \times t)^{1/2}\}] \\ C(0,t) = C_0, C(x,0) &= \mathrm{Ci}, \partial C / \partial x\ (\infty, t) = 0, \delta = 0 \end{aligned} \tag{11}$$

The transport parameters (R, D, and q) can be estimated by fitting the equation to the experimentally obtained breakthrough curve (BTC), using a nonlinear least-squares parameter optimization method with the CXTFIT program, which is included in the STANMOD software package (Simunek et al. 1999). Nonreactive tracers such as Cl^-, Br^-, and ^3H_2O ($K_d = 0$ and $R = 1$) can be used, and these theoretically exhibit asymmetrical BTC with peaks at one pore volume in a homogeneously packed soil column. Deviation of R from 1 is sometimes reported, even when CDE fits the observed symmetrical BTC well. Anion (Cl^- and Br^-) exclusion from the charged soil surface (Green et al. 1995; Mao and Ren 2004; Pot et al. 2005;

Veeh et al. 1994), and ^3H_2O adsorption via hydroxyl charges on a clay lattice (Gaber et al. 1995; Seyfried and Rao 1987) resulted in $R<1$ and $R>1$, respectively. When pesticide leaching is conducted using a conservative tracer, the K_d value of the pesticide can be calculated from the optimized R value by using the column-specific D and q/θ value estimated for the tracer.

Alternatively, the R and D values can be estimated by analyzing the temporal moments (M_p, pth order moment; $p=0, 1, 2, 3$) of the experimental BTCs, when the relevant parameters used in the transport equation are defined in a dimensionless form (Kamra et al. 2001; Vincent et al. 2007). M_0, M_1, M_2, and M_3 represent the mass of solute eluted from a column, and the mean, variance and skewness of the BTC, respectively.

$$M_{\mathrm{p}} = \int_0^\infty T^{\mathrm{p}} \times C(X,T)/C_0\,\mathrm{d}T \tag{12}$$

Where

$C = C/C_0$ (input concentration); $X = x/L$ (column length);

$T = \nu \times t/L$; P (Peclet number) $= \nu \times L/D$

The normalized and central moments μ_1' and μ_{p} can then be expressed below.

$$\mu_1' = \frac{M_p}{M_0} \tag{13}$$

$$\mu_p = (1/M_0) \times \int_0^\infty (T - \mu_1')^{\mathrm{p}} \times C(X,T)/C_0\,\mathrm{d}T \tag{14}$$

For example, the moments μ_1', μ_2, and μ_3 can be described by the transport parameters for the pulse input of a solute with a duration of T_0, when the local equilibrium model is assumed.

$$\mu_1' = R + 1/(2T_0), \quad \mu_2 = 2R^2/P + 1/\left(12T_0{}^2\right), \quad \mu_3 = 12R^3/P^2 \tag{15}$$

Kamra et al. (2001) applied the above two methods to analyze the leaching potential for atrazine (74) and isoproturon (38) in undisturbed soil columns, and reported a better fit by CXTFIT than from using the moment method. The CXTFIT Eq. (10)–(11) and moment Eq. (12)–(15) methods can be used to estimate transport parameters for application to the nonequilibrium transport models described below.

The asymmetrical BTC of a pesticide, with tailing, has been explained by either using a chemical or physical nonequilibrium model. Chemical nonequilibrium is generally supposed when a conservative tracer shows a symmetrical BTC and can be described by the so-called two-site model. In this model, the instantaneous equilibrium adsorption of the pesticide at one site (site 1) and the time-dependent kinetic adsorption at the other site (site 2) are assumed. When the fraction of site 1 is 'F' and a linear adsorption isotherm is assumed, the two-site model can be expressed by Eq. (16)–(18) in accordance with the similar laws taken for the derivation of CDE.

$$C_{S1} = F \times K_d \times C \tag{16}$$

$$\partial C_{S2} / \partial t = \alpha_1 \times \left[(1 - F) \times K_d \times C - C_{S2} \right] \tag{17}$$

$$\begin{gathered}(1 + F \times K_d \times \rho / \theta) \partial C / \partial t + (q / \theta) \partial C / \partial x - (D / \theta) \partial^2 C / \\ \partial x^2 + (\rho / \theta) \partial C_{S2} / \partial t + \delta_s = 0\end{gathered} \tag{18}$$

where

C_{S1} and C_{S2}, pesticide concentration in sites 1 and 2 of soil, respectively;

α_1, first-order kinetic adsorption rate constant; δ_s, apparent first-order degradation rate.

When the BTC of a conservative tracer is asymmetrical with tailing, the physical nonequilibrium process (two-region model) can be supposed to exist. By assuming an equilibrium adsorption, the two-region model divides soil pore water into mobile (region 1) and immobile (region 2) water regions, each of which is in equilibrium with a fraction '*F*' and '1–*F*' of a soil phase. The solute exchange between the two regions is defined by the first-order mass transfer rate coefficient (α_2). The two-region model can be similarly derived as Eq. (10), but without the convection–dispersion term for region 2, as expressed below. Subscripts 'm' and 'im' are the mobile and immobile water regions, respectively.

$$\begin{gathered}\text{Region1}: (1 + F \times K_d \times \rho / \theta_m) \partial C_m / \partial t + (q / \theta_m) \partial C_m / \\ \partial x - (D_m / \theta_m) \partial^2 C_m / \partial x^2 + (\alpha_2 / \theta_m) \times (C_m - C_{im}) + \delta_m = 0\end{gathered} \tag{19}$$

$$\begin{gathered}\text{Region2}: \{1 + (1 - F) \times K_d \times \rho / \theta_{im}\} \partial C_{im} / \\ \partial t - (\alpha_2 / \theta_{im}) \times (C_m ??? C_{im}) + \delta_{im} = 0\end{gathered} \tag{20}$$

Under the same initial and boundary conditions, the dimensionless transport equations of the physical and chemical nonequilibrium models are known to become mathematically identical (van Genuchten and Wagenet 1989). Therefore, the nonequilibrium dimensionless transport equations have been more conveniently utilized to analyze for the BTCs of pesticides (Mao and Ren 2004; Raturi et al. 2003). The following two parameters are used to evaluate the contribution of each nonequilibrium process.

Chemical nonequilibrium (two-site model): Physical nonequilibrium (two-region model):

$$\beta = (1 + F \times \rho \times K_d / \theta) / R \tag{21}$$

$$\omega = \{\alpha_1 \times (1 - \beta) \times R \times L\} / \nu \tag{22}$$

$$\beta = (\theta_m + F \times \rho \times K_d) / (\theta + \rho \times K_d) \tag{23}$$

$$\omega = \alpha_2 \times L / q \tag{24}$$

In the two-site model, β Eq. (21) is the fraction of instantaneous solute retardation and represents the influence of the distribution of sorption between the two sites and ω Eq. (22) is the Damkohler number that describes the ratio of a hydrodynamic residence time to a characteristic time for sorption. The absence of kinetic sorption sites ($F=1$) means $\beta=1$, and a smaller ω value indicates an increased contribution of chemical nonequilibrium. In the two-region model, the parameter β Eq. (23) represents the distribution of soil water between the two regions and ω, as defined in Eq. (24), expresses the ratio of a hydrodynamic residence time to a characteristic time of solute movement within the immobile water region.

6.2 Application of Mathematical Models

For solute transport in a chemical nonequilibrium process, the two-site model has been successfully applied to analyze the asymmetric BTCs of simple benzene derivatives (Angley et al. 1992), triazine herbicides (Gamerdinger et al. 1990; Graber et al. 1997; Suárez et al. 2007), 2,4-D (59) (Baskaran et al. 1996; Estrella et al. 1993), and sulfonylurea herbicides (Gonzalez and Ukrainczyk 1999; Heistermann et al. 2003). The fraction of kinetic sorption sites for triazines increased with increasing organic matter content in soil (Graber et al. 1997), and the mass transfer rate of nicosulfuron (54) was neither correlated with K_d nor soil organic matter content (Gonzalez and Ukrainczyk 1999). Incidentally, the facilitated transport of pesticides by DOM can be evaluated by substituting the K_d value in the transport equations with the apparent adsorption coefficient K_d^{app} that is defined in Eq. (1) (Dunnivant et al. 1992a; Flores-Céspedes et al. 2002; Khan and Thomson (1990); Worrall et al. 2001). The enhanced transport of PCB at higher concentrations of DOM was well simulated by the two-site model using a log K_{DOM} value of 5.1 (Dunnivant et al. 1992a). Magee et al. (1991) reported the importance of further considering the soil adsorption of DOM as an additional process in the DOM-facilitated transport of phenanthrene.

Beigel and Di Pietro (1999) applied the two-site model to describe the asymmetrical BTCs of triticonazole (130) in a packed soil column, in which physical nonequilibrium transport was considered to be unlikely based on the symmetrical BTC of Cl^-. The large α_1 value in the model, indicating quick transport of (130) to kinetic adsorption sites ($F=0.43$), described the first part of the tailing well. However, the model failed to explain the extended slower release of (130) from the column, which might be accounted for by nonequilibrium sorption or bound residue formation. The introduction of a third irreversible adsorption site was necessary to describe the asymmetric BTCs of fluometuron (37) that was observed in soil columns containing either vegetated or no-till soils (Wilson et al. 1998). In addition to the two-site model, other models have also been applied to simulate the chemical nonequilibrium process. Pignatello et al. (1993) introduced a two-compartment spherical diffusion model considering an effective intra-particle diffusion coefficient, to examine the leaching of two aged herbicides in native soils. The release patterns of the herbicides were better described by this model than by the first-order kinetic adsorption model, and >80% of the aged herbicides were estimated to be present in the slower sorption compartment. Other authors have also reported that diffusion into soil aggregates controlled the time-dependent sorption of four pesticides in structured soils (van Beinum et al. 2005, 2006; Villaverde et al. 2009). The asymmetrical BTCs of atrazine (74) were dependent on pore water velocity and column length and were analyzed by assuming γ distribution for both the sorption rate and adsorption coefficient (Chen and Wagenet 1997).

The symmetrical BTC of a conservative tracer does not always indicate the absence of a physical nonequilibrium process in the column leaching experiment. For example, Veeh et al. (1994) obtained the *R* value of 0.7–0.8 through the CXTFIT analysis of the symmetrical Br^- BTC. An anion exclusion effect could not fully account for the *R* values lower than unity, which was well described by the two-region model when immobile water was present. The two-region model was shown to be useful in describing similar leaching profiles to those outlined above obtained in an outdoor lysimeter study with atrazine (74) using conservative tracers (Schoen et al. 1999b), and Seyfried and Rao (1987) used the two-region model to describe the effect of changing water tension at 0–1 kPa on the symmetry in the BTCs of ^3H_2O. By varying pore water velocity in a column leaching experiment, Gaber et al. (1995) examined the relative contribution of chemical and physical nonequilibrium processes in solute transport. The greater contribution of physical nonequilibrium at a higher pore water velocity caused the BTC of ^3H_2O to become more asymmetrical, and this change in symmetry was well described by the two-region model. The authors observed an asymmetrical BTC for (74), with an earlier breakthrough at higher pore water velocity, indicating the involvement of both nonequilibrium processes.

The adsorption coefficient and degradation rate in soil are generally obtained by the batch equilibrium method and incubation in a biometer-like flask or flow-through system, respectively. However, the two-region model is sometimes unable to accurately predict an asymmetrical BTC for a pesticide by using these values. Gaston and Locke (1996) reported that optimization of the degradation rate in each region of this model was necessary to better simulate the asymmetrical BTCs of bentazon (93) in undisturbed soil columns. Kinetic adsorption was introduced to the two-region model by Spurlock et al. (1995) to describe the BTC of monuron (34). Gaston and Locke (2000) similarly introduced kinetic adsorption to the two-region model to describe the leaching of acifluorfen (70) in undisturbed soil columns, the soil degradation rate in the column was also optimized, and this was reported to give a good description of the BTC of (70). Interestingly, preferential flow along root channels in packed soil columns planted with switchgrass was accounted for by the larger dispersion coefficient in the mobile water region of the two-region model (Tsegaye et al. 2007). Poulsen et al. (2006) applied the two-region model to describe the transport of colloids. They reported low *R* values (<0.7), which are soil-independent, together with high pore water velocities, and concluded that a size exclusion mechanism was operational in colloid transport.

In addition to the two-site and two-region models, several other approaches have been developed to analyze solute leaching. The stream tube model (STM) defines the soil as a set of stream tubes wherein advective transport occurs without either local dispersion or interaction with other stream tubes. Vanderborght et al. (2002) applied this model to the preferential flow of two fluorescence tracers in undisturbed soils. Compared to the two-region model, the STM model overpredicted the timing of leaching of the tracers, with leaching occurring too early, and gave a poor fit to their BTCs in the deeper soil cores that have a dense network of macropores, thus indicating the importance of lateral mixing between macropores and the adjacent soil matrix. Hall (1994) further introduced the concept of slow and fast mobile phases for the movement of water, but failed to describe well the leaching behavior of dichlorprop (60) in a lysimeter. A concept has been introduced in the dual permeability (DP) model in which a porous medium is divided into two mobile water regions, conveniently named micropores (matrix) and macropores (fracture region) (Köhne et al. 2006; Pot et al. 2005). The mass transfer rate coefficient at the interface of these two regions is controlled by the shape and characteristic length of soil aggregates. By using the DP model, Köhne et al. (2002) discovered that the low diffusion coefficient of a solute in fine-textured aggregate skins intensifies the preferential solute leaching through macropores. Furthermore, Pot et al. (2005) divided the micropores (matrix) into mobile (M) and immobile (IM) water (two-region DP-MIM model), which could simulate the Br^- BTCs with a dual peak in the undisturbed soils well. With regard to the soil adsorption process, Jørgensen et al. (1998) utilized a two-dimensional model, in which the spacing and aperture of fractures play a role, to investigate the leaching behavior of pesticides in large cores of structured clayey soil; they found that nonequilibrium adsorption to the fracture walls and soil matrix was important. Köhne et al. (2006) added kinetic adsorption into the DP model (DP-KM) to analyze the leaching behavior of isoproturon (38) and terbuthylazine (78). The leaching of both herbicides in the tilled loamy (A_p) soil columns was well described by DP-KM, and only the DP model was able to provide a moderate fit to the extremely early breakthrough curves of these herbicides, which resulted from preferential flow in the no-till sandy (A_h) soil.

7 Mobility of Pesticides in Soil Column Leaching Studies

The mobility of pesticides in various chemical classes has been examined by using the soil column leaching method. Although many of these studies followed regulatory guidelines (i.e., OECD and US EPA), experimental conditions among them varied considerably. Such conditions include column size (diameter and length), the type of elution media, the flow rate and duration of elution, the method of application and soil structure (packed or intact); and the variability in experimental conditions makes it impossible to quantitatively compare pesticide mobility between studies. The retardation factor Eq. (7) is one of the most important and useful parameters when evaluating pesticide mobility; unfortunately, this factor is only available for a limited number of studies, in which mathematical analyses of data were conducted. Therefore, any qualitative analysis or comparison of existing studies is only possible by using the physicochemical properties or test conditions provided for the test pesticides. A representative data set from a range of pesticide soil column leaching studies is presented in Tables 4–7. Dissipation half-lives (DT_{50}) and batch adsorption coefficients (K_d or K_{oc}) measured in the same soils as used in the column leaching studies are useful for calculating a mobility index, and for conducting mathematical modeling, but their availability is limited. Typical values for these parameters can be obtained from the review by Roberts et al. (1998), and the database produced in the EU-funded FOOTPRINT project (PPDB 2009). These values may be useful guides when considering the leaching behavior of pesticides. However, soil characteristics such as pH, clay mineralogy and content of colloids and metal cations affect the existing form of an ionizable pesticide, and result in different soil-pesticide interactions. Furthermore, the possible deviation in K_d (K_{oc}) and DT_{50} from measured values, under flow conditions, should be kept in mind as described in Sect. 4.

