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Preface

The depletion of water resources through environmental contamination has guided scientific community to develop innovative technologies for treating wastewaters. Phytoremediation using aquatic plants has emerged as an eco-friendly and cost-effective alternative. Aquatic plants irrespective free-floating, submerged and emergent possess immense potential for remediation of various organic and inorganic contaminants. The aquatic plants have also shown their efficiency in removing contaminants from wastewaters when used in constructed wetlands. Since aquatic plants play a major role in phytoremediation of wastewaters, the information related to each aspect of this technique needs to be highlighted. The present book provides a detailed overview about the topic with emphasis on every aspect related to this topic.

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In compilation and completion of the major effort of this kind, I would like to acknowledge the scientific community whose literature has been consulted extensively and that only provided the baseline for framing the whole information in form of a book. I wish to express gratitude to the Department of Science and Technology, Ministry of Science and Technology, India, for providing funding and infrastructure. I also acknowledge the website Google for providing pictures of the aquatic plants. Lastly I would like to acknowledge our publishers, Springer India, for their support.

Contents

1 Introduction

Water is a resource that supports life throughout the earth. Contamination of water resulting from anthropogenic activities is a matter of concern worldwide. Various forms of physical, chemical and biological contaminants are reported in polluted waters. Chemical pollutants mainly include inorganic, organic and gaseous pollutants. The nature of the chemical contaminant varies depending upon the nature of anthropogenic activity and the chemicals used in various industrial processes. Discharge of municipal sewage and industrial activities deteriorate water quality in urban areas. Synthetic fertilizers, herbicides, insecticides and plant residues released from agricultural activities change the water quality in rural areas.

1.1 Contaminants in Aquatic Environment

Industrial, municipal and domestic wastewaters contain different types of contaminants. The composition of wastewater depends primarily on the organic and inorganic contaminants (Fig. 1.1).

1.1.1 Physical Contaminants

This mainly includes colour of the wastewater, odour and suspended solids. The level of all the three parameters varies depending upon the source of wastewater. They mainly add sludge and create anaerobic conditions.

1.1.2 Chemical Contaminants

1.1.2.1 Organic Contaminants

Biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) are gross measures of organic content in wastewaters and indicate water quality. BOD is the amount of dissolved oxygen required by microbes (aerobic conditions) to break down organic material present in a given water sample at a certain temperature over a specific time period. It is commonly expressed in milligrammes of oxygen consumed per litre of sample during 5 days of incubation at 20 °C. COD indicates the mass of oxygen consumed per litre of solution. It is expressed in milligrammes per litre (mg L^{-1}). TOC measures total carbon present in the water sample expressed in terms of content of dissolved carbon dioxide and carbonic acid salts. All the three parameters determine the amount of organic pollutants found in surface water (lakes and rivers) or wastewater.

Besides this, a large number of other organic contaminants have been noted in wastewater released from different sources. Some of the other common organic contaminants present in wastewater are listed as:

- Pesticides
- Detergents
- Solvents and cleaning fluids
- Flame retardants
- Hormones and sterols
- Antimicrobials
- Food additives

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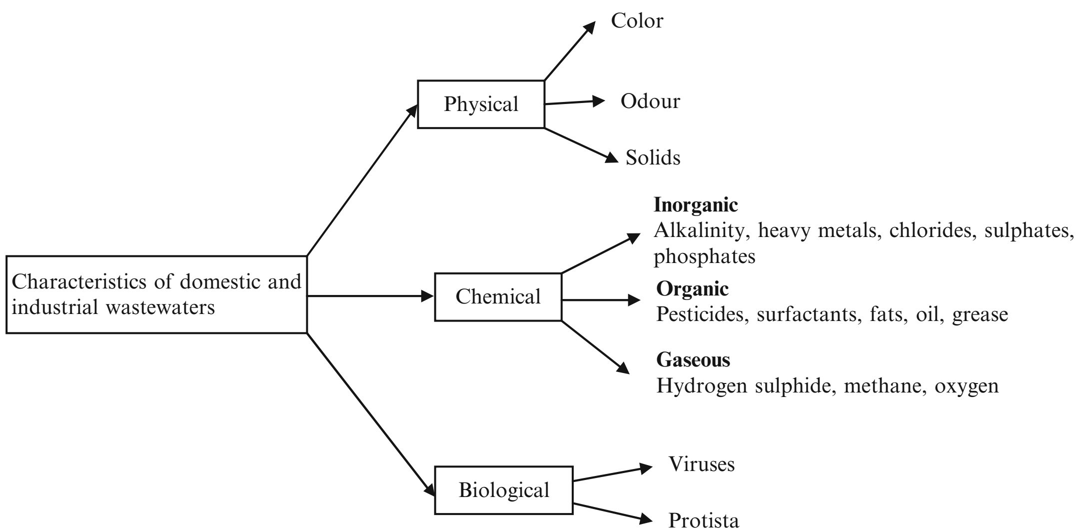

Fig. 1.1 The physical, chemical and biological characteristics of wastewater

Table 1.1 Organic contaminants reported in wastewaters (Petrović et al. 2003)

S. no.	Category	Common compounds/chemicals
1	Personal care compounds	DEET—*N*,*N*-diethyl-meta-toluamide
		Parabens—alkyl esters of *p*-hydroxybenzoic acid
		Triclosan
2	Pharmaceuticals	Veterinary and human antibiotics—ciprofloxacin, erythromycin, sulfamethoxazole, tetracycline
		Drugs—codeine, salbutamol, carbamazepine acetaminophen (paracetamol), ibuprofen
		Others—iopromide, iopamidol
3	Hormones and sterols	Sex hormones—androgens, androstenedione and testosterone, and oestrogens such as oestrone, oestriol, 17 β-oestradiol, 17 α-oestradiol and progesterone
4	Surfactants	Perfluorinated sulphonates and carboxylic acids, perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA)
5	Solvents	Trihalomethanes (THMs) and haloacetic acids (HAAs)
6	Food additives	Triethyl citrate, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT)
7	Chlorinated solvents	Tetrachloroethylene (PCE), trichloroethylene (TCE), 1,1,1-trichloroethane (1,1,1-TCA), dioxin
8	Petroleum hydrocarbons	Polyaromatic hydrocarbons (PAHs), methyl tertiary-butyl ether (MTBE)
9	Pesticides	Chlorinated hydrocarbons (chlordane, EDB)
		Carbamates (aldicarb)
		Organophosphates (malathion)
10	Volatile organic compounds (VOC)	Benzene, toluene, xylene, dichloromethane, trichloroethane, trichloroethylene
11	Endocrine disrupting chemicals (EDC)	Bisphenol A (BPA), oestrone, α-oestradiol and β-oestradiol 4-tert-octylphenol (4-t-OP) and 4-n-nonylphenol (4-n-NP)

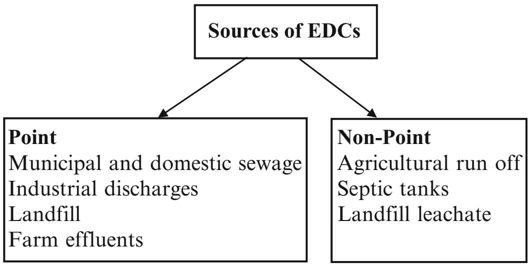

Fig. 1.2 Sources of endocrine-disrupting compounds that pollute the aquatic environment (From Bolong et al. 2009)

Emerging or newly identified contaminants are a major concern for public health and safety as existing conventional water treatment plants are not designed for effective elimination of these unidentified contaminants (Bolong et al. 2009) (Table 1.1). These mainly include

- Endocrine-disrupting chemicals (EDCs) (Fig. 1.2)
- Pharmaceuticals
- Personal care products (PCPs)
- Surfactants
- Various industrial additives

Organic pollutants are also referred to as persistent organic pollutants (POPs) or xenobiotics. Pesticides are the most abundant and common xenobiotics present in wastewaters. These include polychlorinated dibenzodioxins and dibenzofurans (often referred to as *dioxins*) as well as polychlorinated biphenyls (PCBs), aldrin, toxaphene, DDT, chlordane, dieldrin, endrin, HCB, heptachlor and mirex. Concern has arisen because these xenobiotics are extremely stable and persistent, toxic to humans and other organisms, biomagnified along trophic webs and transported over long distances (Carvalho 2006). These xenobiotics are very resilient to biotic and abiotic degradation and cause detectable harmful effects even at relatively low concentrations (Larsen 2006). PAHs and nitroaromatic compounds are of anthropogenic origin and are produced primarily during fuel combustion and manufacture of dyes, explosives, pesticides, fertilizers, etc. Most of the pesticides such as DDT (dichlorodiphenyltrichloroethane), aldrin, lindane, propiconazole and penconazole cause hormonal imbalance and behavioural changes and severely impact reproductive potential in humans. Aromatic and chlorinated hydrocarbons including heptachlor, benzene, bromobenzene, chloroform, camphor, dinitrotoluene, nitrobenzene and styrene are also commonly reported in drinking and wastewaters.

Trace concentrations of endocrine-disrupting chemicals such as oestrone, oestradiol, nonylphenol and ethinyl oestradiol present in effluents cause adverse effects in aquatic biota and hence may have an impact on human health. Exposure route for both humans and animals is by ingestion via food/drink intake which leads to bioaccumulation and biomagnification. EDCs and PCPs affect reproductive potential in humans by altering hormonal level and may prove to be carcinogenic. Besides these, volatile organic compounds (VOC) such as benzene, toluene, xylenes, dichloromethane, trichloroethane (TCA) and trichloroethylene (TCE) also contaminate water bodies through leakage from underground storage tanks. Most of these organic contaminants (including chlorinated solvents, pesticides and hydrocarbons) are known carcinogens and neurotoxins. They cause damage to the central nervous system, irritation of respiratory and gastrointestinal systems and immunological, reproductive and endocrine disorders in children.

1.1.2.2 Inorganic Contaminants

The presence of inorganic contaminants is very common in polluted waters. These mainly include:

- Metals
- Ions/nutrients
- Radionuclides

Heavy Metals

Heavy metals are elements with atomic number >20 that possess metallic properties and mainly include cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), cobalt (Co), iron (Fe), nickel (Ni), manganese (Mn), zinc (Zn) and arsenic (As). They form a major category of polluted waters and have been given due importance due to their higher toxicity. Heavy metals such as cadmium and lead are mainly released from industrial processes, industrial discharges, mining operations and acid mine drainage. Alternate sources of their release are automobile exhaust, urban sewage, petrochemicals, mining and agricultural sources such as fertilizer, fungicidal sprays, pesticides and pharmaceuticals. Leaded gasoline is a major source of atmospheric and terrestrial lead.

Ecological and anthropogenic effects of heavy metals are well reported (Chaney 1988; Wani et al. 2012). Heavy metal accumulation in living organisms proves toxic causing various diseases and disorders. They have tremendous affinity for sulphur and disrupt enzyme function by forming bonds with sulphur groups in enzymes. They also bind protein carboxylic (COOH) and amino ($-NH_2$) groups. Heavy metal ions specifically Cd, Cr, Cu, Pb, As and Hg bind to cell membranes, hindering transport processes through the cell wall. Acute toxicity cause high blood pressure, renal dysfunction, neurological damage, blindness, insanity, chromosome breakage, destruction of testicular and red blood cells and birth defects. Cadmium in particular may replace Zn in some enzymes, thereby altering the stereo-structure of the enzyme and impairing its catalytic activity. Toxicological effects of mercury were neurological damage, including irritability, paralysis, blindness, insanity, chromosome breakage and birth defects.

Ions/Nutrients

Ammonia, nitrite, nitrate, chloride, sulphate, phosphorus and cyanide (CN^-) are the major ions present in contaminated water. Most of them are the product of the decay of nitrogenous organic wastes and are commonly found in groundwater and wastewater. The cyanide ion has a strong affinity for many metal ions. Cyanide is widely used in metal cleaning, electroplating industry and mineral-processing operations. Ammonia is the initial product of the decay of nitrogenous organic wastes. It is a normal constituent of some sources of groundwater and is sometimes added to drinking water to remove the taste and odour of free chlorine. Domestic, municipal and industrial wastewaters contain nitrogen and sulphur in high amounts. Sulphur is mainly present in the form of sulphate and other reduced forms such as hydrogen sulphide, sulphides and thiosulphates. Orthophosphate is the main form of phosphorus present in wastewater streams. Nitrogen is present as nitrate, nitrite or ammonium. Excessive nitrogen and phosphorus loading in wastewater is a major threat to water quality and leads to increased rates of eutrophication. Eutrophication has been identified as a major environmental threat in both freshwater and marine waters all over the globe. Eutrophication-related water quality impairment has a very substantial negative effect on water quality, especially dissolved oxygen (DO) levels. Wastewater also comprises of relatively small concentrations of suspended and dissolved organic and inorganic solids.

Radionuclides

Radionuclides are radioactive isotopes that can occur naturally or result from man-made sources. Natural radiation comes from radioactive elements in the earth's crust, groundwater and surface water. Radionuclides such as uranium or plutonium (Pt) are produced as fission products of heavy nuclei of elements or reaction of neutrons with stable nuclei (Manahan 1994). They are formed in large quantities as waste products in nuclear power generation. Radionuclides found in drinking water sources are isotopes of radium (Ra), uranium (U) and radon (Ro), among others. Radiation exposure can occur by ingesting, inhaling, injecting or absorbing radioactive materials. Radionuclides have a long-term radiological impact due to their long half-life (e.g. 30 years for ^{137}Cs and 2 years for ^{134}Cs) and high biological availability. Half-life is the time required for any given radioisotope to decay to one-half of its original quantity.

Industrial effluents consist of inorganic contaminants such as heavy metals, ammonia, nitrate, nitrite, sulphate and cyanide, while oil, grease, refractory compounds, organochlorides and nitro compounds are the major organic contaminants (Nwoko 2010). Heavy metals, chlorides, sulphate and nitrates are inorganic contaminants commonly reported in groundwater and majority of wastewaters, while pesticides, pharmaceuticals, solvents, food additives, surfactants and petroleum products are the major organic contaminants (Kolpin et al. 2002; Lin et al. 2008; Stuart et al. 2011).

1.1.3 Biological Contaminants

These mainly include viruses, protists and other pathogens such as bacteria present in wastewater.

Excessive contamination in water bodies causes diseases in humans and aquatic biota.

1.2 Wastewater Treatment Methods

Conventional technologies have been used since long for the treatment of organic and inorganic contaminants present in polluted waters. The treatment process consists of three steps: primary, secondary and tertiary.

Primary Treatment—The water is passed through large tanks so that sludge can settle and floating material such as grease and oils can rise to the surface and can be skimmed off. This step produces a homogeneous liquid capable of being treated biologically and a sludge that can be separately treated or processed.

Secondary Treatment—This removes up to 90 % of the organic matter by using biological treatment processes. The microbial growth is suspended in an aerated water mixture where the air is pumped. Aerobic bacteria and other microorganisms break down the organic matter, and most of the organic matter is consumed by bacteria as food.

Tertiary—This helps in raising the effluent quality by minimizing pollution. Various methods such as coagulation sedimentation, filtration and reverse osmosis are used.

This is finally followed by disinfection where chlorination, ultraviolet treatment and ozonation is done to improve water quality (Fig. 1.3).

Each of the water treatment technique is effective for treating a specific contaminant. Heavy metals are removed mainly by alkaline precipitation, ion exchange, electrochemical removal, filtration, reverse osmosis, electrodialysis and adsorption. Organic pollutants such as polychlorinated biphenyls (PCBs) are treated by solvent extraction and thermal alkaline dechlorination. Most of these technologies are based on physical and chemical methods that require input of chemicals, which makes the technology expensive. Moreover, they produce adverse impacts on aquatic ecosystems and human health. Apart from this, most of these techniques are practically infeasible due to the range of the contamination. Over the time, all over the world considerable attention has been paid to select alternate methods/materials particularly biological methods for wastewater treatment. Interest has been generated in the use of biosorbents for treating industrial, municipal and domestic wastewaters (Salt et al. 1995a). Various biological agents including microbes (bacteria), algae, fungi, plants and agricultural residues possess potential for removing various contaminants from environment and treating wastewater

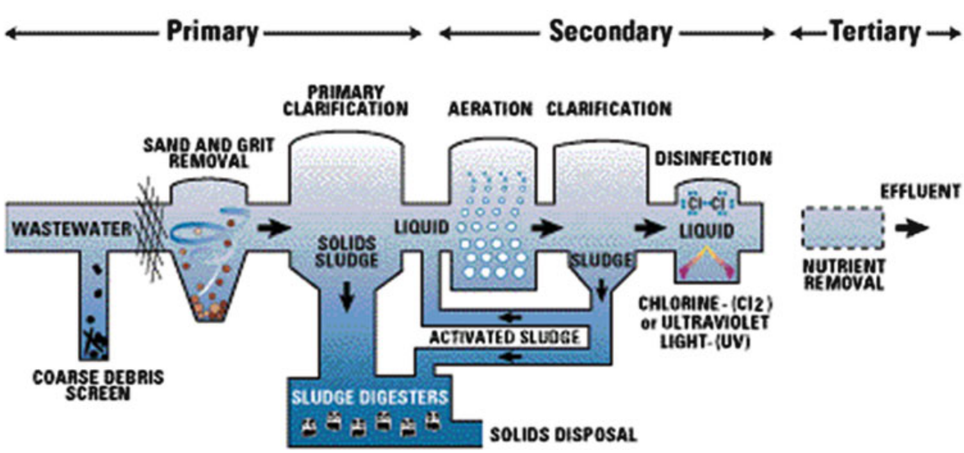

Fig. 1.3 Various steps involved in treatment of wastewater using conventional method (Adapted from http://www.sheffy6marketing.com/index.php?page)

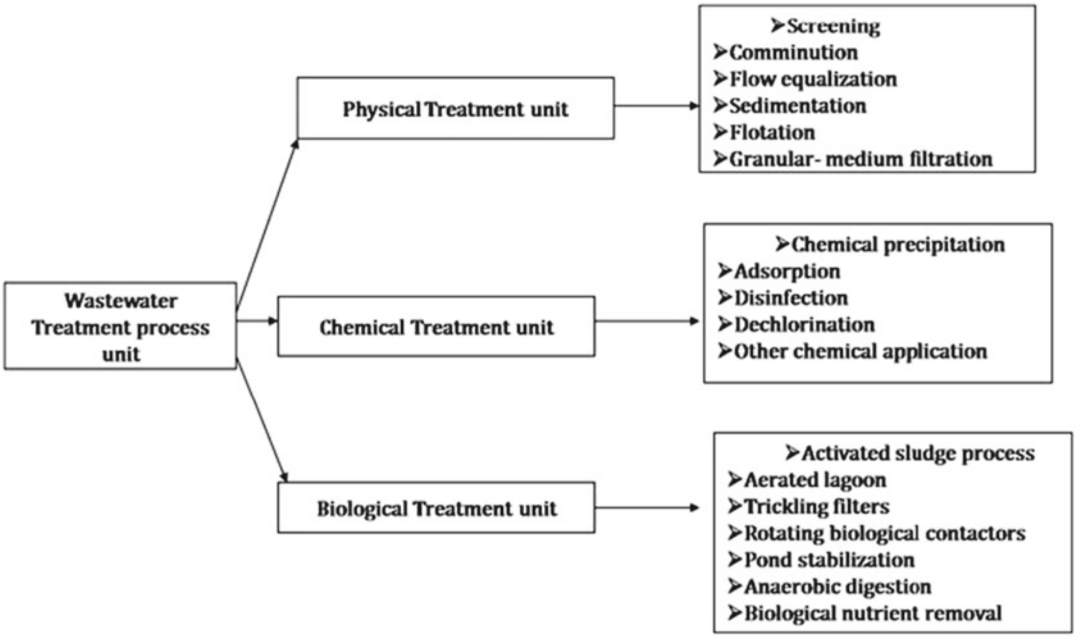

Fig. 1.4 Common wastewater treatment processes (Adapted from Rawat et al. 2011)

generated from dairies, tanneries, sugar factories, pulp and paper industries, palm oil mills, distilleries, etc. (Fig. 1.4).