Although soil column leaching studies provide an indication of the potential mobility of pesticide in soil, the significant leaching of a pesticide from a laboratory soil column does not necessarily mean that contamination of GW under field conditions will occur. When the estimated concentration of a pesticide in GW at 1 m depth exceeds 0.1 ppb, from using FOCUS groundwater simulations, the more reliable outdoor lysimeter studies may be conducted as a refinement step in the EU (re) registration procedure (FOCUS 2011). Maximum concentration data for several currently registered EU pesticides and their metabolites, measured at 1 m depth in outdoor lysimeter studies, were obtained from EU peer-review reports (EFSA 2011; EU 2011). The data were then plotted against their laboratory K_{oc} and DT_{50} values and are shown in Fig. 4. The concentrations of most pesticides, irrespective of their K_{oc} and DT_{50} values, did not exceed the regulatory trigger value of 0.1 ppb, whereas significant breakthrough was reported for a large number of these pesticides in laboratory column leaching studies. Hydrophilic metabolites that had K_{oc} values <100 were more frequently detected at higher concentrations than 0.1 ppb. Soil column leaching studies can provide a good indication of potential pesticide mobility, but the extent of this mobility should be confirmed by an outdoor lysimeter study, because many different factors operate in the field (viz, meteorological conditions and variable soil properties and structure) that cannot easily be created in the laboratory. To make the opposite point, negligible leaching of a pesticide from a laboratory soil column does not necessarily indicate that there is no concern for GW contamination under field conditions. When a pesticide is applied at 100 $g\,ha^{-1}$ to a lysimeter with a surface area of 1 m^2, and the total volume of leachate is 250 L (OECD 2000), the EU trigger value of 0.1 ppb is equal to a 0.25% breakthrough of the applied pesticide. It is usually difficult to trace such a small amount of pesticide with reasonable precision, unless a radiolabeled form of the pesticide is applied in sufficient amounts to allow for quantitation.

Organophosphorus, Carbamate and Pyrethroid Pesticides: A summary literature survey for these groups is presented in Table 4. The organophosphorus pesticides

Table 4 Soil column leaching of organophosphorus, carbamate, pyrethroid pesticides

No.	Pesticide	Species and appl[a]	No. of soil and amendment[b]	DT$_{50}$[c] K[d]	Column properties[e]	Flow medium[f] Flow conditions[g]	Leachate, Soil (%)[h] R[i]	
Organophosphorus								
1	Parathion	^{32}P	8	na	C, d, U, na	DW	na, na	Swoboda and Thomas (1968)
		P, L	cellulose	4.4–13*	2.7 cm id × ^{14}Cm	10.5 cm h^{-1}	na	
2	Fenitrothion	^{14}C	1	20 days	C, d, U and A (60 days), na	DW	16, 85(U); 6–40, 66(A)#	Takimoto et al. (1976)
		P, L		na	2.5 cm id × 20 cm	100 ml	na	
3	Diazinon	ai	1	17–22 days	C, d, U, na	DW	ND, 9–12	Lopetz-Avila et al. (1986)
		P, L		2.2*	4.8 cm id × 40 cm	1.6 cm × 2day^{-1}, 30 days	na	
		^{14}C	2	na	C, d, U, na	DW	30–39, 37–29	Arienzo et al. (1994)
		P, L		1.4–2.0	5 cm id × 30 cm	4.3 mm h^{-1}, 12 days	na	
5	Azinphos-methyl	ai	1 sand	na	C, d, U, na	10 mM CaCl$_2$	70–80, na	Farran and Chentouf (2000)
		C, L	bentonite	26–40	1 cm id × 15 cm	19 cm h^{-1}	na	
6	Methidathion	ai	1	7 days	C, d, U, Cl^{-}	DW	47, 13	Sánchez et al. (2003)
		P, L	TDTMA	45	5.4 cm id × 5 cm	1.3 cm h^{-1},8 h day^{-1},3 days	3.8	
7	Fosthiazate	f	3	na	C, dd, A(2 days), na	DW	0.004–0.09, 5.8–0.4	Karpouzas et al. (2007)
		P, L		na	7.5 cm id × 50 cm	s, 61 days	na	
8	Fenamiphos	^{14}C	3	na	C, d, U, na	5 mM CaCl$_2$	ND, na	Bilkert and Rao (1985)
		P, L		1.2–9.6	4.4 cm id × 40 cm	na	na	
9	Phorate	^{14}C	2	na	C, d, U, na	10 mM CaCl$_2$	ND–6, 93–90	Baskaran et al. (1996)
		P, L		20–34	2.7 cm id × 20 cm	2.1 cm h^{-1}	na	
10	Terbufos	^{14}C	2	na	C, d, U, na	10 mM CaCl$_2$	ND–5, 96–87	Baskaran et al. (1996)
		P, L		24–35	2.7 cm id × 20 cm	2.1 cm h^{-1}	na	
11	Acephate	ai	2	16–29 days	C, d, U, na	5 mM CaSO$_4$	ND–98 ppm, na	Yen et al. (2000)
		P, L		0.02–0.18	7.5 cm id × 27 cm	5 mm day^{-1}, 7 days	na	
		^{14}C	4	na	C, d, U, na	DW	0.6–6.7, 99–46	Sánchez-Camazano et al. (1994)
		P, L		0.7–3.3	5 cm id × 30 cm	0.2 mm h^{-1}, 15 days	na	
12	Methamidophos	ai	2	1.6–12 days	C, d, U, na	5 mM CaSO$_4$	ND–67 ppm, na	Yen et al. (2000)
		P, L		0.25–0.28	7.5 cm id × 27 cm	5 mm day^{-1}, 7 days	na	

12	Methamidophos	f	2times	na	C, d, U, na	5 mM $CaCl_2$	44–61, na	Koleli et al. (2006)
		P, L		0.0–10.2	3 cm id × 30 cm	2.1 cm h^{-1}, 7 days	na	
		^{14}C	2	na	C, d, U, na	DW	ND–7.6, na	Ismail et al. (2002)
		P, L		0.4–0.98	2.5 cm id × 15 cm	10–100 mm, 48 h	na	
15	Glyphosate	ai	1	8–14 days	C, u, U, Cl^-	DW	ND, na	Zhou et al. (2010)
		C, L		na	4 cm id × 15 cm	8 mm h^{-1}, 6.7 days	na	
		ai	3	8–14 days	C, u, A(2 days), na	DW	0.001–0.01, na	Dousset et al. (2004)
		C, L		na	15 cm × 20 cm	0.45 mm h^{-1}, 12 days	na	
16	Glufosinate-NH_4^+	ai	1	11 days¶	C, dd, U, na	DW	0.003, na	Behrendt et al. (1990)
		P, O/L		0.45‡	30 cm × 1 m	s, 260 days	na	
Carbamate								
17	Carbofuran	ai	2	3–10mon	C, d, U, na	5 mM $CaSO_4$	1.2–43, 51–8.2	Yen et al. (1997)
		P, L		0.14–0.44*	18 cm id × 33 cm	0.08 mm h^{-1}, 34–48 days	na	
		ai	2	na	C, d & u, U, na	Deionized water	4–81, 84–9	Farahani et al. (2008)
		P, L		0.9–2.9*	5 cm id × 25 cm	1.1 mm h^{-1}, 14 days	na	
18	Carbaryl	ai	2	na	C, u, U, Br^-	1 mM $CaCl_2$	61–76, na	Raturi et al. (2003)
		P, L	Thatch	1.9–44	10 cm id × 10.7 cm	1 cm h^{-1}, 6–7PV	13–31	
19	Mexacarbate	^{14}C	2	na	C,dd,U and A(30 days), na	Water	ND–10, 86–37	Sundaram (1997)
		P, L		na	5.6 cm id × 30 cm	508 mm, 13–19 h	na	
20	Aldicarb	ai	1	0.8 days	C, d, A(1–11 days), na	10 mM $CaCl_2$	ND–24, na	Fava et al. (2001)
		P, L		0.4*	4 cm id × 30 cm	6.2 mm h^{-1}, 4 days	na	
		ai	4	~2 days	C, u, U, na	Water	20–72#, na	Leistra et al. (1976)
		P, L		na	12 cm id × 25–50 cm	0.5–1.2 mm h^{-1}	na	
		f	1	6–11 days	C, u, U, Br^-	Water	0.4, na	Vink et al. (1997)
		P, L		0.8	29.5 cm id × 51 cm	s, 587 mm, 280 days	na	
		^{14}C	1	na	R, dd, U, na	DW	27–44, na	Morgan et al. (1995)
		P, L		5‡	15 × 5 × 60 cm	0.44 mm h^{-1}, 3–4 L	1.8–2.3	

(continued)

Table 4 (continued)

No.	Pesticide	Species and appl[a]	No. of soil and amendment[b]	DT$_{50}$[c] K[d]	Column properties[e]	Flow medium[f] Flow conditions[g]	Leachate, Soil (%)[h] R[i]	
21	Benthiocarb	ai	1	na	C, d, U, na	10 mM $CaCl_2$	ND, 12	Aktar et al. (2009)
		P, L		na	6 cm id × 30 cm	na, 30 days	na	
		f	2	na	C, u, U and A (31 days), na	Irrigation water	5–10, 79	Doran et al. (2008)
		P, L		na	10 cm id × 10 cm	0.2 mm h^{-1}, 10 days	na	
		ai	2	na	C, d, U, Cl^-	5 mM $CaSO_4$	na, na	Chiang et al. (2001)
		C, L		na	4.35 cm id × 12 cm	1.4 and 2.9 cm h^{-1}	51–110	
22	Molinate	ai	5	na	C, d, U, na	Water	na, 90–84	Gray and Weierich (1968)
		P, L		na	1.7 in. id × 9–24in	8 in.	na	
23	Pirimicarb	ai	2	1.2mon	C, u, A(6 days), Br^-	10 mM $CaCl_2$	2–7, 68–60	Taboada et al. (1994)
		P, L		1.2–2.3	12 cm id × 24 cm	0.8 mm h^{-1}, ~55 cm	na	
24	Carbendazim	ai	1	6.5mon	C, d, U, na	Water	77, na	Aharonson and Kafkafi (1975)
		P, L		3.5	4.5 cm id × 22 cm	107 cm, 12 days	na	
Pyrethroid								
25	Phenothrin	^{14}C	3	1–2 days	C, d, U and A (14 days), na	DW	ND, 95–33#	Nambu et al. (1980)
		P, L		na	2.5 cm id × 20 cm	6–8 cml h^{-1}, 0.3 L	na	
26	Permethrin	^{14}C	2	6–12 days	C, d, U and A (21 days), na	Water	ND–2.6#,100–97#	Kaneko et al. (1978)
		P, L		na	2.5 cm id × 20 cm	1–6 cm h^{-1}, 0.3 L	na	
		ai	6	na	C, d, U, na	Water	0–15, 75–62	Ismail and Kalithasan (2004)
		P, L		11–52	2.5 cm id × 20 cm	7.8 mm day^{-1}, 14 days	na	
		ai	1	na	C, d, U, na	DW	0.04–0.08, 92	Smith and Willis (1985)
		P, L		na	10.2 cm id × 40 cm	2.4 mm h^{-1}, 3PV	na	
27	Bifenthrin	ai	1	na	C, d, U, na	Water	ND, 75	Manoj and Gajbhiye (2007)
		P, L		222	1.1 cm id × 25 cm	3.7 cm h^{-1}, 0.24 L	na	
28	Fenpropathrin	^{14}C	4	11–17 days	C, d, U and A (28 days), na	Water	0.3–47#, 98–41#	Sakata et al. (1990)
		P, L		na	3 cm id × 25 cm	0.4 cm h^{-1}, 1 L	na	

29	Cypermethrin	^{14}C	4	4–56 days	C, d, U and A (30 days), na	Water	0.3–31#, 90–41#	Sakata et al. (1986)
		P, L		na	2.5 cm id × 25 cm	0.6 cm h^{-1}, 1 L	na	
30	*β*-Cyfluthrin	ai	1	16–26 days	C, d, U, na	Water	ND, 75–66	Gupta and Gupta and Gajbhiye (2002b)
		P, L		na	7 cm id × 25 cm	1.6 cm h^{-1}, 2 L	na	
31	Deltamethrin	^{14}C	4	na	C, d, U, $^{3}H_2O$	5 mM $CaCl_2$	3.0–8.8, 93–77	Selim and Zhu (2002)
		P, L		13–98	6.4 cm id × 10 cm	1.3 cm h^{-1}, 3–5PV	na	
		^{14}C	3	na	C, d, U, na	DW	ND, 98–97#	Kaufman et al. (1981)
		P, L		na	7.6 cm id × 30.5 cm	1PV	na	
32	Fenvalerate	^{14}C	4	0.5–3mon	C, d, U and A (30 days), na	Water	ND–1.2#,96–53#	Ohkawa et al. (1978)
		P, L		na	2.5 cm id × 20 cm	0.3 L	na	
		ai	1	na	C, d, U, na	DW	0.04, 97	Smith and Willis (1985)
		P, L		na	10.2 cm id × 40 cm	2.4 mm h^{-1}, 3PV	na	

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[a] Applied with ai (non-labeled), f (formulation) or ^{14}C (radio-label); continuously (C) or as a pulse (P) in laboratory (L) or outdoors (O). [b] TDTMA, tetradecyl trimethyl ammonium bromide. Thatch, bentgrass and zoysiagrass thatch layer. [c] Half-life in aerobic metabolism using the corresponding soils (20–25°C). ¶, estimated values by a mathematical analysis. [d] Adsorption coefficient estimated by the Freundlich ($L^{1/n}\,mg^{1-1/n}\,kg^{-1}$) or linear (*, L kg^{-1}) isotherm. ‡, estimated values by a mathematical analysis. [e] Shape/C, cylinder; R, rectangular: Soil packing/days, disturbed or packed soil; dd, depth-wise packed soil; u, undisturbed or intact soil: Aging/U, unaged; A, aged (period): Tracer. id, internal diameter. [f] DW, distilled water. [g] Flow rate (natural (n)/simulated (s) rainfall or total volume), period. PV, pore volume. [h] Percent of pesticide based on the applied dose. # means total %. [i] R, retardation factor (dimensionless) estimated from a breakthrough curve. na, not available. ND, not detected

Table 5 Soil column leaching of urea and sulfonylurea herbicides

No.	Pesticide	Species and appl[a]	No. of soil and amendment[b]	DT_{50}[c] K[d]	Column properties[e]	Flow medium[f] Flow conditions[g]	Leachate, Soil (%)[h] R[i]	Reference
Urea								
33	Fenuron	ai	1	na	C, d, A(<4 days), Cl^-	5 mM $CaSO_4$($CaCl_2$)	na, na	Spurlock et al. (1995)
		P, L		0.7	8 mm id × 15 cm	80–100PV	1.6–3.7	
34	Monuron	ai	1	na	C,d,A(8–240 days),Cl^-	5 mM $CaSO_4$$CaCl_2$)	na, na	Spurlock et al. (1995)
		P, L		5.2	48 mm id × 15 cm	80–100PV	6.0–6.4	
35	Diuron	ai	1	na	C, d, U, ^3H_2O	5 mM $CaCl_2$	~80, na	Nkedl-Kizza et al. (1987)
		C, L		1.4	2.5 cm id × 30 cm	5.6 cm h^{-1}, na	1.9–4.7	
		ai	1	16 days	C, d, A(7,14 days), na	10 mM $CaCl_2$	30–82, na	Fava et al. (2006)
		P, L		2.7	>4 cm id × 30 cm	0.6 cm h^{-1}, 3 days	na	
		ai	3	4–8mon	C, u, U, na	DW	3–19, 43–27	Landry et al. (2004)
		P, L		na	15 cm id × 20 cm	10PV, 15 days	na	
		ai	4	na	C, u, U, na	rainwater	0.1–0.8, 13–6.6	Landry et al. (2006)
		P, O		na	15 cm id × 20 cm	n, 673 mm, 1y	na	
		^{14}C	1	na	C, d, U, Cl^-	DW	0.1, 107.6	Weber and Whitacre (1982)
		P, L		na	9.7 cm id × 30.5 cm	0.5 mm h^{-1}, 30 days	na	
36	Chlortoluron	ai	2	na	C, d, U, na	DW	23–28, na	Fouqué-Brouard and Fournier (1996)
		C, L		0.7–1.5	1.5 cm id × 30 cm	1.7 cm h^{-1}, 1–3 days	na	
		ai	1	na	C, u, U, na	DW	7, 48	Kördel et al. (1992)
		P, L		~2	11.5 cm id × 36 cm	385 mm, 4 days	na	
		f	1	30 days	C, u, A(1–28 days), Br^-	DW	<1, ~60 (28 days)	van Beinum et al. (2006)
		P, L		7.0	23.7 cm id × 30 cm	30 mm, 5.5 h	na	
37	Fluometuron	ai	2	na	C, d, U, na	5 mM $CaCl_2$	na, na	Crisanto Herrero and Lorenzo Martín (1991)
		P, L		1.5–4.6	8.8 cm id × <30 cm	0.5 mm h^{-1}, 14 days	na	
		f	1	na	C, d, U,	DW	56, na	Hance et al. (1981)
		P, L		1.4–3.0	5 cm id × 30 cm	206 mm	na	

38	Isoproturon	ai	2	na	C, d, U, na	DW	18–19, na	Fouqué-Brouard and Fournier (1996)
		C, L		0.5–1.0	1.5 cm id × 30 cm	1.7 cm h^{-1}, 1–4 days	na	
38	Isoproturon	ai	3	8–25 days$^{\#}$	C, u, U, Br^-	5 mM $CaCl_2$	na, 41–64	Vincent et al. (2007)
		P, L		2–15$^{\#}$	^{14}Cm id × 30 cm	3 mm h^{-1}, 3–9 weeks	2.1–10.8	
		ai	4	33–59 days	C, u, A(3–57 days), na	Water	<0.1–0.5, na (57 days)	Renaud et al. (2004)
		P, O		1.0–3.6	23.5 cm id × 30 cm	24 mm, 8 h	na	
		f	1	na	C, u, U, Br^-	artificial rain	9–38, na	Lennartz (1999)
		P, L		0.65	5.4 cm id × 10 cm	0.23 mm h^{-1}, 6 weeks	4.5–5.4	
39	Linuron	ai	1	na	C, d, U, Cl^-	DW	~50, 17	Sánchez-Camazano et al. (2000)
		P, L		10–51	5 cm id × 40 cm	1.3 mm h^{-1}, 33 days	na	
		ai	1	na	C, d, U, na	DW	8–42, 63–31	Haouari et al. (2006)
		P, L		2.1	5 cm id × 30 cm	1.5 cm h^{-1}, 500 mm	na	
		ai	1	14 days	C, d, A(7,14 days), na	10 mM $CaCl_2$	48–84, na	Fava et al. (2006)
		P, L		5.7	>4 cm id × 30 cm	6.3 mm h^{-1}, 3 days	na	
40	Metobromuron	ai	2	na	C, d, U, na	DW	5–10, na	Fouqué-Brouard and Fournier (1996)
		C, L		0.4–2.1	1.5 cm id × 30 cm	1.7 cm h^{-1}, 12–14 h	na	
41	Chloroxuron	ai	2	na	C, d, U, na	DW	1–4, na	Fouqué-Brouard and Fournier (1996)
		C, L		0.7–7.7	1.5 cm id × 30 cm	1.7 cm h^{-1}, 4–15 days	na	
42	Difenoxuron	ai	2	na	C, d, U, na	DW	4–15, na	Fouqué-Brouard and Fournier (1996)
		C, L		1.9–2.7	1.5 cm id × 30 cm	1.7 cm h^{-1}, 2–3 days	na	
43	Thiazafluron	ai	3	66 days	C, d, U, na	10 mM $CaCl_2$	64–89, na	Cox et al. (1996)
		P, L		0.7–2.0	5 cm id × <30 cm	0.5 mm h^{-1},10 days	na	
		ai	3	15–45 days	C, d, U, na	10 mM $CaCl_2$	72–90, na	Celis et al. (2001)
		P, L		0.7–2.0	2.3 cm id × 20 cm	0.5 mm h^{-1},10 days	na	

(continued)

Table 5 (continued)

No.	Pesticide	Species and appl[a]	No. of soil and amendment[b]	DT_{50}[c] K^d	Column properties[e]	Flow medium[f] Flow conditions[g]	Leachate, Soil (%)[h] R[i]	Reference
44	Tebuthiuron	^{14}C	4	na	C, d, U, Cl^-	DW	0.7–81, 90–17	Weber and Whitacre (1982)
		P, L		na	9.7 cm id × 30.5 cm	0.5 mm h^{-1}, 40 days	na	
45	Buthidazole	^{14}C	4	na	C, d, A (30 days), Cl^-	DW	14–19#, 71–56#	Weber and Peeper (1982)
		P, L		na	9.5 cm id × ~30 cm	0.5 mm h^{-1}, 45 days	na	
Sulfonylurea								
46	Chlorsulfuron	ai	4	na	C, d, U, na	5 mM $CaCl_2$	na, na	Mersie and Foy (1986)
		P, L		1.0–2.4	9.7 cm id × 30 cm	0.5 mm h^{-1}, 14 days	na	
		ai	1	26–46 days	C, d, U, na	DW	na, ~10 (40–50 cm)	Vischetti and Businelli (1992)
		P, L		0.83	na × 50 cm	s, 84 days	na	
		ai	4	na	C, u, U, na	DW	na, na	Beckie and McKercher (1990)
		P, L		na	10 cm id × 40 cm	1 cm h^{-1}, 3–10 h	na	
		^{14}C	2	na	C, d and u, U, Br^-	DW	na, na	Veeh et al. (1994)
		P, L		0.006–0.07	5 cm id × 30 cm	2 mm h^{-1}, 2PV	0.55–1.33	
47	Metsulfuron-Me	ai	2	na	C, d, U, na	DW	na, na	Günther et al. (1993)
		P, L		na	7.5 cm id × 29 cm	2.1 mm h^{-1}, 20 days	na	
		f	2	na	C, d, U, na	DW	ND, 45	Abdulla et al. (2001)
		P, L		5.4–39	11 cm id × 25 cm	0.2 mm h^{-1}, 10 days	na	
		^{14}C	1	66–110 days	C, u, U, Br^-	DW	23–37, 8.2–4.2	Heistermann et al. (2003)
		P, L		0.32#	21 cm id × 28 cm	0.35 mm day^{-1}, ~57 days	na	
49	Triasulfuron	ai	2	na	C, d, U, na	DW	na, na	Günther et al. (1993)
		P, L		na	7.5 cm id × 29 cm	2.1 mm h^{-1}, 28 days	na	
		ai	4	>140 days	C, u, A(3–57 days), na	Water	0.3–9.4, na (57 days)	Renaud et al. (2004)
		P, O		0.03–1.4	23.5 cm id × 30 cm	24 mm, 8 h	na	
50	Primisulfuron-Me	^{14}C,f	4	na	C, u, U, na	Rainwater	0.1–2.3, 59–31#	Weber et al. (2006)
		P, O		na	20 cm id × 91 cm	515–644 mm,128 days	na	

51	Tribenuron-Me	^{14}C	2	na	C, u, U, $^{3}H_2O$	Artificial rain	7–78, 80–12	Riise et al. (1994)
		P, L		0.5–2.3	10 cm id × 24 cm	1 mm h^{-1}, 7 days	na	
52	Ethametsulfuron-Me	ai	3	13–36 days	C, d, U and A (30 days), na	10 mM $CaCl_2$	24–58, 68–25 (U)	Si et al. (2005)
		P, L		1.7–5.5	3.5 cm id × 38 cm	2.1 cm h^{-1}, 25 h	na	
52	Ethametsulfuron	ai	4	na	C, u, U, na	DW	na, na	Beckie and McKercher (1990)
		P, L	Agral 90	na	10 cm id × 40 cm	1 cm h^{-1}, 3–10 h	na	
54	Nicosulfuron	ai	12	na	C, d, U, Cl^-	5 mM $Ca(NO_3)_2$	na, na	Gonzalez and Ukrainczyk (1999)
		P, L		0.9–8.8	2.5 cm id × 15 cm	3.7 cm h^{-1}, 2PV	1.4–10.5	
55	Rimsulfuron	f	2	2.2–7.5 days	C, d, U, Cl^-	DW	na, na	Martins and Mermoud (1999)
		C, L		2.8×10^{-3}	5 cm id × 35 cm	102 cm, 2 weeks	1.0–1.5	
57	Sulfosulfuron	ai	2	na	C, d, U, na	DW	19–22, 76–63	Srivastava et al. (2006)
		P, L		na	8.5 cm id × 36 cm	7.4 mm h^{-1}, 2.5 days	na	
58	Imazosulfuron	^{14}C	4	40 days	C, d, U and A (30 days), na	10 mM $CaCl_2$	<0.3–0.6, 100–81 (U)	Mikata et al. (2001)
		P, L		0.96–1.6	4 cm id × 29 cm	1.6 cm h^{-1}, 35 h	na	

[b] Agral 90, (nonylphenoxy)polyethoxyethanol surfactant. [c] Half-life in aerobic metabolism using the corresponding soils (20–25 °C). The other keys are same as those in Table 4

Table 6 Soil column leaching of arylalkanoate, acetoanilide, diphenyl ether and triazine pesticides

No.	Pesticide	Species and appl[a]	No. of soil and amendment[b]	DT_{50}[c] K[d]	Column properties[e]	Flow medium[f] Flow conditions[g]	Leachate, Soil (%)[h] R[i]	Reference
Arylalkanoate								
59	2,4-D	ai	1	3–9 days	C, d, U, na	DW	39–47, <0.5	Lopetz-Avila et al. (1986)
		P, L		0.14*	4.8 cm id × 40 cm	1.5 cm × 2 day^{-1}, 30 days	na	
		^{14}C	5	na	C, d, U, na	DW	na, na	Grover (1977)
		P, L		0.1–1.3	2 cm id × 25 cm	1.9 cm h^{-1}	na	
		^{14}C	2	na	C, d, U, na	10 mM $CaCl_2$	12–43, 82–55	Baskaran et al. (1996)
		P, L		3.4–17	2.7 cm id × 20 cm	2.1 cm h^{-1}	4.5–20.8	
60	Dichlorprop	ai	3	na	C, d, U, Cl^-	DW	96–100, ND	Matallo et al. (1999)
		P, L		0.4–0.6	9.3 cm id × 10 cm	3–4PV	na	
		^{14}C	2	na	C, u, U, ^3H_2O	DW	59–92, na	Riise et al. (1992)
		P, L		0.5–1.8	10 cm id × 18–25 cm	0.5 mm h^{-1}	na	
61	MCPA	^{14}C	2	na	C, d, U, na	20 mM $CaCl_2$	ND–79, 82–14	Haberhauer et al. (2002)
		P, L		na	4.9 cm id × 10 cm	21 cm	na	
62	Mecoprop	ai	3	na	C, d, U, Cl^-	DW	98–104, ND	Matallo et al. (1999)
		P, L		0.4–0.5	9.3 cm id × 10 cm	3–4PV	na	
63	Triclopyr	ai	2	na	C, u, U, Br^-	1 mM $CaCl_2$	67–84, na	Raturi et al. (2003)
		P, L	Thatch	0.3–2.5	10 cm id × 10.7 cm	1 cm h^{-1}, 6–7PV	2.8–3.2	
		f	1	na	C, d, U, na	DW	ND, 4.5	Lee et al. (1986)
		P, L		na	8.9 cm id × 40 cm	25 mm, every 2nd d	na	
64	Cyhalofop	ai	2	0.6–14 days	C, d, U, na	DW	ND, 85–43	Blasioli et al. (2008)
		P, L		0.5–3.0	3.5 cm id × 16 cm	32 mm h^{-1}, 5 h	na	
Acetoanilides								
65	Alachlor	ai	1	15 days	C, d and u, U, Br^-	DW	0.01–0.6, 33	Heyer and Stan (1995)
		P, L		na	na × 30 cm	2.1 mm h^{-1}, 9 days	na	
		ai	2	4–7 days	C, u, U, Br^-	1 mM $CaSO_4$	na, ND	Sonon and Schwab (2004)
		P, L		na	7.5 cm id × 110 cm	3.5–5PV	na	

65	Alachlor	f	1	17 days	C, u, U, na	n	0.3, na	Walker et al. (1996)
		P, O		1.1	11 cm id × 30 cm	168 days	na	
		^{14}C	3	na	C, d, U, $^{3}H_2O$	5 mM $CaCl_2$	na, na	Selim et al. (2002)
		P, L		0.6–1.8	3.15 cm id × 30 cm	2–3 cm h^{-1}	2.6–4.1	
		^{14}C	1	na	C, u, U, Br^-	Water	14–27, na	Clay et al. (1991)
		P, L		3.2–6.0	15 cm id × 15 cm	5 mm h^{-1}, 11.6PV	na	
67	Metolachlor	ai	1	18 days	C, d, U, na	DW	ND–34, 100–65	Kim and Feagley (1998)
		P, L		1.5	5.4 cm id × 26 cm	1–3PV	na	
		ai	2	na	C, d and u, U, Br^-	Water	16–38, 79–57	Singh et al. (2002)
		P, L		na	8 cm id × 14.5 cm	2–3 cm h^{-1}	na	
		f	1	na	C, u, U, Br^-	Water	2–12, na	Düring and Hummel 1999
		P, L		na	20 cm id × 30–40 cm	0.2–0.4 mm h^{-1}, 4PV	na	
		^{14}C	4	na	C, d, U, na	Deionized water	4–44, 91–51	Weber et al. (2003)
		P, L		1.3–5.6	5 cm id × 30 cm	1.3 cm, every 4 h, 10 days	na	
		^{14}C, f	4	na	C, u, U, na	Rainwater	ND–2.8, 65–42$^{\#}$	Weber et al. (2006)
		P, O		na	20 cm id × 91 cm	515–644 mm,128 days	na	
68	Butachlor	ai	2	na	C, d, U, Cl^-	5 mM $CaSO_4$	na, na	Chiang et al. (2001)
		C, L		na	4.35 cm id × 12 cm	1.4, 2.9 cm h^{-1}	39–90	
69	Metalaxyl	ai	1	66 days	C, d, U, na	10 mM $CaCl_2$	64–69, na	Fernandes et al. (2006)
		P, L		0.3	5 cm id × 20 cm	1.1 mm h^{-1}, 10PV	na	
Diphenyl ether								
70	Acifluorfen	^{14}C	1	74–169 days	C, u, U, Br^-	10 mM $CaCl_2$	35–57, 55–37	Gaston and Locke (2000)
		P, L		0.5–0.8	10.2 cm id × 30 cm	0.65 mm h^{-1}, 40 days	na	
71	Chlomethoxyfen	ai	2	na	C, d, U, Cl^-	5 mM $CaSO_4$	na, na	Chiang et al. (2001)
		C, L		na	4.35 cm id × 12 cm	1.4,2.9 cm h^{-1}	443–1,735	
72	Fomesafen	^{14}C	4	na	C, d, U, Cl^-	Water	ND–11, 87–62	Weber et al. (1993)
		P, L		na	10 cm id × 30.5 cm	0.5 mm h^{-1}, 40 days	na	

(continued)

Table 6 (continued)