1.3 Bioremediation

Bioremediation exploits the natural capability of living organisms to clean environment. It involves the use of microorganisms and other biological materials such as algae, fungi and bacteria to detoxify or remove pollutants from the environment owing to their diverse metabolic capabilities (Volesky and Holan 1995; Matheickal et al. 1999; Ho et al. 2002; Malik 2004). Bioremediation aids in transformation and degradation of contaminants into non-hazardous or less hazardous substances. Bioremediation technology exploits mitigation processes such as biostimulation and bioaugmentation. Biostimulation utilizes indigenous microbial populations to remediate contaminated soils by adding nutrients and other substances to catalyse natural attenuation processes. Bioaugmentation involves introduction of exogenic microorganisms (sourced from outside the soil environment) capable of detoxifying a particular contaminant, sometimes employing genetically altered microorganisms (Biobasics 2006).

Bioremediation has been found effective in mitigating:

- Hydrocarbons
- Halogenated organic solvents
- Halogenated organic compounds
- Non-chlorinated pesticides and herbicides
- Nitrogen compounds
- Metals (lead, mercury, chromium)
- Radionuclides

1.3.1 Microbes

Degradation of organic contaminants using biodegradation mechanism of microbes results in complete mineralization of organic contaminants into carbon dioxide, water and inorganic compounds, while transformation mechanism converts complex organic contaminants to other simpler organic compounds. Biodegradation of toxic organic pollutants such as pesticides, hydrocarbons, halogenated organic compounds and phenolic or anilinic compounds has been facilitated by enzymes present in microbes. Enzymes cleave chemical bonds and assist the transfer of electrons from a reduced organic substrate (donor) to another chemical compound (acceptor). Enzymes such as oxygenases or oxidoreductases and laccases mediate oxidative coupling through polymerization, copolymerization with other substrates or binding to humic substance (Karigar and Rao 2011). Anaerobic microbes are important for degrading the halogens and nitrosamine, reducing epoxides and nitro groups. Bacteria such as *Pseudomona*s, *Bacillus*, *Neisseria*, *Moraxella*, *Trichoderma*, *Aerobacter*, *Micrococcus* and *Burkholderia* and *Acinetobacter* are able to degrade DDT, dieldrin and endrin. *Anabaena* (a cyanobacterium), *Pseudomonas spinosa*, *Pseudomonas aeruginosa* and *Burkholderia* can degrade endosulfan.

Microorganisms employ a variety of mechanisms to resist and cope with toxic metals. *Oscillatoria* spp., *Chlorella vulgaris* and *Chlamydomonas* spp., *Arthrobacter*, *Agrobacter*, *Enterobacter* and *Pseudomonas aeruginosa* are some metal-reducing microbes. The principal mechanism of resistance of inorganic metals by microbes are oxidation, reduction, methylation, demethylation, enzymatic reduction, metal–organic complexion, metal ligand degradation, intracellular and extracellular metal sequestration, metal efflux pumps, exclusion by permeability barrier and production of metal chelators such as metallothioneins and biosurfactants. Microorganisms do not biodegrade inorganic metals, but transform their oxidation state. Transformation of oxidation states of toxic metals increases their bioavailability in the rhizosphere (root zone), thus facilitating their absorption and removal. Generally, microbial transformations and detoxifications of metals occur by either redox conversions (reduction) of inorganic forms or conversions from inorganic to organic forms and vice versa. Reduction of metals can occur through dissimilatory metal reduction, where microbes utilize metals as terminal electron acceptor for anaerobic respiration. Till date As, Cr, Hg, U and Se have been detoxified by microbial reduction.

Microbial remediation of toxic metals occurs in two ways:

1. Direct reduction by the activity of the bacterial enzyme 'metal reductase'. It is applied for groundwater decontamination. This *ex situ* method is very expensive and has low metal extraction efficiencies.
2. Indirect reduction by biologically produced hydrogen sulphide (H_2S) by sulphate-reducing bacteria to reduce and precipitate the metals. This *in situ* method is environmentally sound and inexpensive.

The mechanism by which bioremediation of metals occurs includes:

1. Biosorption and bioaccumulation

   Biosorption is sequestration of the positively charged heavy metal ions (cations) to the negatively charged microbial cell membranes and polysaccharides secreted in most of the bacteria on the outer surfaces through slime and capsule formation. The metals are transported into the cell cytoplasm through the cell membrane with the aid of transporter proteins.
2. Immobilization

   Metal ions get fixed to iron (Fe) oxides and into organic colloids inside the microbial cells become immobilized. This is achieved by enzymatic reduction by microbes.
3. Solubilization

   Metal-reducing bacteria enzymatically reduce and also solubilize oxide minerals.

1.3.2 Fungi

Penicillium, *Aspergillus wentii*, *Aspergillus niger Rhizopus oryzae*, *Mucor*, *Saccharomyces*, *Phanerochaete chrysosporium* (white rot fungi), *Trametes versicolor*, *Pleurotus ostreatus* and *Pleurotus sajor-caju* biosorb metals and radionuclides (Bishnoi and Garima 2005). Biosorption of metal ions on cell surface occurs by ion exchange and complexation with functional groups such as carboxylate, hydroxyl, amines, amide, phosphate and sulphydryl. Extracellular enzymes such as oxidoreductases, laccases, ligninases and peroxidases present in fungus assist

Table 1.2 Bacteria capable of destroying hazardous wastes and chemicals by biodegradation

Organisms	Chemicals degraded
Bacteria	
Flavobacterium spp.	Organophosphates
Cunniughamella elegans and *Candida tropicalis*	PCBs (polychlorinated biphenyls) and PAHs (polycyclic aromatic hydrocarbons)
Alcaligenes spp. and *Pseudomonas* spp.	PCBs, halogenated hydrocarbons, alkylbenzene sulphonates, PCBs, organophosphates, benzene, anthracene, phenolic compounds, 2,4-D, DDT and 2,4,5-trichlorophenoxyacetic acid etc
Actinomycetes	Raw rubber
Nocardia tartaricans	Chemical detergents (ethylbenzene)
Arthrobacter and *Bacillus*	Endrin
Closteridium	Lindane
Trichoderma and *Pseudomonas*	Malathion
Fungi	
Phanerochaete chrysosporium	Halocarbons such as lindane and pentachlorophenol
P. sordida and *Trametes hirsuta*	DDT, DDE, PCBs, 4,5,6-trichlorophenol, 2,4,6-trichlorophenol, dichlorphenol and chlordane
Zylerion xylestrix	Pesticides/herbicides (aldrin, dieldrin, parathion and malathion)
Yeast (*Saccharomyces*)	DDT
Mucor	Dieldrin

degradation of xenobiotic compounds including lignocellulosic materials, phenols PAHs, PCBs, nitroaromatics, pesticides, herbicides and dyes (Magan et al. 2010). Fungal peroxidases and dioxygenases are involved in biodegradation of pentachlorophenol. White rot fungi in particular produce lignin-degrading enzymes that catalyse oxidation of xenobiotics such as endosulfan in addition to their ability to degrade lignin. *Aspergillus flavus*, *Fusarium oxysporum*, *Mucor aternans*, *P. chrysosporium*, *Trichoderma viride*, etc. degrade DDT. Biodegradation of pesticides is regulated by environmental factors including pH, temperature, nutrient supply and oxygen availability. Biodegradation occurs via two strategies: (1) the use of the target compound as a carbon source and (2) enzymatic transformation of the target compound (co-metabolism) (Table 1.2).

1.3.3 Algae

Algae acts as indicators of water pollution and play a role in treating wastewater. Algae such as *Chlamydomonas reinhardtii*, *Chlorella*, *Ankistrodesmus* and *Scenedesmus* have been successfully used for the treatment of olive oil, mill, paper industry and domestic wastewater. Removal of contaminants occurs by bioaccumulation and biodegradation. The unicellular green algae *Chlorella fusca* var. vacuolata and *Chlamydomonas reinhardtii* are able to bioaccumulate, biotransform and biodegrade the herbicide metfluorazon and prometryne and remove nutrients such as nitrogen and phosphorus. *Ankistrodesmus* and *Scenedesmus* species have also shown potential for biotransforming organic compounds such as naphthalene.

Algal species such as *Chlorella*, *Anabaena inaequalis*, *Westiellopsis prolifica*, *Stigeoclonium tenue* and *Synechococcus* sp. tolerate heavy metals. Several species of *Chlorella*, *Anabaena* and marine algae have been used for the removal of heavy metals. Metals are taken up by algae through adsorption. At first, the metal ions are quickly adsorbed over the cell surface in a few seconds or minutes; this process is called physical adsorption. Then, these ions are transported slowly into the cytoplasm in a process called chemisorption. Polyphosphate bodies in algae enable freshwater unicellular algae to

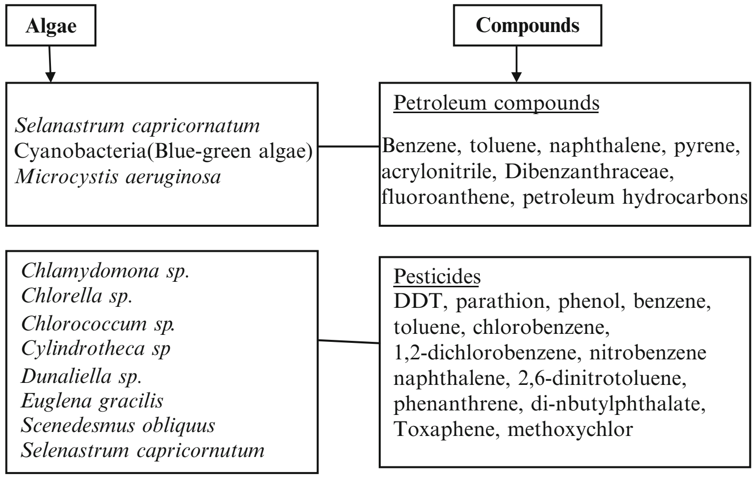

Fig. 1.5 Degradation of organic compounds by algae

store other nutrients. Several researchers have established that metals such as Ti, Pb, Mg, Zn, Cd, Sr, Co, Hg, Ni and Cu are sequestered in polyphosphate bodies in green algae. These bodies perform two different functions in algae: provide a 'storage pool' for metals and act as a 'detoxification mechanism'. *Microcystis* microalgae are capable to synthesize peptides and metallothioneins, mainly the post-transcriptionally synthesized class III metallothioneins or phytochelatins, which effectively bind to heavy metal (Dwivedi 2012). Among them, microalgae have proved to possess high metal-binding capacities due to the presence of polysaccharides, proteins or lipid on the surface of their cell walls containing some functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals. Marine algae are capable of biosorbing radionuclide such as radium, thorium and uranium (Priyadarshani et al. 2011). Biosorption of uranium by *Cystoseira indica*, a brown alga, has also been reported (Fig. 1.5).

1.3.4 Other Materials

Agricultural products/by-products are natural sorbent materials that have also shown the capacity to remove contaminants from wastewater. They can serve as a replacement of costly methods for wastewater treatment. Agro residues and biomaterials such as leaf powder, straw and bran, fruit residues, fibres obtained from crop plants, fruit plants and tree species have been evaluated with an aim of developing low-cost wastewater treatment technology (Ho and Ofomaja 2006; Ofomaja and Ho 2007; Amuda et al. 2007; Kahraman et al. 2008; Schiewer and Patil 2008). These materials have been found effective in removing heavy metals; inorganic ions such as nitrate, ammonia and phosphate; and organic compounds including dyes and phenol (Sun and Xu 1997; Abdelwahab et al. 2005; Ho et al. 2005; Eberhardt and Min 2008; Mohd Din et al. 2009; Liu et al. 2010). Removal of contaminants occurs by adsorption, chelation and ion exchange (Gardea-Torresday et al. 1999). These materials are composed of lignin, cellulose, hemicellulose, pectin and tannins that possess functional groups such as alcohols, hydroxyls, aldehydes, ketones, carboxylates and phenols that contribute to native ion exchange capacity (Abia et al. 2002). High adsorption capacity, availability in bulk and low economic value are advantages associated with the use of agro residues.

Terrestrial as well as aquatic plant species show ability to remove/transform/degrade contaminants. Crop plants, tree species, weeds and other wild plants with their natural ability in removing various contaminants from the environment have been demonstrated.

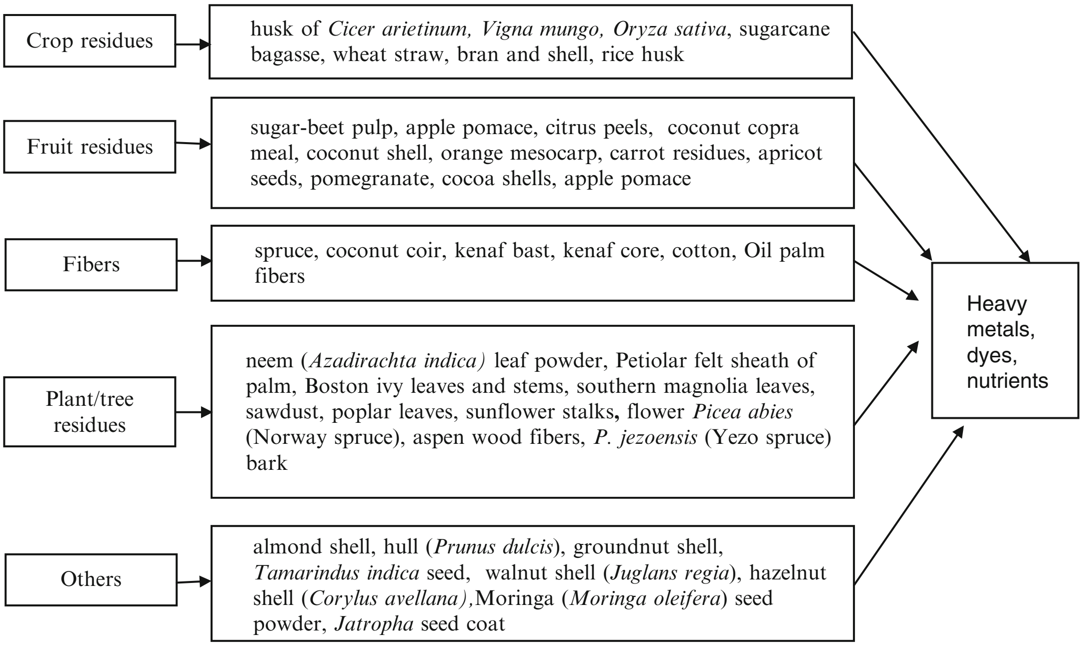

Fig. 1.6 Various agricultural residues used for removing contaminants from wastewater

Bioremediation techniques, although requiring more time, usually require less capital (~10–50 % cheaper) than the physical and chemical treatment methods. Bioremediation has been listed among top ten technologies because of its potential for sustainable mitigation of environmental pollution and cost effectiveness. In the era of bioremediation, vegetation/plants as a biological resource with immense capacity for removing variable contaminants from various components of ecosystem have been studied. Plants remove or degrade selected contaminants present in soil, sludge, sediment, groundwater, surface water and wastewater by utilizing their metabolic and hydraulic processes, thereby improving the environment quality that is termed as 'phytoremediation' (Fig. 1.6).

1.4 Phytoremediation

Plant root systems together with the translocation, bioaccumulation and contaminant degradation abilities aid the technique. Over the time, green technology became a promising alternate for treating both organic and inorganic contaminants present in water and soil and hence can be an affordable technological solution for wastewater treatment. The high purification activity of the plants is due to a rapid growth in polluted wastewater and capacity to remove contaminants (Miretzky et al. 2004). Plants possess efficient capacity for removing/treating variety of contaminants- metals, pesticides, chlorinated solvents, explosives, crude oil, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, landfill leachates, munitions and radionuclides through processes such as extraction, degradation, or including military sites, agricultural fields, industrial units, mine tailings, and sewage and municipal wastewater treatment plants. Bioremediation technologies, including phytoremediation, have been estimated to be 4–1,000 times cheaper, on a per volume basis, than current non-biological technologies (Sadowsky 1999). Phytoremediation has been studied extensively in research and small-scale demonstrations, but full-scale applications are currently limited to a small number of projects (Cunningham and Ow 1996).

The uptake of contaminants by plants is affected by several factors. Major factors include:

- Plant species—The physical characteristics of plants play an important role in the uptake/removal of contaminants. Genetic adaptations and biological processes including metabolic and absorption capabilities transport systems help in uptake of nutrients or contaminants selectively from the growth matrix (soil or water). Higher biomass production and species with higher adaptability to climatic and soil conditions are a necessary requirement for good phytoremediation capacity. Plant processes and associated rhizosphere microbes help in degradation/detoxification/transformation of contaminants. Selection of the plant species whether annuals or perennials, monoculture or deciduous is an important consideration. The seeds or plants should be from, or adapted to, the climate of the phytoremediation site. Therefore, the selection of plant variety is critical to ensure superior and effective remediation. For metal remediation, identification and selection of suitable hyperaccumulator plant species is required (Schnoor et al. 1995).
- Physical properties—Physicochemical parameters such as pH, organic matter, redox potential, contaminant concentration and the mineral content of the soil and water affect the removal/degradation of the contaminant.
- Root zone—Root length and root diameter affect contaminant uptake and degradation. Degradation of contaminants in the soil is facilitated by plant enzymes and root exudates. Plant roots exude organic acids such as citrate and oxalate that affect the bioavailability of metals. The type, amount and effectiveness of exudates and enzymes produced by a plant's root vary between species and even within subspecies or varieties of one species.
- Chelating agent—Chelating agents such as EDTA and micronutrients increase the bioavailability of contaminants especially heavy metals and stimulate the heavy metal-uptake capacity of the plant so that remediation is faster.
- Plant biomass—The high-biomass-producing plants possess higher contaminant removal potential.