No.	Pesticide	Species and appl^{a}	No. of soil and amendment^{b}	DT$_{50}$^{c} K^{d}	Column properties^{e}	Flow medium^{f} Flow conditions^{g}	Leachate, Soil (%)^{h} R^{i}	Reference
72	Fomesafen	^{14}C	1	na	C, u, U, na	n	ND–100	Guo et al. (2003)
		P, O		1.74	7.5 cm id × 50 cm	367 mm, 2mon	na	
73	Oxyfluorfen	ai	6	15–242 days	C, d, U, na	10 mM $CaSO_4$	ND, ~70	Yen et al. (2003)
		P, L		52–755	7 cm id × 21 cm	1.1 mm h^{-1}, 30 days	na	
Traizines								
74	Atrazine	ai	1	73–78 days	C, d, U, na	DW	48–53 (total)	Lopetz-Avila et al. (1986)
		P, L		0.5*	4.8 cm id × 40 cm	1.5 cm × 2 day^{-1}, 30 days	na	
		ai	1	na	C, d, U, $^{3}H_2O$	5 mM $CaCl_2$	~90, na	Nkedl-Kizza et al. (1987)
		C, L		0.15	2.5 cm id × 30 cm	5.6 cm h^{-1}, na	1.4–2.0	
		ai	1	na	C, u, U, Cl^-	DW	~100, na	Zhou et al. (2010)
		C, L		na	4 cm id × 15 cm	8 mm h^{-1}, 6.7 days	4.6	
		f	3	2–23 mon	C, d, U, Br^-	Deionized water	<0.1–4.6, 65–43	Bedmar et al. (2004)
		P, L		2.6–3.1*	15.3 cm × 30 cm	900 mm, 40 days	7.5–8.8	
		f	1	22 days	C, u, U, na	n	1.8, na	Walker et al. (1996)
		P, O		0.95	11 cm id × 30 cm	168 days	na	
		^{14}C	2	na	C, d, U, na	10 mM $CaCl_2$	22–28, 69–65	Baskaran et al. (1996)
		P, L		2.7–3.0	2.7 cm id × 20 cm	2.1 cm h^{-1}	na	
		^{14}C	2	na	C, d, U, na	Deionized water	75–81, <27	Abu-Zreig et al. (2000)
		P, L		na	5 cm id × 19 cm	14–16 mm h^{-1}, 40 h	na	
		^{14}C	1	6–77 days	C, dd, U, na	n + irrigation	7, ~18	Cherrier et al. (2005)
		P, O		1.0*	19.8 cm id × 30 cm	65 days	na	
		^{14}C	2	na	C, u, U, $^{3}H_2O$	Artificial rain	18–95, 73–3	Riise et al. (1994)
		P, L		0.3–3.1	10 cm id × 24 cm	1 mm h^{-1}, 7 days	na	
		^{14}C,f	4	na	C, u, U, na	Rainwater	ND–1.7, 47–39$^{\#}$	Weber et al. (2006)
		P, O		na	20 cm id × 91 cm	515–644 mm,128 days	na	

75	Simazine	ai	2	50 days	C, d, U, na	Water	~40, ND	Calderón et al. (2004)
		P, L		1.3	5 cm id × 25 cm	0.6 mm h^{-1}	na	
75	Simazine	f	2	na	C, d, U, na	DW	28–33 (total, 8 days)	Hogue et al. (1981)
		P, L		na	4 cm id × 30 cm	4 mm h^{-1}, 2–8 days	na	
		f	1	na	C, d, U,	DW	7.5, na	Hance et al. (1981)
		P, L		2.3–3.2	5 cm id × 30 cm	20.6 cm	na	
		f	1	20–25 days	C, u, U, Br^{-}	Water	0.1, na	Vink et al. (1997)
		P, L		4.8	29.5 cm id × 51 cm	s, 587 mm, 280 days	na	
76	Cyanazine	f	1	20 days	C, u, A(1–28 days), Br^{-}	DW	ND, ~40 (28 days)	van Beinum et al. (2006)
		P, L		2.9	23.7 cm id × 30 cm	30 mm, 5.5 h	na	
77	Prometon	^{14}C	1	na	C, d, U, Cl^{-}	DW	0.1, 87.4	Weber and Whitacre (1982)
		P, L		na	9.7 cm id × 30.5 cm	0.5 mm h^{-1}, 30 days	na	
78	Terbuthylazine	ai	2	na	C, d and u, U, Br^{-}	Water	3–11, 91–81	Singh et al. (2002)
		P, L		na	8 cm id × 14.5 cm	2–3 cm h^{-1}, 0.6 L	na	
		f	1	na	C, u, U, Br^{-}	artificial rain	na, na	Lennartz (1999)
		P, L		2.1	5.4 cm id × 10 cm	5.5 mm day^{-1}, 6weeks	11.1	
		f	2	63 days$^{\#}$	C, u, U, Br^{-}	Water	na, na	Köhne et al. (2006)
		P, L		3.7–12	14.7 cm id × 15 cm	30 mm × 3–4	na	
80	Terbutryn	ai	3	na	C, d, U, na	Water	na, na	Wu and Santelmann (1975)
		P, L		na	5.5 cm id × 30 cm	127 mm	na	

[b] The keys are same as those in Table 4

Table 7 Soil column leaching of miscellaneous pesticides

No.	Pesticide	Species and appl[a]	No. of soil and amendment[b]	DT$_{50}$[c] K^{d}	Column properties[e]	Flow medium[f] Flow conditions[g]	Leachate, Soil (%)[h] R[i]	Reference
83	Dicamba	ai	1	73–77 days	C, d, U, na	DW	62–86, ND	Lopetz-Avila et al. (1986)
		P, L		0.11*	4.8 cm id × 40 cm	1.5 cm × 2 day^{-1}, 30 days	na	
		ai	1	10–17 days#	C, dd, U, Br^{-}	Water	37–63, na	Krzyszowska et al. (1994)
		P, L		na	8.4 cm id × 50 cm	0.5 mm h^{-1}, 3 days	na	
		^{14}C	1	38 days	C, d, U and A (~42 days), Br^{-}	3 mM CaCl$_2$	10–85, 57–9	Comfort et al. (1992)
		P, L		0.01–0.06#	5 cm id × 29 cm	5 mm h^{-1}, 2PV	1.0–1.2	
84	Picloram	ai	4	>>5 days	C, d, U, na	DW	90–96, na	Celis et al. (2005)
		P, L		na	3 cm id × 20 cm	9 mm h^{-1}, 4–5PV	na	
		ai	1	13–87 days#	C, dd, U, Br^{-}	Water	36–52, na	Krzyszowska et al. (1994)
		P, L		<0.26	8.4 cm id × 50 cm	0.5 mm h^{-1}, 3 days	na	
85	Clopyralid	ai	3	stable	C, d, U, na	10 mM CaCl$_2$	82–90, na	Cox et al. (1996)
		P, L		0.01–0.05	5 cm id × <30 cm	0.5 mm h^{-1}, 10 days	na	
		ai	3	na	C, d, U, na	10 mM CaCl$_2$	>90, na	Celis et al. (2001)
		P, L		0.01–0.05	2.3 cm id × 20 cm	2.5 mm h^{-1}, 10 days	na	
86	Pyrithiobac	^{14}C	4	na	C, u, U, Br^{-}	5 mM Ca(NO$_3$)$_2$	0.04–1, 73–28	Matocha and Hossner (1999)
		P, L		na	10 cm id × 20 cm	1.5–11 cm h^{-1}, 2PV	na	
87	Imazethapyr	ai	1	na	C, u, U, Br^{-}	Deionized water	62–64, na	O'Dell et al. (1992)
		P, L		0.1–1.2*	30 cm id × 68 cm	1.3 mm h^{-1}, 2PV	na	
		^{14}C	1	>30 days	C, d, U and A (~28 days), na	Water	na, 95–65	Johnson et al. (2000)
		P, L	pH	0.5–14*	2.2 cm id × 15 cm	1.5PV	na	
88	Imazaquin	ai	3	na	C, d, U, na	DW	85–97, na	Undabeytia et al. (2004)
		P, L		0.06–0.6	3 cm id × 24 cm	1.5 mm h^{-1}, 0.4 L	na	
		^{14}C	2	na	C, d, U, na	Water	0.3–73, 100–26	Regitano et al. (2002)
		P, L		1.4–1.9	5 cm id × 30 cm	400 mm, 4 days	na	

		^{14}C	4	na	C, d, U, na	Deionized water	52–94, 44–6	Weber et al. (2003)
		P, L		0.6–2.4	5 cm id × 30 cm	1.3 cm, every 4 h, 10 days	na	
89	Bromacil	^{14}C	1	na	C, d, U, Cl$^-$	DW	4.8, 86.8	Weber and Whitacre (1982)
		P, L		na	9.7 cm id × 30.5 cm	0.5 mm day^{-1}, 30 days	na	
		^{14}C, f	1	na	C, d, U, na	Water	100, na	Tan and Singh (1995)
		P, L		na	7 cm id × 8 cm	2.4 cm h^{-1}, 4PV	na	
90	Terbacil	ai	4	na	C, d, U, na	10 mM CaCl$_2$	87–101, na	Mora et al. (1997)
		P, L		0.2–1.1	5.5 cm id × 20 cm	0.5–1.1 mm h^{-1}, 2 months	2.1–4.7	
		f	2	na	C, d, U, na	DW	65–82, 16–6	Hogue et al. (1981)
		P, L		na	4 cm id × 30 cm	0.42 cm h^{-1}, 2–8 days	na	
91	Lenacil	ai	1	46 days	C, u, U, Br$^-$	Water	ND, na	Cuevas et al. (2008)
		P, L		1.6	20 cm id × 24 cm	18 mm	na	
92	Hexazinone	ai	2	47–91 days	C, d, U, na	Water	83–97, ND	Calderón et al. (2004)
		P, L		0.2–0.7	5 cm id × 25 cm	0.6 mm h^{-1}	na	
		ai	3	20–91 days	C, u, A (2 days), na	DW	2–14, na	Dousset et al. (2004)
		C, L		na	15 cm × 20 cm	0.45 mm h^{-1}, 12 days	na	
93	Bentazone	ai	3	>1mon	C, d, U, Cl$^-$	Water	na, na	Romero et al. (1996)
		P, L		0.04–0.6	9 cm id × 10 cm	0.6–1.1 cm h^{-1}, 26 days	0.9–1.3	
		ai	1	na	C, d, U, na	10 mM CaCl$_2$	76, 1	Hua et al. (2009)
		P, L		na	5.4 cm id × 34 cm	200 mm, 48 h	na	
		f	1	41 days	C, u, A (1–28 days), Br$^-$	DW	13, ~80 (28 days)	van Beinum et al. (2006)
		P, L		0	23.7 cm id × 30 cm	30 mm, 5.5 h	na	
94	Metribuzin	ai	1	na	C, d, U, na	DW	75, ~16	Smith and Willis (1985)
		P, L		na	10.2 cm id × 40 cm	2.4 mm h^{-1}, 3PV	na	
		ai	1	16 days	C, d, U, na	DW	ND–89, 81–11	Kim and Feagley (1998)
		P, L		1.1	5.4 cm id × 26 cm	1–3PV	na	
		ai	2	5–6 days	C, dd, U, na	Water	na, 34 (7 days)	Khoury et al. (2003)
		P, L		0.2–1.0	3 cm id × 30 cm	0.3–0.4 mm h^{-1}, 15 days	na	

(continued)

Table 7 (continued)

No.	Pesticide	Species and appl^a	No. of soil and amendment^b	DT$_{50}$^{c} K^d	Column properties^e	Flow medium^f Flow conditions^g	Leachate, Soil (%)^h R^i	Reference
94	Metribuzin	f	3	2–5months	C, d, U, Br$^-$	Deionized water	15–83, 2–0.6	Bedmar et al. (2004)
		P, L		1.1–2.1*	15.3 cm × 30 cm	900 mm, 40 days	3.6–5.6	
		f	1	11 days	C, u, U, na	*n*	3.4, na	Walker et al. (1996)
		P, O		0.7	11 cm id × 30 cm	168 days	na	
		^{14}C	1	na	C, u, U, Cl$^-$	Deionized water	12, 6	Locke et al. (1994)
		P, L		0.4	10 cm id × 10 cm	1.3–2.5cm × 6, every 7 days	2.2	
95	Metamitron	ai	1	na	C, d, U, na	10 mM CaCl$_2$	93, na	Goicolea et al. (1991)
		P, L		0.3	9 cm id × 30 cm	3.5 mm h^{-1}, 5PV	na	
		ai	3	14 days	C, d, U, na	10 mM CaCl$_2$	12–63, na	Cox et al. (1996)
		P, L		0.6–2.2	5 cm id × <30 cm	0.5 mm h^{-1},10 days	na	
		ai	1	<1 days	C, d, U, na	10 mM CaCl$_2$	16, na	Cox et al. (1997)
		P, L		4.1*	5 cm id × 20 cm	5.3 mm h^{-1}, 1.5PV	na	
		f	1	na	C, u, U, Br$^-$	Water	0.3–12, na	Düring and Hummel 1999
		P, L		na	20 cm id × 30–40 cm	4–10 mm day^{-1}, 4PV	na	
96	Chloridazon	ai	1	na	C, d, U, na	10 mM CaCl$_2$	83, na	Goicolea et al. (1991)
		P, L		0.4	9 cm id × 30 cm	3.5 mm h^{-1}, 5PV	na	
		ai	1	83 days	C, u, U, Br$^-$	Water	ND, na	Cuevas et al. (2008)
		P, L		2.6	20 cm id × 24 cm	18 mm	na	
97	Norflurazon	ai	4	na	C, d, U, na	DW	41–99, 17–1	Morillo et al. (2004)
		P, L		0.4–2.8	3 cm id × 24 cm	1.5 mm h^{-1}, 25PV	na	
		^{14}C, f	1	na	C, d, U, na	Water	48, na	Tan and Singh (1995)
		P, L		na	7 cm id × 8 cm	2.4 cm h^{-1}, 4PV	na	

98	Trifluralin	ai	1	na	C, d, U, na	DW	0.003, 40	Smith and Willis (1985)
		P, L		na	10.2 cm id × 40 cm	2.4 mm h^{-1}, 3PV	na	
		ai	1	43 days	C, d, U, na	DW	<0.1, 100–75	Kim and Feagley (1998)
		P, L		10	5.4 cm id × 26 cm	1–3PV	na	
99	Pendimethalin	ai	1	na	C, d, U, na	10 mM CaCl$_2$	ND, 29	Aktar et al. (2009)
		P, L		na	6 cm id × 30 cm	na, 30 days	na	
		ai	1	na	C, d, U, na	Water	0.4, >90	Chopra et al. (2010)
		P, L		na	5 cm id × 60 cm	2.1 mm h^{-1}, 6 days	na	
100	Oryzalin	ai	1	na	C, d, U, na	10 mM CaCl$_2$	ND, 85	Aktar et al. (2009)
		P, L		na	6 cm id × 30 cm	na, 30 days	na	
		ai	3	1.2 months	C, u, U, na	DW	ND–4, 22–15	Landry et al. (2004)
		P, L		na	15 cm id × 20 cm	10PV, 15 days	na	
		ai	4	na	C, u, U, na	rainwater	0.02–0.4, 5–1	Landry et al. (2006)
		P, O		na	15 cm id × 20 cm	*n*, 673 mm, 1y	na	
101	DDT	^{14}C	3	na	C, d, U, na	10 mM CaCl$_2$	1–22, 9	Lalah et al. (2009)
		P, L		280	4.7 cm id × 17 cm	4–5 mm h^{-1}, 48 h	na	
102	Chlorobenzilate	ai	2	4–9 days	C, d, U, na	5 mM CaSO$_4$	ND, 100–90	Wang et al. (1994)
		P, L		8–26*	8 cm id × 30 cm	8 mm h^{-1}, 18 days	na	
103	Endosulfan	^{14}C	2	na	C, d, U, na	DW	ND–0.12, na	Ismail et al. (2002)
		P, L		6.7–19	2.5 cm id × 15 cm	10–100 mm, 48 h	na	
105	Flurtamone	^{14}C	3	na	C, d, U, Cl^{-}	Deionized water	ND, 120–80	Mueller and Banks (1991)
		P, L		2.7–6.2	7 cm id × 28 cm	2PV	na	
106	Dithiopyr	f	1	11–19 days	C, d, U, na	Water	0.02–0.04, ~100	Gupta and Gajbhiye (2002a)
		P, L		0.2–0.7	7 cm id × 25 cm	1.6 cm h^{-1}, 2.5 L	na	

(continued)

Table 7 (continued)