Phytoremediation technology can treat both organic and inorganic contaminants, though uptake mechanisms in plants vary for each contaminant (Barceló and Poschenrieder 2003). Treatment of organic contaminants mainly involves phytostabilization, rhizodegradation, rhizofiltration, phytodegradation and phytovolatilization mechanisms, while phytostabilization, rhizofiltration, phytoaccumulation and phytovolatilization mechanisms are involved in the treatment of inorganic contaminants (Fig. 1.7; Table 1.3).

A number of different methods lead to contaminant degradation, removal (through accumulation or dissipation) or immobilization:

1. Degradation (destruction or alteration of organic contaminants)—rhizodegradation and phytodegradation
2. Accumulation (removal of organic and/or metal contaminants)—phytoextraction and rhizofiltration
3. Dissipation (removal of organic and/or inorganic contaminants into the atmosphere)—phytovolatilization
4. Immobilization (containment of organic and/or inorganic contaminants)—phytostabilization

1.4.1 Phytoextraction

It is defined as uptake/absorption and translocation of contaminants by plant roots into the aboveground portions of the plants (shoots) that can be harvested. Plant species absorb and hyperaccumulate metal contaminants and/or excess nutrients in harvestable root and shoot tissue. This process is applicable for metals (Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Zn), metalloids (As, Se), radionuclides (^{90}Sr, ^{137}Cs, ^{234}U, ^{238}U), non-metals (B, Mg) and organic contaminants present in soils, sediments and sludges (Brooks 1998a). It is also referred to as phytoaccumulation, phytoabsorption, phytosequestration, phytomining or biomining. Thompson et al. (1998) reported phytoaccumulation of organic contaminants, mainly explosive hexahydro-1,3,5-trinitro-1,3,5-triazine

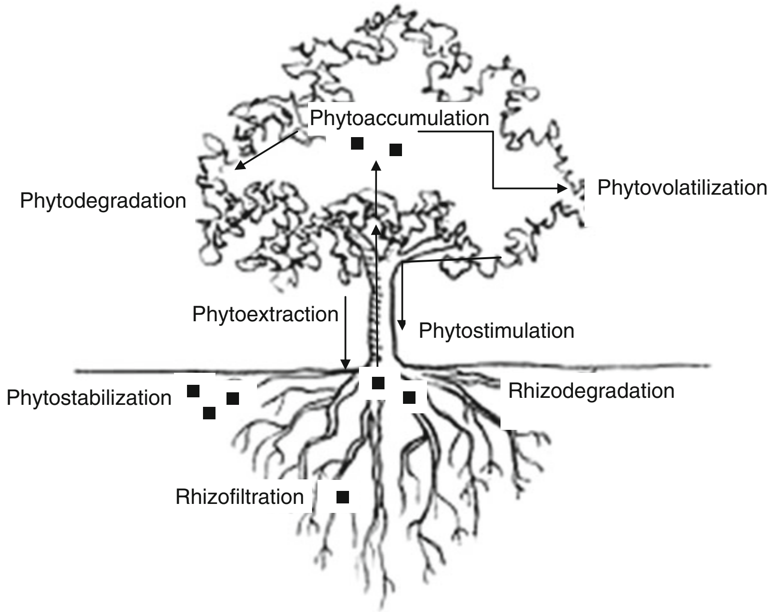

Fig. 1.7 Phytoremediation processes

Table 1.3 Phytoremediation processes

Process	Description	Media	Contaminants	Plants
Rhizodegradation/ phytodegradation	Microbial degradation in the rhizosphere stimulated by plants	Soil, sediments, sludges	Organic—aromatic, aliphatic and petroleum hydrocarbons, chlorinated solvents, TNT, pesticides	Grasses, alfalfa, hybrid poplar, *Brassica*, *Typha*, *Jatropha*, *Cassia*
Phytostabilization	Stabilization of contaminants by binding/complexation	Soil, sediments, sludges	Inorganic—metals (As, Cd, Cr, Cu, Pb, Zn)	Sunflower, *Chenopodium*
Phytoextraction	Uptake of contaminants into roots by accumulation or harvestable shoots	Soil, sediments, sludges	Inorganic—metals (Cr, Cu, Ni, Zn, Cd, Ag), radionuclides	*Alyssum*, *Brassica* *Thlaspi*, sunflower
Rhizofiltration	Removal of contaminant by plant roots	Groundwater, surface water, wastewater	Inorganic—metal, radionuclides (^{137}Cs, ^{230}Pb, ^{238}U)	*Eichhornia*, *Lemna*
Phytovolatilization	Volatilization of contaminant by leaves	Soil, sediments	Organic/inorganic (Se, Hg, As)	*Poplar*, *Phragmites*, *Scirpus*

(RDX), in an unaltered form in the leaves of hybrid poplar from a hydroponic solution.

1.4.1.1 Hyperaccumulators

Plants that possess the capacity to accumulate high quantities of metals than required for plant growth are termed as 'hyperaccumulators'. The concentration noted in these plants are about 10–100-fold higher than the levels noted in 'ordinary' non-hyperaccumulator plants (Erakhrumen 2007; Wani et al. 2012). The minimum concentration of metal a plant needs to contain to be termed a hyperaccumulator varies for each metal (Reeves and Brooks 1983; Baker and Brooks 1989). They

Table 1.4 Range of elemental concentrations in non-hyperaccumulator and hyperaccumulator plants (Reeves 2003)

Element	Normal range (mg g^{-1})	Element limit (mg g^{-1})	Hyperaccumulator species
As	0.01–5	1,000	*Pteris vittata*
Cd	0.03–20	100	*Eichhornia crassipes*,
			Thlaspi caerulescens
Co	0.05–50	1,000	*Alyssum* sp.
Cu	1–100	1,000	*Elodea nuttallii*
Mn	5–2,000	10,000	*Alyssum* sp.
			Phytolacca acinosa
Ni	0.2–100	1,000	*Berkheya coddii*,
			Alyssum bertolonii
Cr	0.05–30	1,000	*Spirodela polyrhiza*,
			Dicoma niccolifera
			Sutera fodina
Pb	0.5–30	1,000	*Thlaspi rotundifolium*
			Minuartia verna
			Brassica sp.
			Sesbania drummondii
Se	0.01–10	100	*Astragalus bisulcatus*
			Stanleya pinnata
Zn	0–0.1	10,000	*Thlaspi caerulescens*
			Eichhornia crassipes

are defined as plants that complete their life cycle with foliar metal concentrations exceeding (mg kg^{-1} dry weight, DW) Cd > 100, Ni and Cu > 1,000 and Zn and Mn > 10,000 (Table 1.4). This is physiologically possible because they possess high tolerance capacity (Brooks 1998a, b). Most of the metal taken up by them is exported to shoots, while a lower proportion of them are stored in root vacuoles. Some of the most studied hyperaccumulator plant species include *Thlaspi*, *Pteris vittata*, and *Brassica* species (Brooks 1998a, b). These plants can accumulate metals in concentrations 100,000 times greater than in the associated water. Maximum number of hyperaccumulators have been reported from families Brassicaceae, Lamiaceae, Scrophulariaceae, Cyperaceae, Poaceae, Apocynaceae, Euphorbiaceae, Flacourt iaceae, Fabaceae and Violaceae.

1.4.2 Phytostabilization

It is defined as the use of plants to immobilize the contaminants in the soil and groundwater through absorption and accumulation in plant tissues, adsorption onto roots or precipitation within the root zone preventing their migration in soil. The plant root exudates stabilize, demobilize and bind the contaminants in the soil matrix, thereby reducing their bioavailability. This process is suitable for organic contaminants and metals present in soils, sediments and sludges. Contaminants are adsorbed onto roots or bind to humic (organic) matter through the process of humification. Phytostabilization of organic contaminants or metabolic by-products can be achieved by attaching to plant components such as lignin. This is referred to as 'phytolignification' (Cunningham et al. 1995). Phytostabilization of metals is generally intended to occur in the soil, whereas phytostabilization of organic contaminants through phytolignification occurs aboveground. Metals within the root zone can be stabilized by changing from a soluble to an insoluble oxidation state, through root-mediated precipitation. Plant root exudates and microbes present in root zone alter the soil pH by the production of CO_2, possibly changing metal solubility and mobility, thus impacting the dissociation of organic compounds. This technique does not require disposal of hazardous materials or biomass. Moreover, ecosystem restoration is enhanced by the vegetation. The only limitation is long-term maintenance of the vegetation.

1.4.3 Rhizofiltration (Phytofiltration)

It is the removal of contaminants in surface water by plant roots. It involves adsorption or precipitation onto plant roots or absorption followed by sequestration in the roots. This process is applicable for removal of metals (Pb, Cd, Cu, Fe, Ni, Mn, Zn, Cr), excess nutrients and radionuclide (^{90}Sr, ^{137}Cs, ^{238}U, ^{236}U) present in groundwater, surface water and wastewater (Dushenkov et al. 1995, 1997a, b). It is generally applicable for treating large volumes of water with low contaminant concentrations (ppb). It can be conducted *in situ* or *ex situ* to remediate contaminated surface water bodies. Parameters such as pH, flow rate and contaminant concentration can alter the efficiency of this process. Applications of rhizofiltration are currently at the pilot-scale stage. Phytotech tested a pilot-scale rhizofiltration system in a greenhouse at the Department of Energy uranium-processing facility in Ashtabula, Ohio, and engineered ex situ system used sunflowers to remove uranium from contaminated groundwater and/or process water (Dushenkov et al. 1997a, b). Proper disposal of the contaminated plant biomass could be a limitation.

1.4.4 Phytovolatilization

It is defined as the plant's ability to absorb, metabolize and subsequently volatilize the contaminant into the atmosphere. Growing trees and other plants take up water along with the contaminants, pass them through the plants leaves and volatilize into the atmosphere at comparatively low concentrations. This process is used for removing metal contaminants present in groundwater, soils, sediments and sludge medium. This process is applicable for complex organic molecules that are degraded into simpler molecule contaminants. The degradation product or modified volatile form is less toxic than the main contaminant. Examples include the reduction of highly toxic Hg species to less toxic elemental Hg or transformation of toxic Se (as selenate) to the less toxic dimethyl selenide gas. Genetically modified tobacco (*Nicotiana tabacum*) and *Arabidopsis thaliana* contain a gene for mercuric reductase that convert ionic mercury (Hg(II)) to the less toxic metallic mercury (Hg(0)) and volatilize it (Meagher 2000).

1.4.5 Rhizodegradation

It is defined as the breakdown of contaminants in the soil through microbial activity localized in the root zone. This process uses microorganisms to consume and digest organic substances for nutrition and energy. Natural substances/exudates released by plant roots include sugars, alcohols, amino acids, organic acids, fatty acids, sterols, growth factors, nucleotides and flavanones; contain organic carbon that provides food for soil microorganisms; and establish a dense root mass that takes up large quantities of water. Organic contaminants in soil can often be broken down into daughter products or completely mineralized to inorganic products such as carbon dioxide and water by naturally occurring bacteria, fungi and actinomycetes. Plant roots increase the size and variety of microbial populations in the soil surrounding the roots (the rhizosphere) or in mycorrhizae (associations of fungi and plant roots). The increased microbial populations and activity in the rhizosphere result in increased contaminant biodegradation in the soil, and degradation of the exudates can stimulate co-metabolism of contaminants in the rhizosphere. Plant root exudates also alter geochemical conditions in the soil, such as water content, aeration, structure, temperature and pH, which may result in changes in the transport of inorganic contaminants creating more favourable environments for soil microorganisms. Perhaps the most serious impediment to successful rhizodegradation is the depth of the root zone. A wide range of organic contaminants such as petroleum hydrocarbons, PAHs, pesticides, chlorinated solvents, PCP, polychlorinated biphenyls (PCBs), benzene, toluene, o-xylene and surfactants can be removed by this technique (Donnelly et al. 1994; Gilbert and Crowley 1997).

1.4.6 Phytodegradation (Phytotransformation)

It is defined as the metabolization and degradation of contaminants within the plant or the degradation of contaminants in the soil, sediments, sludges, groundwater or surface water by enzymes produced and released by the plant. Organic compounds such as munitions (trinitrotoluene), chlorinated solvents, herbicides, insecticides and inorganic nutrients are reported to be removed by this technique (Burken and Schnoor 1997; Thompson et al. 1998; Campos et al. 2008). Plant-produced enzymes metabolize contaminants that may be released into the rhizosphere. Plant-formed enzymes found in plant sediments and soils include dehalogenase, nitroreductase, peroxidase, laccase and nitrilase (Schnoor et al. 1995). Nitroreductase enzyme present in *Myriophyllum aquaticum* degrades TNT concentrations (Schnoor et al. 1995). Hybrid poplar trees metabolized TNT to 4-amino-2,6-dinitrotoluene (4-ADNT), 2-amino-4,6-dinitrotoluene (2-ADNT) and other unidentified compounds in laboratory hydroponic and soil experiments (Thompson et al. 1998). Pilot-scale field demonstration studies of phytodegradation have been conducted for a number of sites, primarily army ammunition plants (AAPs) contaminated with munitions waste, including the Iowa AAP, Volunteer AAP and Milan AAP, and emergent aquatic plants have shown potential to decrease TNT concentrations.

1.4.7 Advantages of Phytoremediation Technique

Over the last few years, phytoremediation emerged as a publicly acceptable, aesthetically pleasing and solar-energy-driven cleanup technology with minimal environmental disruption. This is because it possesses certain advantages such as:

- Capacity in reducing a wide range of contaminants both organic and inorganic.
- Cost-effective technology as it does not require expensive biosorbent materials and highly specialized personnel and equipment. It is cost-effective for large volumes of water having low concentrations of contaminants and for large areas having low to moderately contaminated surface soils.
- Can be applied *in situ* to remediate shallow soil, groundwater and surface water bodies.
- Does not have destructive impact on environment and benefits the soil, leaving an improved, functional soil ecosystem at costs estimated at approximately one-tenth of those currently adopted technologies.
- Can be used in much larger-scale cleanup operations.
- Organic pollutants may be degraded to CO_2 and H_2O removing environmental toxicity.
- Can decontaminate heavy metal-polluted soils and biomass produced during the phytoremediation process could be economically valorized in the form of bioenergy. The use of metal-accumulating bioenergy crops might be suitable for this purpose.

1.5 Plant Species Used in Phytoremediation Technology

Terrestrial and aquatic plant species have been exploited for phytoremediation. Terrestrial species have been found effective for phytoremediation as they possess larger root systems which facilitate higher uptake of contaminants. Trees and grass species are commonly used for phytoremediation. Alfalfa has been used widely for its deep rooting and root zone metabolic activity. Poplar (or hybrid poplar) and cottonwood (*Populus deltoides*) trees, Indian mustard *Brassica juncea*, sunflower (*Helianthus annuus*), *Thlaspi* sp. including *T. caerulescens* and *T. rotundifolium* have been explored because of the characteristics such as high biomass production

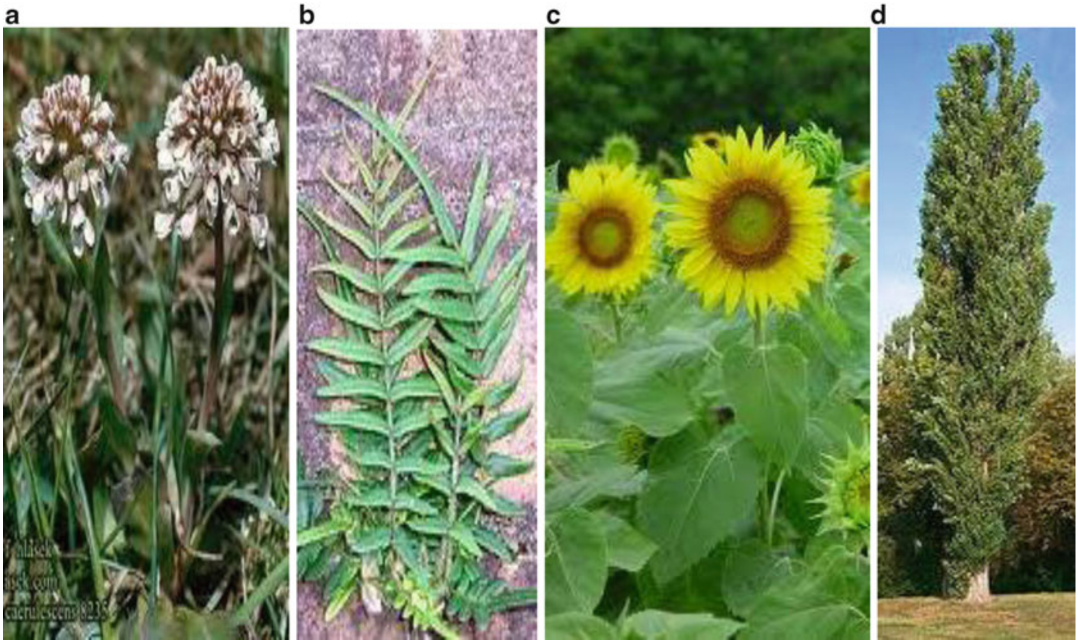

Fig. 1.8 Some of the terrestrial species used in phytoremediation: (**a**) *Thlaspi*, (**b**) Pteris, (**c**) Helianthus and (**d**) Populus

and fast growth (EPA 1998; Schnoor 2000). Several fast-growing tree plantations have been established and are under active study for their potential use in wastewater cleanup in land discharge systems. Some grasses such as ryegrass, prairie grasses and fescues have been investigated for rhizodegradation and phytostabilization due to their widespread growth and their extensive root systems. Efficacy of phytoremediation varies according to varieties, cultivars or genotypes and type of pollutant (Dipu et al. 2011).

Each plant species depicts a variation in its ability to remove contaminants from the environment. Plants such as *Pteris vittata*, *Sutera fodina*, *Alyssum* and *Thlaspi rotundifolium* possess the capacity to remove heavy metals such as As, Cr, Ni, Zn and Cd, while *Zea mays*, *Setaria faberi*, *Solanum melongena*, *Spinacia oleracea*, *Raphanus sativus*, *Ocimum basilicum* and *Oryza sativa* have shown the ability to transform and bioaccumulate herbicides and pesticides like DDT and endosulfan. *Hordeum vulgare* and *Conyza canadensis* have shown sequestration of herbicide metolachlor and glyphosate in vacuoles (Fig. 1.8).

Some plants that have shown high potential for phytoremediation have been listed below:

1. The vetiver grass (*Vetiveria zizanioides*)

   The plant was able to treat (biological) 16,000 tonnes of soils contaminated with polyaromatic hydrocarbons (PAHs) at the Scott Lumber Company site in Missouri, USA. The PAH concentration was effectively reduced by 70 %.
2. The brake fern (*Pteris vittata*)

   The Edenspace System Corporation in the USA used the Chinese brake fern, and it showed potential to treat 1.5-acre site contaminated with arsenic (As) in New Jersey, North Carolina. The fern phytoextracted more than 200-fold of arsenic (As) in the above-ground part.
3. Hybrid poplar (*Populus* × *canadensis*)

   Ecolotree Inc. used the hybrid poplar trees to phytoremediate soil and groundwater contamination with petroleum-related organics, PAHs and chlorinated organics released by accidental spills in 2000 in Milwaukee, Wisconsin, USA. The poplar trees were buried up to 10 ft below the surface, and a subsurface aeration system was provided to encourage deep rooting into groundwater. Ecolotree Inc. used the hybrid poplar to treat soil contaminated with chemical fertilizer and pesticides in Illinois, USA, in 1999. Some 440 trees of about 12–18 ft tall bare root poplar were planted into 6-ft-deep trenches.