No.	Pesticide	Species and appl[a]	No. of soil and amendment[b]	DT_{50}[c] K[d]	Column properties[e]	Flow medium[f] Flow conditions[g]	Leachate, Soil (%)[h] R[i]	Reference
108	Azoxystrobin	ai	1	na	C, d and u, U, na	DW	ND, 100–90	Ghosh and Singh (2009)
		P, L		na	5.9 cm id × 30 cm	3.7 cm h^{-1}, 1–3PV	na	
		f	1	61 days	C, u, A (1–28 days), Br^{-}	DW	0.1, 95 (28 days)	van Beinum et al. (2006)
		P, L		11	23.7 cm id × 30 cm	30 mm, 5.5 h	na	
109	Fipronil	f	2	na	C, u, U and A (31 days), na	Irrigation water	10–20, ~72	Doran et al. (2008)
		P, L		na	10 cm id × 10 cm	5 mm day^{-1}, 10 days	na	
110	Flumetsulam	^{14}C	2	na	C, d, U and A (3,5 days),na	Deionized water	6–45, 78–39	Tingle et al. (1999)
		P, L		na	5 cm id × 25 cm	1PV	na	
111	Sulfentrazone	ai	6	na	C, d, U, na	Water	0–23, 100–80	Ohmes and Mueller (2007)
		P, L		0.01–0.7*	7.6 cm id × 27 cm	1PV	na	
112	Buthiobate	^{14}C	2	1–3mon	C, d, A (35 days), na	Water	0.2–1.3#, 100–99#	Ohkawa et al. (1976)
		P, L		na	2.5 cm id × 20 cm	51 cm	na	
113	Thifluzamide	ai	1	>30 days	C, d, U, na	Water	0.1–5, 77–72	Gupta and Gajbhiye (2004)
		P, L		9.6	7 cm id × 25 cm	7.8 mm h^{-1}, 2 L	na	
114	Napropamide	^{14}C	1	na	C, u, U, Cl^{-}	4 mM $CaSO_4$	na, na	Elabd et al. (1986)
		P, L		2.0	10 cm id × 15 cm	1.7 mm h^{-1}, 38 days	10.1	
115	Procymidone	ai	1	na	C, u, U, Br^{-}	Water	24–90, na	Dousset et al. (2010)
		P, L		4.2*	5 cm id × 20 cm	183 cm × 3, every 2 weeks	na	
117	Imidacloprid	f	1	na	C, d, U, na	Water	29–45, 71–56	Gupta et al. (2002)
		P, L		na	7 cm id × 25 cm	1.6 cm h^{-1}, 2.5 L	na	
118	Thiamethoxam	ai, f	1	46–301 days	C, d, U, na	Water	66–79, na	Gupta et al. (2008)
		P, L		na	7 cm id × 25 cm	1.1 cm h^{-1}, 2.5 L	na	

120	Sulcotrione	^{14}C	1	16–74 days	C, dd, U, na	n + irrigation	15, ~8	Cherrier et al. (2005)
		P, O		1.3*	19.8 cm id × 30 cm	65 days	na	
123	Fenpropimorph	^{14}C	2	58 days	C, d, U, na	Deionized water	ND, ~100	Stockmaier et al. (1996)
		P, L		46–79*	5 cm id × 30 cm	20 cm, 48 h	na	
124	Fentin acetate	^{14}C	1	~40 days	C, d, U, na	Water	ND, 19	Barnes et al. (1973)
		P, L		na	2.5 cm id × 25 cm	2.4 cm h^{-1}, 6 weeks	na	
125	Imazalil	^{14}C	2	na	C, d, U, Cl^-	5 mM $CaSO_4$	ND, 99–81	van Leemput et al. (1986)
		P, L		na	4.2 cm id × 40 cm	4 mm h^{-1}, 3 h day^{-1}, 6 days	200–1,222	
126	Procloraz	^{14}C	1	na	C, u, U, Br^-	10 mM $CaCl_2$	0.02–5.8, 98–80	de Jonge et al. (1998)
		P, L		48	20 cm id × 20 cm	10 mm h^{-1}, 27 h	na	
128	Triadimefon	ai	1	na	C, d, U, na	DW	ND, 94	Singh (2005)
		P, L		1.4	5.9 cm id × 20 cm	2.2 cm h^{-1}, 3PV	na	
		ai	2	8–13 days	C, dd, U, na	Water	na, 23–20$^{\#}$	Khoury et al. (2001)
		P, L		1.9–11	3 cm id × 30 cm	580–825 mm, 18 days	na	
130	Triticinazole	^{14}C	1	na	C, d, U, Cl^-	Milli-Q water	na, na	Beigel and Di Pietro (1999)
		P, L		1.3–1.7$^{\#}$	5.5 cm id × 6.5 cm	5.2 cm h^{-1}, 16PV	3.3–4.0	
132	Tricyclazole	ai	1	97 days	C, d, U, na	10 mM $CaCl_2$	9–19, 28–26	Fernandes et al. (2006)
		P, L		3.6	5 cm id × 20 cm	1.1 mm h^{-1}, 10PV	na	

[a] pH, the pH effect was examined. The other keys are same as those in Table 4

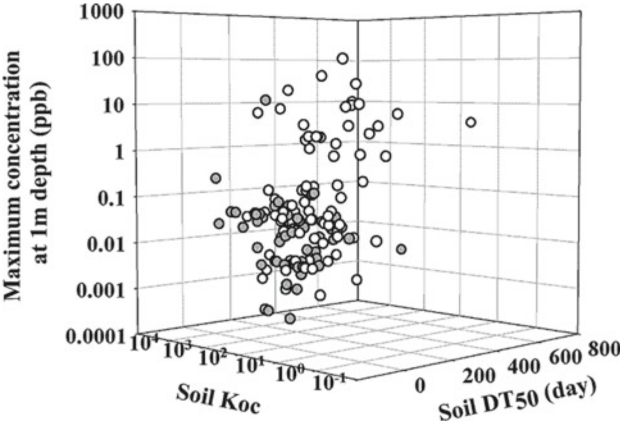


Fig. 4 Outdoor lysimeter results of the existing pesticides in the European Union Pesticide (gray circle), metabolite (open circle). K_{oc}, arithmetic mean; DT_{50}, geometric mean

include a variety of chemical structures, and members of the group exhibit a wide range of soil adsorption properties (log K_{oc} of 1–4) and are characterized by rapid to moderate degradation in soil. Hydrophobic phorate (9) and terbufos (10) were predominantly retained in disturbed soil columns, whereas very hydrophilic acephate (11) and methamidophos (12), with log $K_{oc} < 1$, exhibited a higher leaching rate. Significant breakthrough was reported for nonionizable but hydrophilic diazinon (3), azinphos-methyl (5), and methidathion (6), whereas insignificant amounts were detected in the leachates for the much more hydrophilic compounds glyphosate (15) and glufosinate (16). The ionizable (15) and (16) scarcely leached from soil columns; this behavior was accounted for by their tight adsorption to soil organic matters via Ca^{2+}-bridging and iron oxides on clay surfaces (Behrendt et al. 1990; Dousset et al. 2004). Although a higher flow rate may account for the larger breakthrough of the former pesticides, these observations highlight the difficulty in comparing leaching results obtained under different conditions. Insufficient, or lack of data on K_{oc} and DT_{50} values in the soil used for leaching also makes such comparisons more difficult. The effect of aging was demonstrated for fenitrothion (2), in which degradation to more hydrophilic metabolites increased the amount of leached ^{14}C, leaving lower amounts of ^{14}C retained in the soil. Carbamates generally have moderate adsorption and persistence in soil, resulting in significant leaching from soil columns, as observed for carbofuran (17) and carbendazim (24). Microbial degradation during aged soil column leaching experiments reduced the leaching of mexacarbate (19) (Sundaram 1997), aldicarb (20) (Fava et al. 2001), and benthiocarb (21) (Doran et al. 2008). As compared to laboratory column leaching study results at higher flow rates, a significant reduction in leaching was reported in a long-term lysimeter study with aldicarb (20), in which natural rainfall events (Vink et al. 1997) were simulated. (Leistra et al. 1976; Morgan et al. 1995). These results most likely indicate either an increased contribution from preferential flow at higher flow rates or an increased opportunity for microbial pesticide degradation under discontinuous flow conditions. Although the chemical structure of the carbamates is similar to that of the amides and ureas, no information concerning their facilitated transport by DOM and colloids have been reported. The pyrethroid insecticides are characterized by having very high hydrophobicity, and having DT_{50} values of approximately 1 month (Laskowski 2002). Hence, they are generally resistant to leaching, (Table 4). The increased leaching of ^{14}C as a result of aging was observed to occur or cypermethrin (29), fenpropathrin (28), and permethrin (26); this increased mobility resulted from the formation of more polar metabolites.

Urea and Sulfonylurea Herbicides: These classes of herbicides are characterized by high water solubility and low soil adsorption, and therefore the mobility of these groups in soil is generally classified as being “very high” to “medium” (McCall et al. 1981). Significant amounts of urea herbicides, up to 90% of the applied dose, were detected in column eluates (Table 5). The leaching rate of these herbicides is highly dependent on both individual pesticide properties, such as water solubility, dissociation constant, and leaching conditions. Slow and discontinuous water flow was shown to markedly decrease, not only the leaching of nonionic diuron (35) but also ionizable tebuthiuron (44) and buthidazole (45) (Landry et al. 2006; Weber and Peeper 1982; Weber and Whitacre 1982), whereas the effect of water flow rate was unclear for linuron (39). Interactions with clay resulted in more retention of (45) in the soil column. By contrast, a slower water flow rate was reported to increase the leaching of isoproturon (38) (Lennartz 1999). The increase was accounted for by the contribution from preferential flow in the undisturbed soil column. Sulfonylurea has a pK_a of ~4 and is primarily dissociated under neutral conditions, which implies high potential for leaching. However, monitoring of its mobility in soil has frequently been conducted by bioassay using herbicide-sensitive plant seedlings. This approach limits the availability of quantitative data on the compound’s distribution in soil and eluates. A moderate degradation rate, combined with high mobility resulted in significant leaching for metsulfuron-methyl (47) (Heistermann et al. 2003), triasulfuron (49), tribenuron-methyl (51), ethametsulfuron-methyl (52), and sulfosulfuron (57) (Table 5). The microbial degradation of metsulfuron-methyl (47) in the soil column produced low recovery of ^{14}C (<40%), and this caused a marked decrease in leaching (Abdulla et al. 2001). In a controlled leaching study performed with ^{14}C-imazosulfuron (58), Mikata et al. (2001) showed that the microbial processes of mineralization and bound residue formation resulted in reduced leaching of (58). Furthermore, because the main metabolites of (58) are less mobile than are the parent compounds, reduced elution of ^{14}C was observed after aging.

Arylalkanoate, Acetoanilide, Diphenyl Ether and Triazine Pesticides: Arylalkanoate herbicides have a dissociable carboxyl group. Hence, their mobility is generally classified as being “very high” to “high” (McCall et al. 1981), because of their extremely low soil adsorption. Considerable amounts of applied arylalkanoates have been detected in column eluates (Table 6). However, the leaching behavior of MCPA (61) was greatly influenced by soil humic matter, possibly from cation-bridged adsorption (Haberhauer et al. 2002). Lee et al. (1986) reported reduced leaching of triclopyr (63) caused by discontinuous water flow, which facilitated microbial degradation in the soil column. The contribution of microbial degradation was also indicated by the low recovery of 2,4-D (59) in soil columns (Lopetz-Avila et al. 1986). The relatively high K_{oc} value, and faster biodegradation rate of cyhalofop (64) among class members of these herbicides greatly reduced its leaching. Similar leaching behavior was also reported for the acetanilide pesticides, with significant breakthrough observed under continuous water flow conditions, but reduced leaching was observed under discontinuous and lower water flow conditions, especially in outdoor studies. Among the diphenyl ethers, the benzoic acid derivative acifluorfen (70) exhibited the most significant leaching. Detectable amounts of fomesafen (72), which has a low soil adsorption coefficient, was observed in leachates under continuous water flow conditions, but leaching was reported to be insignificant in an outdoor study that utilized natural rainfall. Most of the other hydrophobic diphenyl ethers were primarily retained in the soil column. Because of their high mobility and persistence in soil, the triazine herbicides have the potential to contaminate GW and the unsaturated zone of soil profiles. They have frequently been detected in GW monitoring studies, as have their metabolites (Cohen et al. 1984; Hancock et al. 2008). Because of such detections, many column leaching studies have been conducted on members of this class, especially atrazine (74) and simazine (75). In laboratory column leaching studies conducted under continuous water flow conditions, more than 75% of the applied (74) was detected in the leachates (Abu-Zreig et al. 2000; Nkedl-Kizza et al. 1987; Zhou et al. 2010). However, as was the case for other pesticides that are susceptible to leaching, slow and discontinuous water flow conditions were shown to enhance the microbial degradation of (74) and (75), and hence, only minimal amounts of these compounds were detected in eluates collected under these conditions (Cherrier et al. 2005; Vink et al. 1997; Walker et al. 1996; Weber et al. 2006). In acidic soils, adsorption of the protonated species to negatively charged clay surfaces may reduce triazine herbicide leaching (Calderón et al. 2004). The higher K_{oc} values of cyanazine (76) and terbuthylazine (78) resulted in less breakthrough of these compounds compared to (74) and (75).

Miscellaneous Pesticides: Six herbicides, including dicamba (83) and imazaquin (88), possess a carboxyl group and are characterized by very low rates of soil adsorption that is similar to the arylalkanoate herbicides. When these substances do not rapidly biodegrade in soils, they show significant leaching in soil columns (Table 7). However, reduced mobility of (87) and (88) was observed to occur in soils that retained higher acidity, or a higher content of humic materials and clay, because such materials more strongly adsorb the undissociated or cation-bridging forms of these compounds (Regitano et al. 2005; Weber et al. 2003). A time lag after the herbicide application to soil and a drier state of soil also reduced the leaching of these herbicides (Comfort et al. 1992; Johnson et al. 2000; O'Dell et al. 1992; Regitano et al. 2002). What accounted for the difference in leaching was the kinetic adsorption and enhanced interactions with humic substances and clay due to their increased surface acidity. Four uracil-like herbicides, including bromacil (89) and hexazinone (92), were primarily recovered from column eluates, although aging (Dousset et al. 2004) or slower elution (Weber and Whitacre 1982), allowed them to degrade, resulting in reduced leaching. The inverse relationship that exists between the terbacil (90) mobility and soil organic matter or clay content indicates not only that a hydrophobic interaction is occurring but also shows that cation-bridging interactions occur with soil constituents (Mora et al. 1997). *N*-heterocycles, including the triazinone and pyridazinone skeletons, bentazone (93)–norflurazon (97), exhibited similar behavior to that of the uracil-like herbicides. The degradation rates of metribuzin (94) and metamitron (95) showed a large variability in leachability, probably because of differences in microbial activity between the test soils, which resulted in a wide range of breakthrough curves for these pesticides in soil columns. No relationship was observed between leached amounts and water flow rates for (95) and chloridazon (96), but for both compounds, the lowest amount of leaching was observed in soil columns that had the largest radius, even at the highest water flow rate (Cuevas et al. 2008; Düring and Hummel 1999). Increased degradation over a longer residence time caused by increased tortuosity and the presence of immobile water in the undisturbed thicker soil columns may account for these differences. Chloridazon (96) had a high affinity for clay minerals (Cuevas et al. 2008), while Fe- and Al oxides exhibited the opposite effects on the adsorption of (97) to soils (Morillo et al. 2004). This indicates that clay mineralogy is also an important factor for determining probable soil mobility of this pesticide class. Insignificant leaching was reported for hydrophobic pesticides that had K_{oc} values of >1,000, such as the dinitroaniline herbicides (98)–(100) and the organochlorine insecticides (101)–(104). A larger breakthrough amount was reported for DDT (101) and likely occurred because of its facilitated transport with DOM. The azole fungicides (125)–(130), which are generally persistent in soil, were scarcely detected in leachates, because of their high adsorption to soil.

8 Summary

In this review, I address the practical and theoretical aspects of pesticide soil mobility. I also address the methods used to measure mobility, and the factors that influence it, and I summarize the data that have been published on the column leaching of pesticides.

Pesticides that enter the unsaturated soil profile are transported downwards by the water flux, and are adsorbed, desorbed, and/or degraded as they pass through the soil. The rate of passage of a pesticide through the soil depends on the properties of the pesticide, the properties of the soil and the prevailing environmental conditions. Because large amounts of many different pesticides are used around the world, they and their degradates may sometimes contaminate groundwater at unacceptable levels. It is for this reason that assessing the transport behavior and soil mobility of pesticides before they are sold into commerce is important and is one indispensable element that regulators use to assess probable pesticide safety. Both elementary soil column leaching and sophisticated outdoor lysimeter studies are performed to measure the leaching potential for pesticides; the latter approach more reliably reflects probable field behavior, but the former is useful to initially profile a pesticide for soil mobility potential.