The Occidental Petroleum Corporation, LA, and the University of Washington, USA, used hybrid polar to treat several sites in the USA contaminated with 'trichloroethanol'. Hybrid polar trees were successfully used by other commercial companies like Phytokinetics Inc. in the USA to treat groundwater contaminated with chlorinated volatile organics including dichlorobenzidine at several superfund sites. Technical University of Denmark used poplar trees to phytoremediate soils contaminated by gasoline and diesel compounds at an old gas filling station at Axelved, Denmark, and cyanide, PAHs, oil and BTEX (benzene, toluene, ethylbenzene and xylene) contaminated soil at a former municipal gas work site in Denmark. The Polish Academy of Sciences used the poplar trees to remove pesticides stored in bunkers at a resort in Niedzwiada, Poland.

4. Sunflower (*Helianthus annuus*)

   Sunflower plants has been used to treat lead-contaminated soil with lead (Pb) ranging from 75- to 3,450-mg kg^{-1} soil at its Detroit Forge Site in 1998. In a single season of crop growth, the lead contents in the soil were brought down to 900 mg kg^{-1} of soil, and subsequently it was removed completely after successive crop growth. The total cost of phytoremediation treatment by sunflower was US $ 50.00 per cubic yard, which saved more than US $ 1.1 million compared to the estimated cost of physicochemical treatment by soil excavation and disposal in landfills.

   Sunflower and the Indian mustard plant (*Brassica juncea*) were used to phytoremediate the lead (Pb)-contaminated soil at an industrial facility in Connecticut, USA. The Edenspace System Corporation in the USA used the sunflower and the Indian mustard to treat various sites in the USA contaminated with heavy metals. The company also used this plant to remediate uranium (U)-contaminated soils (47 mg kg^{-1} of soil) at the US Army Sites at Aberdeen, Maryland. The sunflower plants bioaccumulated uranium at the rate of 764 mg kg^{-1}–1,669 mg kg^{-1} of soil.

5. Indian mustard (*Brassica juncea*)

   The Edenspace System Corporation, USA, used the Indian mustard plant to treat the radionuclide strontium (Sr89/90)-contaminated soil at Fort Greely in Alaska, USA. The plants bioaccumulated more than 10–15-fold of strontium (Sr89/90) higher than in soil. They also used the Indian mustard with sunflower to treat various sites in the USA contaminated with heavy metals. They accumulated more than 3.5 % of heavy metals of their dry weight. They also used the Indian mustard to remove caesium-137 (Cs^{137}) from the contaminated pond waters after the Chernobyl Nuclear Power Plant disaster in Ukraine in 1986.

   The Brookhaven National Lab, New Jersey, USA, used Indian mustard to remove radionuclides cesium-137 (Cs^{137}) and strontium-90 (Sr90) by phytoextraction from contaminated soil. The Phytotech, Florida, USA, used the Indian mustard plant to remediate lead (Pb)- and cadmium (Cd)-contaminated soil at the Czechowice Oil Refinery, Katowice, in Poland. Indian mustard plant was used with sunflower (*Helianthus annuus*) to phytoremediate the lead (Pb)-contaminated soil at an industrial facility in Connecticut, USA.

Literature demonstrates many success stories related to removal of variable contaminants at various sites across the world (Table 1.5).

Realizing the potential of terrestrial species, aquatic plant species have been explored and studied extensively for their phytoremediation capacity. A number of aquatic plant species and their associated microorganisms have been used for more than a decade in constructed wetlands for municipal and industrial wastewater treatment. The aquatic plant biomass represents an abundantly available biological material. The features such as easily cultivation, high biomass production, faster growth rate, surplus availability and high tolerance to survive adverse environmental conditions together with higher bioaccumulation potential establish them as potential agents for phytotechnology. Aquatic

Table 1.5 Sites demonstrating phytoremediation of various contaminants

Location	Application	Pollutant	Medium	Plants
Edgewood, MD	Phytovolatilization	Chlorinated solvents	Groundwater	Hybrid poplar
	Rhizofiltration			
	Hydraulic control			
Forth Worth, TX	Phytodegradation	Chlorinated solvents	Groundwater	Eastern cottonwood
	Phytovolatilization			
	Rhizodegradation			
	Hydraulic control			
Ogden, UT	Phytoextraction	Petroleum	Soil	Alfalfa, poplar
	Rhizodegradation	Hydrocarbons	Groundwater	Juniper, fescue
Portsmouth, VA	Phytodegradation	Petroleum	Soil	Grasses
	Rhizodegradation			Clover
Trenton, NJ	Phytoextraction	Heavy metals	Soil	Hybrid poplar
		Radionuclides		Grasses
Anderson, ST	Phytostabilization	Heavy metals	Soil	Hybrid poplar, grasses
Ashtabula, OH	Rhizofiltration	Radionuclides	Groundwater	Sunflower
Milan, TN	Phytodegradation	Explosives	Groundwater	Duckweed, parrot feather
Amana, IA	Phytodegradation	Nitrates	Groundwater	Hybrid poplar
Upton, NY	Phytoextraction	Radionuclides	Soil	Indian mustard, cabbage
Chernobyl, Ukraine	Rhizofiltration	Radionuclides	Groundwater	Sunflowers

Source: Adapted from EPA (1998) and the website (http://arabidopsis.info/students/dom/mainpage.html)

plants also referred to as aquatic macrophytes consist of/include assemblage of diverse taxonomic groups including pteridophytes (ferns) and bryophytes (mosses, hornworts and liverworts) and angiosperms (flowering plants). They dominate in wetlands, shallow lakes, ponds, marshes, streams and lagoons. They play key functions in biochemical cycles, through organic carbon production, phosphorous, mobilization and the transfer of other trace elements and act as carbon sinks. They directly influence the hydrology and sediment dynamics of freshwater ecosystems through their effects on water flow.

Macrophytes are broadly classified into three types depending upon their habit of growth:

1. *Free-floating plant species*—They are further classified as:
   (a) Floating unattached—Plants that float on the surface of water and roots/submerged leaves hang free in the water, i.e. they are not anchored to the bottom. Some of the well-studied species in this category are *Lemna*, *Eichhornia*, *Pistia*, *Salvinia*, *Azolla* and *Spirodela*.
   (b) Floating attached—Plants that have leaves floating on the surface, stems beneath the surface and roots anchoring to the substrate.
2. *Submerged plant species*—They include species where the entire plant is below the surface of the water. Some of well-explored species in this category include *Potamogeton*, *Ceratophyllum* and *Myriophyllum*
3. *Emergent plant species*—They include species whose stems and leaves are found above the water, while the roots grow underwater. Some common species in this category are *Typha*, *Elodea*, *Phragmites* and *Scirpus*.

The aquatic and wetland plant species—in particular, free-floating, submerged (rooted) and semiaquatic/emergent (rooted)—gained importance worldwide as they depict exorbitant efficiency to remove contaminants from wastewaters, though the degree of potential for removal varies from species to species. Aquatic macrophytes possess immense potential for removal/degradation of variety of contaminants, including heavy metals, inorganic/organic pollutants, radioactive wastes and explosives. Aquatic plants form a major part of the natural and constructed wetlands as they possess immense potential for removing variable contaminants from wastewaters/aqueous solutions. Realizing the exorbitant abilities of aquatic macrophytes, their role in environmental cleanup is highlighted.

Literature Cited

Abdelwahab O, Nemr A, El Sikaily A, Khaled A (2005) Use of rice husk for adsorption of direct dyes from aqueous solution: a case study of direct f. Scarlet. Egypt J Aquat Res 31:1–11

Abia AA, Horsfall M, Didi O (2002) The use of agricultural byproduct for the removal of trace metals from aqueous solutions. J Appl Sci Environ Manag 6(2): 89–95

Amuda OS, Giwa AA, Bello IA (2007) Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. Biochem Eng J 36: 174–181

Baker AJM, Brooks RR (1989) Terrestrial higher plants which hyperaccumulate heavy elements: a review of their distribution, ecology and phytochemistry. Biorecovery 1:81–126

Barceló J, Poschenrieder C (2003) Phytoremediation: principles and perspectives. Contrib Sci 2(3):333–344

Biobasics (2006) The science and the issues. 9 Feb–24 Nov 2006. http://www.biobasics.gc.ca/english/View.asp?x=741

Bishnoi NR, Garima (2005) Fungus-an alternative for bioremediation of heavy metal containing wastewater – a review. J Sci Ind Res 64:93–100

Bolong N, Ismail AF, Salim MR, Matsuura T (2009) A review of the effects of emerging contaminants in wastewater and options for their removal. Desalination 239:229–246

Brooks RR (1998a) Plants that hyperaccumulate heavy metals: their role in phytoremediation, microbiology, archaeology, mineral exploration and phytomining. CAB International, Oxford

Brooks RR (1998b) Plants that hyperaccumulate heavy metals. CAN International, Wallington, p 379

Burken JG, Schnoor JL (1997) Uptake and metabolism of atrazine by poplar trees. Environ Sci Technol 31:1399–1406

Campos M, Merino I, Casado R, Pacios LF, Gómez L (2008) Review. Phytoremediation of organic pollutants. Spanish J Agric Res 6(Special issue):38–47