Soil is physically heterogeneous. The structure of soil varies both vertically and laterally, and this variability affects the complex flow of water through the soil profile, making it difficult to predict with accuracy. In addition, macropores exist in soils and further add to the complexity of how water flow occurs. The degree to which soil is tilled, the density of vegetation on the surface, and the type and amounts of organic soil amendments that are added to soil further affect the movement rate of water through soil, the character of soil adsorption sites and the microbial populations that exist in the soil. Parameters that most influence the rate of pesticide mobility in soil are persistence (DT_{50}) of the pesticide, and its sorption/desorption (K_{oc}) characteristics. These parameters may vary for the same pesticide from geographic site-to-site and with soil depth. The interactions that normally occur between pesticides and dissolved organic matter (DOM) or WDC are yet other factors that may complicate pesticide leaching behavior.

The soil mobility of pesticides is normally tested both in the laboratory and in the field. Lab studies are initially performed to give researchers a preliminary appraisal of the relative mobility of a pesticide. Later, field lysimeter studies can be performed to provide more natural leaching conditions that emulate the actual field use pattern. Lysimeter studies give the most reliable information on the leaching behavior of a pesticide under field conditions, but these studies are time-consuming and expensive and cannot be performed everywhere. It is for this reason that the laboratory soil column leaching approach is commonly utilized to profile the mobility of a pesticide, and appraise how it behaves in different soils, and relative to other pesticides.

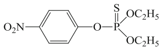
Because the soil structure is chemically and physically heterogenous, different pesticide tests may produce variable DT_{50} and K_{oc} values; therefore, initial pesticide mobility testing is undertaken in homogeneously packed columns that contain two or more soils and are eluted at constant flow rates. Such studies are done in duplicate and utilize a conservative tracer element. By fitting an appropriate mathematical model to the breakthrough curve of the conservative tracer selected, researchers determine key mobility parameters, such as pore water velocity, the column-specific dispersion coefficient, and the contribution of nonequilibrium transport processes. Such parameters form the basis for estimating the probable transport and degradation rates that will be characteristic of the tested pesticide. Researchers also examine how a pesticide interacts with soil DOM and WDC, and what contribution from facilitated transport to mobility is made as a result of the effects of pH and ionic strength.

Other methods are used to test how pesticides may interact with soil components to change mobility. Spectroscopic approaches are used to analyze the nature of soil–pesticide complexes. These may provide insight into the mechanism by which interactions occur. Other studies may be performed to determine the effect of agricultural practices (e.g., tillage) on pesticide leaching under controlled conditions using intact soil cores from the field. When preferential flow is suspected to occur, dye staining is used to examine the contribution of macropores to pesticide transport. These methods and others are addressed in the text of this review.

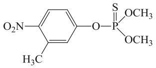
9 Appendix 1: Chemical Structures

Organophosphorus pesticides

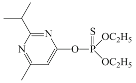
(1) Parathion



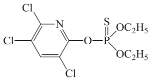
(2) Fenitrothion



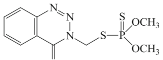
(3) Diazinon



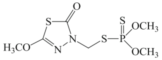
(4) Chlorpyrifos



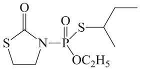
(5) Azinphos-methyl



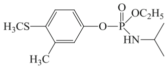
(6) Methidathion



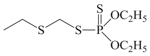
(7) Fosthiazate



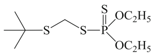
(8) Fenamiphos



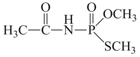
(9) Phorate



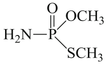
(10) Terbufos



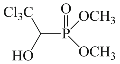
(11) Acephate



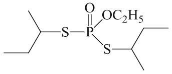
(12) Methamidophos



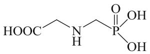
(13) Trichlorfon



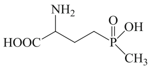
(14) Cadusafos



(15) Glyphosate

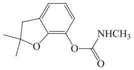


(16) Glufosinate

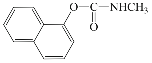


Carbamates

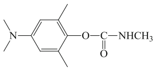
(17) Carbofuran



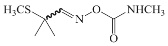
(18) Carbaryl



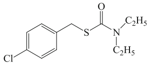
(19) Mexacarbate



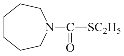
(20) Aldicarb



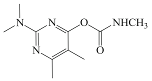
(21) Benthiocarb



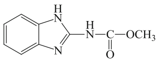
(22) Molinate



(23) Pirimicarb

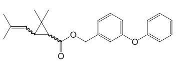


(24) Carbendazim

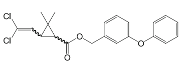


Pyrethroid insecticides

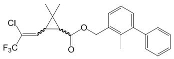
(25) Phenothrin



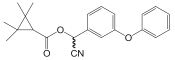
(26) Permethrin



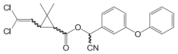
(27) Bifenthrin (*Z*)-(1*RS*)-*cis*



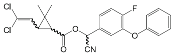
(28) Fenpropathrin



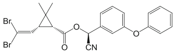
(29) Cypermethrin



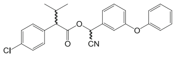
(30) *β*-Cyfluthrin
(1*R*)-*cis,trans*-(α*S*), (1 *S*)-*cis,trans*-(α*R*)



(31) Deltamethrin
(1*R*)-*cis*-(α*S*)

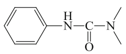


(32) Fenvalerate

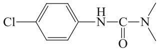


Urea herbicides

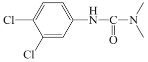
(33) Fenuron



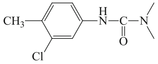
(34) Monuron



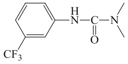
(35) Diuron



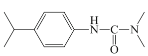
(36) Chlortoluron



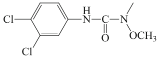
(37) Fluometuron



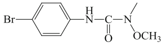
(38) Isoproturon



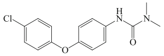
(39) Linuron



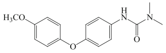
(40) Metobromuron



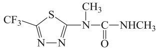
(41) Chloroxuron



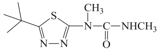
(42) Difenoxuron



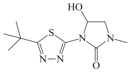
(43) Thiazafluron



(44) Tebuthiuron

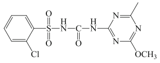


(45) Buthidazole

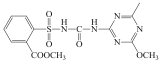


Sulfonylurea herbicides

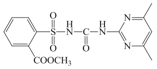
(46) Chlorsulfuron



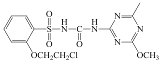
(47) Metsulfuron-methyl (Me)



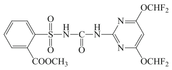
(48)Sulfometuron-methyl(Me)



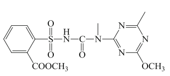
(49) Triasulfuron



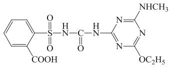
(50)Primisulfuron-methyl(Me)



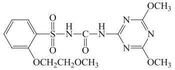
(51) Tribenuron-methyl (Me)



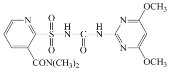
(52) Ethametsulfuron



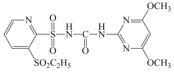
(53) Cinosulfuron



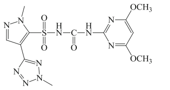
(54) Nicosulfuron



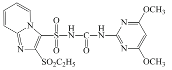
(55) Rimsulfuron



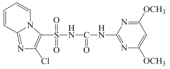
(56) Azimsulfuron



(57) Sulfosulfuron

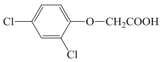


(58) Imazosulfuron

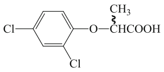


Arylalkanoate herbicides

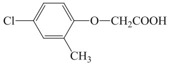
(59) 2,4-D



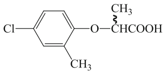
(60) Dichlorprop



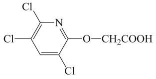
(61) MCPA



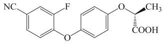
(62) Mecoprop



(63) Triclopyr

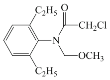


(64) Cyhalofop (*R*)

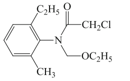


Acetoanilide herbicides

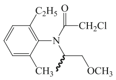
(65) Alachlor



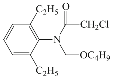
(66) Acetochlor



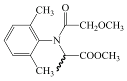
(67) Metolachlor



(68) Butachlor

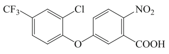


(69) Metalaxyl

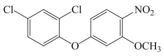


Diphenylether herbicides

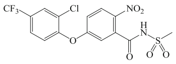
(70) Acifluorfen



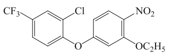
(71) Chlomethoxyfen



(72) Fomesafen

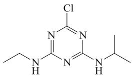


(73) Oxyfluorfen

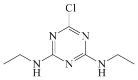


Triazine herbicides

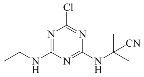
(74) Atrazine



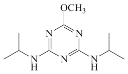
(75) Simazine



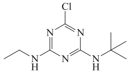
(76) Cyanazine



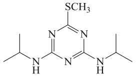
(77) Prometon



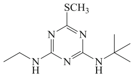
(78) Terbuthylazine



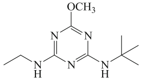
(79) Prometryn



(80) Terbutryn

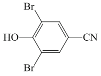


(81) Terbumeton

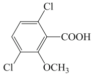


Miscellaneous pesticides

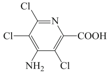
(82) Bromoxynil



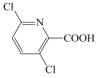
(83) Dicamba



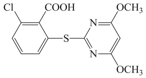
(84) Picloram



(85) Clopyralid

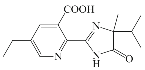


(86) Pyrithiobac

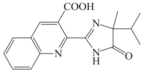


Miscellaneous pesticides

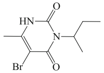
(87) Imazethapyr



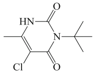
(88) Imazaquin



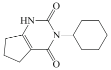
(89) Bromacil



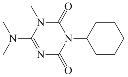
(90) Terbacil



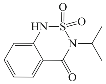
(91) Lenacil



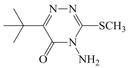
(92) Hexazinone



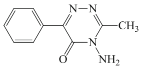
(93) Bentazon



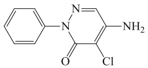
(94) Metribuzin



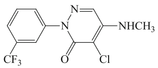
(95) Metamitron



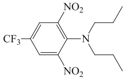
(96) Chloridazon



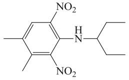
(97) Norflurazon



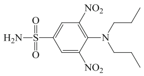
(98) Trifluralin



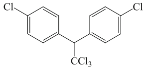
(99) Pendimethalin



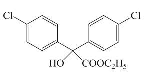
(100) Oryzalin



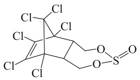
(101) DDT



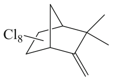
(102) Chlorobenzilate



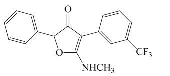
(103) Endosulfan



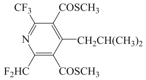
(104) Toxaphene



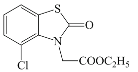
(105) Flurtamone



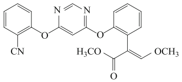
(106) Dithiopyr



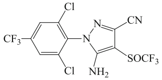
(107) Benazolin-ethyl



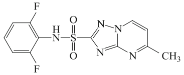
(108) Azoxystrobin (*E*)



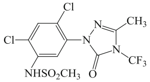
(109) Fipronil



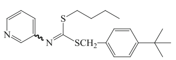
(110) Flumetsulam



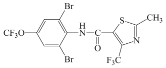
(111) Sulfentrazone



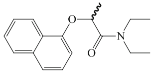
(112) Buthiobate



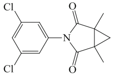
(113) Thifluzamide



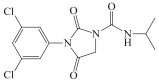
(114) Napropamide



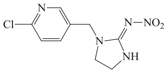
(115) Procymidone



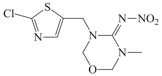
(116) Iprodione



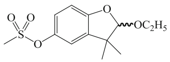
(117) Imidacloprid



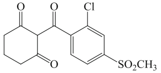
(118) Thiamethoxam (*E*)



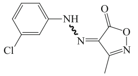
(119) Etofumesate



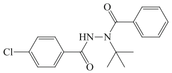
(120) Sulcotrione



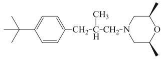
(121) Metazoxolon



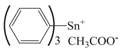
(122) Halofenozide



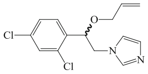
(123) Fenpropimorph (*cis*)



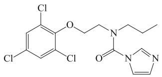
(124) Fentin acetate



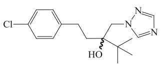
(125) Imazalil



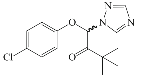
(126) Procloraz



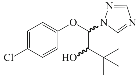
(127) Tebuconazole



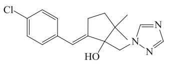
(128) Triadimefon



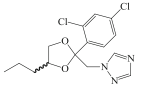
(129) Triadimenol



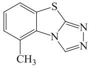
(130) Triticinazole (*E*)



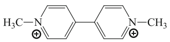
(131) Propiconazole



(132) Tricyclazole



(133) Paraquat



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Behavior and Impact of Zirconium in the Soil–Plant System: Plant Uptake and Phytotoxicity

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1 Introduction

Because of the large number of sites they pollute, toxic metals that contaminate terrestrial ecosystems are increasingly of environmental and sanitary concern (Uzu et al. 2010, 2011; Shahid et al. 2011a, b, 2012a). Among such metals is zirconium (Zr), which has the atomic number 40 and is a transition metal that resembles titanium in physical and chemical properties (Zaccone et al. 2008). Zr is widely used in many chemical industry processes and in nuclear reactors (Sandoval et al. 2011; Kamal et al. 2011), owing to its useful properties like hardness, corrosion-resistance and permeable to neutrons (Mushtaq 2012). Hence, the recent increased use of Zr by industry, and the occurrence of the Chernobyl and Fukashima catastrophe have enhanced environmental levels in soil and waters (Yirchenko and Agapkina 1993; Mosulishvili et al. 1994; Kruglov et al. 1996).

Zr is the twentieth most common element in the earth's crust (Fodor et al. 2005). Zr is generally considered to be immobile in soil (Muhs et al. 2007, 2010; Muhs and Budahn 2009; Aznar et al. 2009; Feng 2010, 2011; Little and Lee 2010; Hao et al. 2010; Bern et al. 2011), because it has low water solubility and a strong tendency to polymerize (Clearfield 1964). Moreover, Zr forms strong complexes with soil components, via zirconium dioxide and zirconocene dichloride, among others. The rate of adsorption/desorption of Zr to soil depends on its speciation and the characteristics of the soil involved. This element can be mobile in soil under a wide range of geological settings such as tropical weathering (Duvallet et al. 1999; Kurtz et al. 2000; Hodson 2002; Davydov et al. 2006).

Soil–plant transfer is an important link in the chain of events that leads to radionuclide entry into the human food chain. However, few studies have been performed on Zr transfer to plants (Shi and Guo 2002). Such soil–plant transfer may be influenced by both the characteristics of the plants (species, variety, maturity, etc.) and soils involved. Generally, plants absorb elements as ions or small complexes (Kabata-Pendias and Pendias 1992) in the soil solution.

Compared to other fission products (e.g., Sr, Cs, and Co), few data exist on the environmental behavior and fate of Zr (Couture et al. 1989; Garnham et al. 1993). Our goal in this review is to describe the following aspects of Zr: (1) isotopes and sources; (2) retention, mobility, and bioavailability in soils; (3) speciation in soil; (4) plant uptake and translocation to aerial parts; and finally (5) phytotoxicity.

2 Zr Minerals, Isotopes, and Sources

Relative to other inorganic trace elements, Zr has a high natural abundance in the earth's crust (Jones 1998; Martínez Cortizas et al. 2003; Chow et al. 2003; Alleman et al. 2010; Kumpiene et al. 2011). The natural level of Zr in soils varies from 32 to 850 mg/kg (Kabata-Pendias and Pendias 1992; Fodor et al. 2005). Bowen (1979) gave 400 mg/kg as an average Zr soil concentration, and Pais and Jones (1983) reported a value of 250 mg/kg. In soil, Zr is more than twice as abundant as copper and zinc and has ten times the abundance of lead. Its geochemistry is dominated by its lithophilic nature: Zr occurs in more than 140 recognized mineral species, but zircon ($ZrSiO_4$) and baddeleyite (ZrO_2) are the main naturally observed compounds (Ryzhenko et al. 2008). The order of Zr content in various types of rock is ultrabasic rocks < granite rocks < alkaline rocks (Kovalenko and Ryzhenko 2009). A-type granite is characterized by having high concentrations of Zr, and accessory minerals such as zircon and monazite (Jung et al. 2000; Sako et al. 2009). The highest Zr content values appear in agpaitic nepheline syenites, carbonatites, and peralkaline granites: 34 mg/kg in ultra basic rocks, 150 mg/kg in intermediate rocks, 200 mg/kg in silicic rocks, 820 mg/kg in alkaline rocks, and 1,120 mg/kg carbonatites (Ryzhenko et al. 2008). Zircon and baddeleyite are weathering resistant and form placers, which are the main commercial sources of Zr (Ryzhenko et al. 2008).

Naturally occurring Zr contains five stable isotopes (Ryzhenko et al. 2008; Caffau et al. 2010). Among these, ^{90}Zr is the most common form, comprising 51% of natural Zr. The other four stable isotopes and their relative abundances are ^{91}Zr (11%), ^{92}Zr (17%), ^{94}Zr (17%), and ^{96}Zr (2.8%) (Ryzhenko et al. 2008). In addition to these stable natural isotopes of Zr, 28 artificial isotopes have been manufactured, ranging in atomic mass from 78 to 110. Among these artificial isotopes, ^{93}Zr is the longest-lived [half-life ($T_{1/2}$) of 1.53×10^6 years] and ^{110}Zr is the heaviest and shortest-lived artificial isotope ($T_{1/2}$ 30 ms). ^{93}Zr decays to niobium (^{93}Nb) by emitting a beta particle of 0.02 million electron volts radiation energy. Nb, in turn, decays by isomeric transition by emitting beta and gamma particles of 0.028 and 0.0019, respectively. The Zr isotopes, with mass numbers between 88 and 104, have been characterized by high fission yields ranging from 5.8 to 6.3%.

Both geogenic and anthropogenic sources for Zr exist, the first generally being more abundant (Abollino et al. 2002; Schulin et al. 2007; Brun et al. 2008; Little and Lee 2010). The unique physical–chemical properties of Zr has enhanced its industrial use and has produced higher anthropogenic emissions to the environment from several sources: nuclear fallout, ceramic dusts, and heavy metal mining, improper waste dumping, abandoned industrial activity sites, incidental release (e.g., leakage, corrosion), and atmospheric fallout (Chow et al. 2003; Schulin et al. 2007; Little and Lee 2010; Bhuiyan et al. 2010). The Zr applications most valued by include uses that require high resistance to corrosive agents, component use in vacuum tubes, alloying agent for steel, surgical instrument applications, photoflash bulbs, explosive primers, lamp filaments and as a component of gems. The alloys of Zr are utilized as refractory materials, a cladding material for nuclear fuel elements, and a component of explosive primers, rayon spinnerets and superconductive magnets (Yau 2010). Recently, Dou et al. (2011) reported that a granular zirconium–iron oxide alloy can be used to remove fluoride from drinking water. The increased use of Zr by many industries has increased annual production from mines where it is sourced (Fig. 1; USGS 2012).

Zr has a diversity of uses. Zr is known as an ideal material for nuclear reactor applications, due to its low absorption cross-section for neutrons (Mushtaq 2012). The use of Zr in commercial nuclear power generation now accounts for as much as

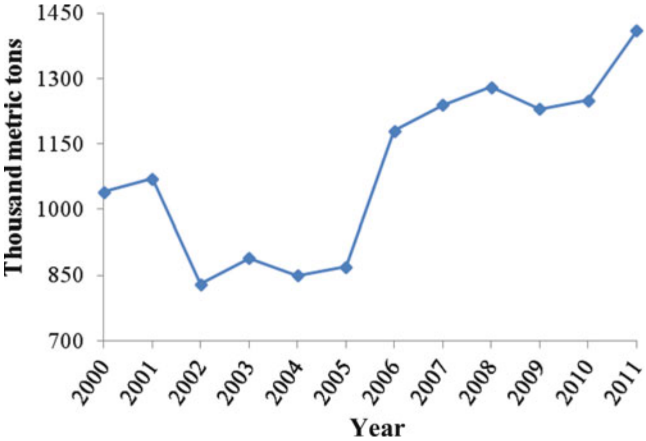

Fig. 1 Annual world mine production of Zr in 000 metric t (from USGS 2012)

90% of the Zr metal that is produced. The ^{93}Zr isotope is long-lived ($T_{1/2}$ of 10^6 years). This isotope occurs largely in radioactive wastes as a fission reaction by-product (Naudet 1974). Because of its relatively short half-life, the ^{89}Zr isotope ($T_{1/2}$ of 78.4 h) is a promising positron-emitting surrogate for ^{90}Y in radio immunotherapy (Verel et al. 2003). Zr is also used for its incendiary effect in weapons such as the BLU-97/B combined effects bomb. Moreover, Zr is detected in phosphate fertilizers and in calcium cyanamide (range 0.38–8.24 mg/kg) (Senesi et al. 1988). Traces of Zr also exist in sewage sludge (5–90 mg/kg), limestone (20 mg/kg), and animal manure (5 mg/kg) (Kabata-Pendias 1993).

Abollino et al. (2002) and Bhuiyan et al. (2010) reported that anthropogenic activities can modify the amount and nature of Zr that is present in soils and should be considered as a possible soil pollutant. Finally, the growing environmental abundance of Zr has increased researcher interest in measuring the levels at which it exists in living organisms (Ghosh et al. 1992).

3 Retention, Mobility, and Bioavailability of Zr in Soils

Metal bioavailability is defined as the fraction of total metal in soil that can be absorbed by a biological target (Shahid et al. 2012b). The degree to which a metal is bioavailable depends on its soil mobility. Opinions vary on how mobile/bioavailable Zr is in soil. Certain authors (Chadwick et al. 1990; Bain et al. 1994; Hodson 2002) believe that Zr is very slightly mobile in soils as a result of its binding to highly insoluble oxides, chloride, and silicates that are resistant to weathering (Kabata-Pendias 1993; Smith and Carson 1978; Prisyagina et al. 2008). Blumenthal (1963), in contrast, believes that zirconium oxide is almost insoluble in water, acid and alkali solutions, and organic solvents and therefore is not mobile. Indeed, the mobility and/or bioavailability of Zr depend on its chemical form. Certain chemical forms of Zr (e.g., zirconium carbide and zirconium oxychloride) are slightly soluble, whereas others are insoluble in water (zirconium oxide, zirconium hydroxide, and zirconium phosphate) (Venable 1922).

Zr has a fixed crystalline structure in many of the minerals in which it appears (Horvath et al. 2000). This structure of Zr changes very slowly over time from the effects of weathering. The more Zr minerals are weathered the more they change. Hence, one can use the degree of weathering of Zr-containing minerals that appear in soil to track the geologic age of some minerals. Therefore, Zr is used as a tool to estimate long-term weathering rate for rocks that exist in soils (Hill et al. 2002; Egli and Fitze 2001; Patino et al. 2003; Zaccone et al. 2008).

The total quantity of an immobile element in a given soil horizon is not unaffected by the weathering processes (Hodson 2002), although the element's concentration may change from loss or addition of other elements or from the addition of organic matter. Goldich (1938) and Pettijohn (1941) investigated the durability of Zr in weathered rock and found that zircon was the most persistent mineral in a wide range of igneous, metamorphic and sedimentary rocks. Tejan-Kella et al. (1991) recorded etch-pitted zircon grains only in soils that were 100,000 years old. The chemical composition of zircon mineral is used to elaborate many magmatic processes, including the interaction with hydrothermal fluids (Thomas et al. 2002; Hoskin 2005), crystal fractionation (Pettke et al. 2005; Lowery Claiborne et al. 2006), and/or magma mixing (Wang et al. 2002; Belousova et al. 2006), as well as being a potential source indicator (Aja et al. 1995; Belousova et al. 2002; Gagnevin et al. 2009).

Zr is highly resistant to acidic weathering and is widely used to predict the structure of parent rocks (Valeton et al. 1987; Kurtz et al. 2000; Panahi et al. 2000; Calagari and Abedini 2007). The ratio of Zr to other metals like Hf or Ti is highly useful to determine the crystallization sequences of rocks (Zaraisky et al. 2009). Therefore, Zr/Hf and Ti/Zr concentration ratios are employed to trace possible precursor rock(s) that exist in ores (Kurtz et al. 2000; Zaraisky et al. 2008, 2009; Hao et al. 2010; Bern et al. 2011). The ratios of immobile elements (e.g., Ti/Zr) in bauxite are similar to those of the parent rock (Valeton et al. 1987) and can be used to determine source rocks (Calagari and Abedini 2007). The concentration ratios of other element combinations have been successfully used to infer the derivation of soils (Sommer et al. 2000).

In contrast to the opinion of other researchers mentioned above, Whitfield (2011) and Bern et al. (2011) concluded that Zr was mobile in soils. The mobility of Zr relative to Nd in commercial reactors was also reported by Maeck et al. (1975). Hill et al. (2002) and Kurtz et al. (2000) have shown that immobile elements like Zr (or Y and Th) are redistributed within the weathered soil profile. This redistribution may result from physical, chemical, and biological processes that operate on the earth's surface (Anderson et al. 2002; Che et al. 2012). Petrographic evidence (Rubin et al. 1993; Flohr and Ross 1990) suggests that Zr may be mobile in soil under a wide range of geological settings (Hao et al. 2010; Malandrino et al. 2011; Ribeiroa et al. 2010; Liu et al. 2010).

In addition to origin (whether natural or anthropogenic), several other factors influence the mobility of Zr in soils, such as soil characteristics, interactions with organic matter, and climate (Ferrand et al. 2006; Davydov et al. 2006). These factors, separately or in combination, affect the bioavailability of Zr, particularly when adsorption/desorption processes are involved (Klechkovsky and Gulyakin 1958; Schulin et al. 2007).

The effects of pH greatly influences metal partitioning between the soil solid and solution phases (Peng et al. 2009; Shahid et al. 2011b). Soil pH affects adsorption/desorption reactions, speciation, and mobility of heavy metals in soils (Davydov et al. 2006; Wu and Hendershot 2010; Zou et al. 2009; Bali et al. 2010; Shahid et al. 2011c). In strongly acidic solutions, the polynuclear hydrolysis species are formed and control Zr solubility and mobility in solution. Under less acidic conditions, mononuclear hydrolysis species are more predominate. Under alkaline solutions, solubility increases form the formation of the zirconate ion.

Soil texture also influences the behavior of Zr. Metals generally have a strong affinity for the soil-clay fraction (Owojori et al. 2010), and that fine soil fraction is often pollutant enriched. In contrast, Zr is mainly present as zircon grains in the coarse fractions of soils (Stiles et al. 2003; Caspari et al. 2006). However, Zr sorption onto the solid surfaces of soil may influence its mobility and bioavailability (Klechkovsky and Gulyakin 1958; Udovic and Lestan 2009; Rascio and Navari-Izzo 2011). Competing ions (viz., H, Ca, Mg, Na, Fe, and K) affect these adsorption reactions.

Soil organic matter (*SOM*) also plays a key role in governing the mobility/bioavailability of metals in soil (Dessureault-Rompré et al. 2010). Soil organic content affects the mobilization of Zr, because this element may be adsorbed by it, or may form stable complexes with it (Ferrand et al. 2006). Such interactions may result from the interaction of metal ions with the acidic binding sites on carboxylic and phenolic hydroxyl groups of SOM (Oliva et al. 1999; Viers et al. 2000; Pokrovsky and Schott 2002). Oliva et al. (1999) and Viers et al. (2000) recorded relatively high Zr concentrations (0.01–0.6 g/kg) in organic-rich soils (10–35 μg/g dissolved organic carbon). Oliva et al. (1999) measured high Zr concentrations in a small tropical watershed in South Cameroon and believed that they were the result of zircon weathering that was enhanced by organic matter. LeRiche (1973) detected Zr in hydrogen peroxide extracts of soils, which indicated that Zr may be associated with the organic matter fraction of soils. SOM also indirectly affects metal mobility in soil via its effects on soil properties (i.e., pH, cation exchange capacity, particle size distribution, cracking pattern and porosity, soil solution composition, microbial and enzyme activities) (Shahid et al. 2012b).

The extent of Zr mobility also varies according to climatic conditions. Under temperate and tropical weathering conditions, biotite is decomposed and zircon is released into the soil column, and it is subsequently redeposited in deep horizons (Swindale and Jackson 1956; Cornu et al. 1999). Under low rainfall, Zr may precipitate or coprecipitate with Fe oxides and become immobilized. In contrast, Zr may become mobile under more severe weathering conditions and the presence of high organic matter content (Dupré et al. 1996; Hodson 2002; Braun et al. 2005).

In soils exposed to intensive chemical weathering, topsoil generally contains higher amounts of Zr as zircon minerals, compared to deeper horizons (Hodson 2002; Stiles et al. 2003). Abollino et al. (2002) reported higher concentrations of Zr in chemically weathered surface than in deep soil samples. Hence, there is a notion that the mobility of Zr is site-specific.

4 Zr Speciation

The biogeochemical behavior of an inorganic element in an ecosystem, and its potential effects on plants, are strongly influenced by its speciation (Stojilovic et al. 2005; Fodor et al. 2005; Davydov et al. 2006; Dumat et al. 2006; Ryzhenko et al. 2008; Prisyagina et al. 2008; Kopittke et al. 2008; Louvel et al. 2009; Uzu et al. 2009; Shahid et al. 2012b, c). Speciation is the existence of a metal in different chemical forms as a result of being exposed to different environmental conditions (Dumat et al. 2006; Louvel et al. 2009; Shahid et al. 2011c). As mentioned, Zr speciation strongly depends on soil pH and SOM interactions. Zr exists in several forms in the soil and in liquid media, and these forms have different levels of solubility and bioavailability (Fodor et al. 2005; Davydov et al. 2006; Ryzhenko et al. 2008; Prisyagina et al. 2008; Louvel et al. 2009). Different Zr species affect the solubility, mobility, and uptake of Zr by plants (Davydov et al. 2006; Ferrand et al. 2006; Ryzhenko et al. 2008). Therefore, although it is relatively easier to measure, one cannot rely on the total Zr content in a plant as an indicator of uptake and toxicity (Shahid et al. 2012b). Therefore, to improve the understanding of risk and what constitutes realistic remediation depends heavily upon measuring the relevant species of Zr that exists in soil as well as those taken into plants.

Zr presents different oxidation states (varies from +2 to +4), +4 being the form of the predominant stable valence; bonding with oxygen is the prevailing and most common reaction for Zr (Kabata-Pendias 1993). The Zr crustal abundance ranges from 20 to 500 mg/kg, and its aqueous chemistry is dominated by the quadrivalent oxidation state (valence electron configuration $4d2\ 5s'$) (Ryzhenko et al. 2008). The lower oxidation states of Zr (0, I, II, and III) occur only in nonaqueous solvents and fused salts (Cotton and Wilkinson 1980). Due to high ionic potential (22.54 e^2/Å), Zr is the most polarizing among the heavier transition and post-transition quadrivalent cations. The extent of hydrolysis and polymer stoichiometry depends on the nature of the ionic media (Davydov et al. 2006), with tetramer and trimer forms being the most common stoichiometry. Moreover, hydrolysis and polymerization reactions dominate in the presence of high field strength cations that are capable of rupturing H–O bonds. Similarly, hydrolysis and polymerization is promoted in alkaline solutions and with increasing temperatures.

How Zr reacts in aqueous media (soil solution) is still the subject of controversy. The zirconium oxide and hydroxide have low solubility and precipitate at low pH. This is because Zr hydrolyses and precipitates as polynuclear species in strongly acidic solutions ($\text{pH}<1$) (Baes and Mesmer 1986; Ekberg et al. 2004). Davydov et al. (2006) and Ryzhenko et al. (2008) evaluated the hydrolysis and precipitation of Zr as a function of pHs between 0 and 14 and generally show that Zr precipitation reactions occur at low pH (about 2) (Ryzhenko et al. 2008; Prisyagina et al. 2008). In the pH range 0.6–2.3, potentiometric measurements indicated the presence of both the mononuclear form $[Zr(OH)_3]^+$ (at a low Zr concentration) and the polymeric species $[Zr_4(OH)_8]^{8+}$ and $[Zr_2(OH)_6]^{2+}$. This latter polymeric species predominated at low total Zr concentrations (10^{-5} M). At higher pH, solvent extraction measurements indicated the presence of three mononuclear species: $[Zr(OH)_2]^{2+}$, $[Zr(OH)_3]^+$, $Zr(OH)_4$ (Davydov et al. 2006; Ryzhenko et al. 2008). Under tetravalent oxidation conditions, Zr acts as a hard acid: electrostatic, rather than covalent forces dominate its complexation with inorganic ligands in the following order of decreasing stability: $OH^- > F^-\ PO_4^{2-} > ClO_4^{2-} > SO_4^{2-} > CO_2^- > NO_3^- > Cl^- > ClO_4^-$. Complexation reactions involving OH^- and F^- ions have received the most attention, and speciation studies have generally been conducted in perchlorate media.

5 Plant Uptake of Zr from Soil and Translocation to Aerial Parts

Soil–plant transfer is an important link in the chain of events that leads to the entry of metals into the food chain. Unfortunately, little data are available concerning the transfer of Zr to plants (Wang et al. 2000; Shi et al. 2002). Zr is less soluble than other metals (e.g., Pb and Cd) and tends to exist as an insoluble particulate. Consequently, only a small fraction of zirconium is available for plant uptake (Ferrand et al. 2006; Uzu et al. 2009; Hao et al. 2010; Muhs et al. 2010; Feng 2011; Bern et al. 2011), because of strong binding with organic and inorganic ligands in soils (Sammut et al. 2010; Vega et al. 2010; Shahid et al. 2012b). By contrast, Sako et al. (2009) stated that the least mobile elements (e.g., Zr, Ti, Sc, Al, and Th) have a low residence time in the soil solution. However, Tematio et al. (2009) concluded that Zr is more strongly available in the B soil horizons.

Unlike other heavy metals (e.g., Pb, Cd, and Ni), the way Zr enters plants is not well understood. The main pathway by which Zr is taken up by plants is soil–root transfer (Ferrand et al. 2006). Zr is mainly taken up as the tetravalent cation in soil solution (Whicker and Schultz 1982). Zr adsorption on root surfaces (Chaignon and Hinsinger 2003) is a minor phenomenon and such absorption is mainly driven by nonselective water and nutrient fluxes (Ferrand et al. 2006). Zr may enter roots passively and follow translocating water streams. At the molecular level, the mechanism by which Zr enters roots is still unknown. Zr can enter the plant roots via different pathways, especially through ionic channels as does Pb. Entry into plants by Zr may depend on the functioning of an H^+/ATPase pump to maintain a strong negative membrane potential in rhizoderm cells (Hirsch et al. 1998). Some authors suggested that kinetic-dependant absorption of the metal occurs; the initial phase representing rapid entry into root-free space and binding to the cell walls, and the subsequent slower phase resulting from transport across the plasma membrane into the cytoplasm (Maria and Cogliatti 1988).

The rate of Zr entry into plant roots significantly depends on its chemical form in the soil solution. Ferrand et al. (2006) observed higher Zr concentrations in the roots of *Pisum sativum* and in tomato plants for the acetate and oxychloride forms than the hydroxide or oxide forms. Shi and Guo (2002) studied the absorption of Zr by *Brassica rapa* that was cultivated on a loamy soil. They observed that when Zr was applied by soil surface irrigation, ^{95}Zr was distributed equally between root and shoot. However, when Zr was applied as spray on plant leaves, Zr concentration was greater in roots than shoot. Zirconium ascorbate has been reported by Fodor et al. (2003) to be accumulated from nutrient solution at a significant rate by *Chlorella pyrenoidosa* cells (Simon et al. 1998). This phenomenon may have practical importance in removing Zr from contaminated aquatic environments. Interactions between organic ligands and metals in natural media have been extensively studied because of their affect on metal availability (Ferrand et al. 2006; Quenea et al. 2009; Yip et al. 2010). Synthetic or natural organic ligands have been extensively used to enhance plant uptake of metals in remediation studies (Evangelou et al. 2007; Saifullah et al. 2009, 2010; Yip et al. 2010; Shahid et al. 2012b). In addition to organic ligands, plant root exudates, which generally include acetic, oxalic, fumaric, citric, and tartaric acids, also affect Zr solubility in soil and its uptake by plants (Hinsinger et al. 2009, 2011). Langmuir and Herman (1980) showed that for thorium (a chemical analogue of Zr), oxide solubility and availability were increased by organic ligand addition.

The penetration of an element into a plant can be assessed by assessing the transfer factor (TF) from soil to plant (TF is generally defined as the ratio between the concentration in plants and the soil) (Arshad et al. 2008; Bi et al. 2010; Liu et al. 2010). This TF depends on soil physical and chemical properties and plant type (Arshad et al. 2008; Bi et al. 2010; Liu et al. 2010). The TF value permits researchers to integrate information on the initial total stock of Zr, and therefore to better compare Zr availability under various experimental conditions (Ferrand et al. 2006). A TF value equal to 0.01 corresponds to a low metal absorption rate and a TF value of 10 indicates that the plant accumulates the metal. The mean TF value obtained by Tome et al. (2003) for Zr uptake by grass-pasture grown in soils near a uranium mine was 0.09. Actually, several authors have reported that Zr accumulates in various food crop parts if the crops were grown on Zr-contaminated soil (Sanzharova and Aleksakhin 1982; Fodor et al. 2002). Sanzharova and Aleksakhin (1982) concluded that Zr was taken up by barley, corn, and alfalfa. Gundersen et al. (2000) observed that Zr was absorbed by *P. sativum* (between 0.425 and 5.29 μg/kg of Zr per fresh wt). In any event, plants accumulate significantly lower Zr concentrations than exists in the soil in which they grow (Smith and Carson 1978; Sanzharova and Aleksakhin 1982). Kabata-Pendias (1993) indicated that the Zr levels found in food plants vary from 0.005 to 2.6 mg/kg.

After penetrating the central plant cylinder, metals translocate to shoots via the water flow of the vascular system (Krzeslowska et al. 2010). While passing through the xylem, Zr may form complexes with amino acids such as histidine, or organic acids, as do Pb and Cd (Ferrand et al. 2006; Vadas and Ahner 2009; Maestri et al. 2010; Rascio and Navari-Izzo 2011), or may be transferred in inorganic form. Transportation of metals from the roots to the shoots requires movement through the xylem (Verbruggen et al. 2009) and is probably driven by transpiration (Liao et al. 2006; Shahid et al. 2011b). The translocation rate of Zr in higher plants is low (Sanzharova and Aleksakhin 1982; Kabata-Pendias 1993; Ferrand et al. 2006). Like Pb, generally more that 90% or more of absorbed Zr is accumulated in plant roots (Kabata-Pendias and Pendias 1992; Wang et al. 2000; Shi et al. 2002; Klechkovsky and Gulyakin 1958; Ferrand et al. 2006; Yan et al. 2010; Gupta et al. 2010; Jiang and Liu 2010).

Restrictions in metal translocation may result from blockage by the Casparian strip, accumulation in plasma membrane, precipitation as insoluble Zr or immobilization by negatively charged exchange sites within the cell wall, or sequestration in the vacuoles of rhizodermal and cortical cells. Kabata-Pendias and Pendias (1992) reported a higher increase of Zr content in nodules and roots of legumes than in aerial parts. Wang et al. (2000) found the same result for soybean plants that were cultivated in a radio contaminated soil, even for a longer growing period (up to 60 days after sowing). Shi et al. (2002) found that Zr in *Oryza sativa* was concentrated in the roots and lower part of the stem. Ferrand et al. (2006) observed a several fold increase in the accumulation of Zr in root of *P. sativum* and *Solanum lycopersicum* plants, when the plants were grown in Zr-spiked soil. Enhanced sequestration in root cells, with limited translocation to shoot tissues is a typical feature of metal excluders (Baker 1981). A low Zr concentration in the edible parts of plants, even in very contaminated soils is an important result in terms of sanitary risk linked to vegetable eating. Additional studies on Zr that address movement and accumulation in numerous other plant species are needed. In particular, data are needed on the distribution of Zr in leafy or root vegetables and should emphasize the consumed parts of the vegetables.

6 Zr Toxicity to Plants

Metal toxicity depends not only on total concentration but also on metal speciation and interactions with soil components. Zr has no known biological function in plant or animal metabolism (Blumental 1976). Although effects vary with Zr dose and speciation, exposure has produced either stimulatory or toxic effects in algae, yeasts, bacteria, fish, and higher plants (Smith and Carson 1978; Couture et al. 1989; Abollino et al. 2002; Shi and Chen 2002; Shi and Li 2003; Fodor et al. 2005). Although data are scarce, it appears that the stable isotopes of Zr have low toxicity to organisms (Blumental 1976; Couture et al. 1989). Zr caused slight toxicity in young *Hordeum vulgare* by decreasing biomass (Davis et al. 1978). A significant influence of Zr–Ascorbate on intracellular chemical composition or chlorophyll content was observed to occur in various plants exposed to Zr: *C. pyrenoidosa* or *Triticum aestivum* (Simon et al. 1998; Fodor et al. 2005). Ferrand et al. (2006) reported a slight decrease in dry weight of *P. sativum* and *S. lycopersicum* plants from a high accumulation of Zr.

Zr is also reported to stimulate or inhibit enzymes in plant cells. Inhibition of Zr-induced phosphate-dependent enzymes was reported by Smith and Carson (1978). Fodor et al. (2005) reported a Zr-induced increase in peroxidase (POD) activity, whereas decreased ascorbate peroxidase (APX) and glutathione reductase (GR) activities occurred in *T. aestivum*. Simon et al. (1998) reported a Zr-induced modification of enzymatic activity in *C. pyrenoidosa*. Similar results were obtained by Ti-ASC (which has similar physical and chemical activities as that of Zr) in *T. aestivum* and *Zea mays* (Pais 1983) and in *Capsicum annuum* (Carvajal et al. 1994). Furthermore, after Zr application, Fodor et al. (2005) reported a marked decrease in the total phenol content of plant tissues.

The mechanism behind Zr-induced inhibition of growth or modification in enzyme activities is not known, but may be explained in terms of the possible mechanisms responsible for these physiological changes in plants. Heavy metal accumulation in plant tissue is toxic to most plants and interferes with various morphological, physiological, and biochemical process (Shahid 2010). Inside a cell, these metals impair photosynthesis, respiration, mineral nutrition, and enzymatic reactions (Maestri et al. 2010; Ali et al. 2011). The primary response of plants to heavy metal toxicity is the generation of reactive oxygen species (ROS) (Pourrut et al. 2008; Mirza et al. 2010; Rascio and Navari-Izzo 2011; Ali et al. 2011; Xu et al. 2011). Such ROS include, superoxide radicals ($O_2^{\bullet -}$), hydroxyl radicals ($^{\bullet}OH$), and hydrogen peroxide (H_2O_2) and are also produced during normal cell metabolism in the chloroplast, either as by-products of the reduction of molecular oxygen (O_2) or its excitation in the presence of highly energized pigments. Excess ROS formed within cells from heavy metal exposure can provoke oxidation and modification of cellular amino acids, proteins, membrane lipids, and DNA and produce oxidative stress (Pourrut et al. 2008; Grover et al. 2010; Yadav 2010; Qureshi et al. 2010; Rascio and Navari-Izzo 2011).

To combat oxidative damage and prevent cell injury and tissue dysfunction, plants employ protective mechanisms (Benekos et al. 2010; Xu et al. 2011). First, plants may resist metal entry into their cells by exclusion or by binding them to the cell wall or other ligands such as organic acids and amino acids, thereby rendering them harmless, as happens with Pb (Wu et al. 2011; Xu et al. 2011; Zeng et al. 2011). Preventing metal entrance into roots is the first and major protective mechanism adopted by plants against harmful metal effects (Meyers et al. 2008; Jiang and Liu 2010). Metal complexation with carboxyl groups of pectins that exist in plant cell walls is the most important plant-cell resistant reaction to most metals like lead (Patra et al. 2004; Kopittke et al. 2007; Meyers et al. 2008; Krzeslowska et al. 2009, 2010; Jiang and Liu 2010). In this manner, metals are accumulated in root cells and are not translocated to shoot tissues. Although Zr is generally not considered to be a toxic metal, its entry into plants via roots is blocked by its bonding with cell wall exchange sites (Ferrand et al. 2006). Several authors have reported that Zr accumulates in plant root cells and thereby reduces the amount translocated to shoot tissues (Kabata-Pendias 1993; Sanzharova and Aleksakhin 1982).

A secondary defense system against metal toxicity is manifested via antioxidants that combat increased production of ROS that are caused by metal exposure.

These antioxidant enzymes include superoxide dismutase (SOD), catalase (CAT), peroxidase (POD), ascorbate peroxidase (APX), and glutathione reductase (GR). There are also antioxidants of low molecular weight such as proline (PRO), cysteine (Cys), nonprotein thiol (NPT), ascorbic acid (AsA), and glutathione (GSH) that scavenge ROS, thereby prohibiting cell injury and tissue dysfunction (Lyubenova and Schröder 2011; Mou et al. 2011; Lomonte et al. 2010; Ali et al. 2011).

7 Conclusions and Perspectives

Zr is a typical lithophile element that has special properties that render it useful for several former and present industrial and other applications. In this chapter, we address the biogeochemical behavior of Zr in soil–plant systems and its impact on the plants. The conclusions we reached from having performed this review are as follows.

1. Zr is abundant in the earth's crust and forms stable complexes in soil with many different compounds, particularly with inorganic ligands like Cl^- and SO_4^{2-}. The behavior of Zr is strongly affected by its geologic origin and speciation. Low pH and complexation with soil organic matter affects zirconium behavior in soils and increases its phytoavailability. The recent growing use of Zr in different industrial processes has produced increased concentrations in different environmental compartments and in some cases has modified the speciation of Zr.
2. Despite its presence and retention at quite high quantities in ecosystems, Zr has not yet been accused of affecting the specific metabolic system of any organisms. Although zirconium enters plants, mainly through the roots from the soil solution, its mechanisms for doing so are still unknown. Once in the roots, Zr becomes sequestered in root cells and a limited amount is translocated to plant shoots. Depending on its speciation, Zr can induce phytotoxicity, such as affecting chlorophyll content or modifying enzyme activity. Plant antioxidant enzymes may be a protective strategy against the toxicity of Zr.
3. Finally, our review has disclosed that more data on the plant–soil behavior of Zr are needed. In particular, new plant species that are cultivated on different soil types that contain Zr are needed. Future studies should emphasize the mechanisms that are involved in uptake and phytotoxicity of Zr and should assess the potential health risks associated with Zr-polluted plants that are consumed by humans. These are important goals in the context of the increasing amounts of Zr emissions to the environment.

8 Summary

Zirconium (Zr) is a transition metal that has both stable and radioactive isotopes. This metal has gained significant attention as a major pollutant of concern, partly because it has been prominent in the debate concerning the growing anthropogenic

pressure on the environment. Its numerous past and present uses have induced significant soil and water pollution. Zr is generally considered to have low mobility in soils. The behavior of Zr particularly depends on the characteristics of the media in which it exists, and even its presence in the biosphere as a contaminate may affect its behavior. In this chapter, we describe the relationship between the behavior of Zr and its speciation in soils, its uptake and accumulation by plants, its translocation and toxicity inside plants, and mechanisms by which plants detoxify it.

Zr is abundant and occurs naturally in the earth's crust. Zr emissions to the atmosphere are increasing from anthropogenic activities such as its use in industry and nuclear reactors. Zr forms various complexes with soil components, which reduces its soil mobility and phytoavailabilty. The mobility and phytoavailabilty of Zr in soil depend on its speciation and the physicochemical properties of soil that include soil pH, texture, and organic contents. Despite having low soil mobility and phytoavailability, amounts of Zr are absorbed by plants, mainly through the root system and can thereby enter the food chain.

After plant uptake, Zr mainly accumulates in root cells. Zr does not have any known essential function in plant or animal metabolism. Although little published data are available, we conclude that the phytotoxicity of Zr is generally low. Notwithstanding, Zr can significantly reduce plant growth and can affect plant enzyme activity. When exposed to Zr-induced toxicity, plants possess numerous defense mechanisms to cope with the toxicity. Such strategies include Zr sequestration in plant roots and activation of various antioxidants. Because Zr may have impact on the biosphere, we believe it deserves to be evaluated in supplementary studies that will enhance the understanding of its behavior in soil–plant systems.

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