Carvalho FP (2006) Agriculture, pesticides, food security and food safety. Environ Sci Policy 9:685–692

Chaney RL (1988) Metal speciation and interactions among elements affect trace element transfer in agricultural and environmental food-chains. In: Kramer JR, Allen HE (eds) Metal speciation: theory, analysis and applications. Lewis Publishers Inc., Chelsea, pp 218–260

Cunningham SD, Ow DW (1996) Promises and prospects of phytoremediation. Plant Physiol 110:715–719

Cunningham SD, Berti WR, Huang JW (1995) Phytoremediation of contaminated soils. Trends Biotechnol 13:393–397

Dipu S, Kumar AA, Salom Gnana Thanga V (2011) Potential application of macrophytes used in phytoremediation. World Appl Sci J 13:482–486

Donnelly PK, Hedge RS, Fletcher JS (1994) Growth of PCB-degrading bacteria on compounds from photosynthetic plants. Chemosphere 128:984–988

Dushenkov V, Kumar PBAN, Motto H, Raskin I (1995) Rhizofiltration: the use of plants to remove heavy metals from aqueous streams. Environ Sci Technol 29:1239–1245

Dushenkov S, Vasudev D, Kapulnik Y, Gleba D, Fleisher D, Ting KC, Ensley B (1997a) Removal of uranium from water using terrestrial plants. Environ Sci Technol 31:3468–3474

Dushenkov S, Vasudev D, Kapulnik Y, Gleba D, Fleisher D, Ting KC, Ensley B (1997b) Phytoremediation: a novel approach to an old problem. In: Wise DL (ed) Global environmental biotechnology. Elsevier Science B.V, Amsterdam, pp 563–572

Dwivedi S (2012) Bioremediation of heavy metal by algae: current and future perspective. J Adv Lab Res Biol 3:228–233, Issn 0976–7614

Eberhardt TL, Min S (2008) Biosorbents prepared from wood particles treated with anionic polymer and iron salt: effect of particle size on phosphate adsorption. Bioresour Technol 99:626–630

EPA (1998) A citizen's guide to phytoremediation. EPA 542-F-98-011. United States Environmental Protection Agency. p 6. http://www.bugsatwork.com/XYCLONYX/EPA_GUIDES/PHYTO.PDF

Erakhrumen A (2007) Phytoremediation: an environmentally sound technology for pollution prevention, control and remediation in developing countries. Educ Res Rev 2(7):151–156

Gardea-Torresday JL, Tiemann KJ, Gamez G, Dokken K (1999) Effect of chemical composition for multi-metal binding by Medicago sativa (Alfalfa). J Hazard Mater 1369:41–51

Gilbert ES, Crowley DE (1997) Plant compounds that induce polychlorinated biphenyl biodegradation by *Arthrobacter* sp. strain B1B. Appl Environ Microbiol 63:1933–1938

Ho Y, Porter J, McKay G (2002) Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems. Water Air Soil Pollut 141:1–33

Ho YS, Ofomaja AE (2006) Biosorption thermodynamics of cadmium on coconut copra meal as biosorbents. Biochem Eng J 30:117–123

Ho YS, Chiang TH, Hsueh YM (2005) Removal of basic dye from aqueous solution using tree fern as a biosorbents. Process Biochem 40:119–124

Kahraman S, Dogan N, Erdemoglu S (2008) Use of various agricultural wastes for the removal of heavy metal ions. Int J Environ Pollut 34:275–284. http://www.inderscience.com/browse/index.php?journalID=9&year=2008&vol=34&issue=1/2/3/4

Karigar CS, Rao S (2011) Role of microbial enzymes in the bioremediation of pollutants: a review. Enzyme Res Article ID 805187, 11 p. doi:10.4061/2011/805187

Kolpin D, Furlong E, Meyer MT, Thurman EM, Zaugg SD, Barber LB, Buxton HT (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: a national reconnaissance. Environ Sci Technol 36:1202–1211

Larsen JC (2006) Risk assessments of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and dioxin-like polychlorinated biphenyls in food. Mol Nutr Food Res 50:885–896

Lin AY, Yu T, Lin C (2008) Pharmaceutical contamination in residential, industrial, and agricultural waste streams: risk to aqueous environments in Taiwan. Chemosphere 74:131–141

Liu H, Donga Y, Liu Y, Wang H (2010) Screening of novel low-cost adsorbents from agricultural residues to remove ammonia nitrogen from aqueous solution. J Hazard Mater 178:1132–1136

Magan N, Fragoeiro S, Bastos C (2010) Environmental factors and bioremediation of Xenobiotics using white rot fungi. Mycobiology 38(4):238–248

Malik A (2004) Metal bioremediation through growing cells. Environ Int 30(2):261–278

Manahan S (1994) Environmental chemistry, 6th edn. Lewis Publishers, New York, p Pp 811

Matheickal J, Yu Q, Woodburn G (1999) Biosorption of cadmium (II) from aqueous solutions by pre-treated biomass of marine alga *Durvillaea potatorum*. Water Res 33:335–342

Meagher RB (2000) Phytoremediation of toxic elemental and organic pollutants. Curr Opin Plant Biol 3(2):153–162

Miretzky P, Saralegui A, Cirelli AF (2004) Aquatic macrophytes potential for simultaneous removal of heavy metals (Buenos Aires, Argentine). Chemosphere 57:997–1005

Mohd Din AT, Hameed BH, Ahmad AL (2009) Batch adsorption of phenol onto physiochemical-activated coconut shell. J Hazard Mater 161:1522–1529

Nwoko CO (2010) Trends in phytoremediation of toxic elemental and organic pollutants. Afr J Biotechnol 9(37):6010–6016

Ofomaja AE, Ho YS (2007) Effect of pH on cadmium biosorption by coconut copra meal. J Hazard Mater 139:356–362

Petrović M, Gonzalez S, Barceló D (2003) Analysis and removal of emerging contaminants in wastewater and drinking water. Trends Anal Chem 22:685–696

Priyadarshani I, Sahu D, Rath B (2011) Microalgal bioremediation: current practices and perspectives. J Biochem Technol 3(3):299–304

Rawat I, Kumar R, Mutanda T, Bux F (2011) Dual role of microalgae: phycoremediation of domestic wastewater and biomass production for sustainable biofuels production. Appl Energy 88:3411–3424

Reeves RD (2003) Tropical hyperaccumulators of metals and their potential for phytoextraction. Plant Soil 249(1):57–65

Reeves RD, Brooks RR (1983) Hyperaccumulation of lead and zinc by two metallophytes from a mining area of Central Europe. Environ Pollut Ser A 31:277–287

Sadowsky MJ (1999) In phytoremediation: past promises and future practices. In: Proceedings of the 8th international symposium on microbial ecology, Halifax, pp 1–7

Salt DE, Blaylock M, Kumar PBAN, Dushenkov V, Ensley BD, Chet I, Raskin I (1995a) Phytore mediation: a novel strategy for the removal of toxic metals from the environment using plants. Biotechnology 13:468–475

Salt DE, Prince RC, Pickering IJ, Raskin I (1995b) Mechanisms of cadmium mobility and accumulation in Indian mustard. Plant Physiol 109:1427–1433

Schiewer S, Patil SB (2008) Pectin-rich fruit wastes as biosorbents for heavy metal removal: equilibrium and kinetics. Bioresour Technol 99:1896–1903

Schnoor JL (2000) Phytostabilization of metals using hybrid poplar trees. In: Raskin I, Ensley BD (eds) Phytoremediation of toxic metals – using plants to clean-up the environment. Wiley, New York, pp 133–150

Schnoor JL, Licht LA, McCutcheon SC, Wolfe NL, Carreira LH (1995) Phytoremediation of organic and nutrient contaminants. J Environ Sci Technol 29:318A–323A

Stuart ME, Manamsa K, Talbot JC, Crane EJ (2011) Emerging contaminants in g groundwater. Groundwater science programme open report OR/11/013. British Geological Survey

Sun G, Xu X (1997) Sunflower stalks as adsorbents for color removal from textile wastewater. Ind Eng Chem Res 36:808–812

Thompson PL, Ramer LA, Schnoor JL (1998) Uptake and transformation of TNT by hybrid poplar trees. Environ Sci Technol 32:975–980

Volesky B, Holan Z (1995) Biosorption of heavy metals. Biotechnol Program 11:235–250

Wani SH, Sanghera GS, Athokpam H, Nongmaithem J, Nongthongbam R, Naorem BS, Athokpam HS (2012) Phytoremediation: curing soil problems with crops. Afr J Agric Res 7(28):3991–4002

2 Aquatic Plant Species and Removal of Contaminants

The aquatic and wetland plant species possess exorbitant efficiency to remove various inorganic and organic contaminants including heavy metals, radionuclides, nutrients, explosives and hydrocarbons from wastewaters. The removal of contaminants varies from species to species and is also dependent upon concentration of the contaminant and duration of exposure. The present chapter highlights the variety of contaminants removed by aquatic plants. Well studied plant species in each category are also listed (Fig. 2.1).

2.1 Contaminants Removed by Aquatic Plants

2.1.1 Inorganic Contaminants

2.1.1.1 Heavy Metals

Heavy metals form one of the largest categories of contaminants that are efficiently removed by aquatic plants. Living and nonliving biomass of aquatic plants treat heavy metals in a sustainable way. Aquatic macrophytes, irrespective of free-floating, submerged or emergent plant species, sequester heavy metals (Tables 2.1, 2.2 and 2.3). Free-floating aquatic plant species, namely, *Eichhornia crassipes* (water hyacinth), *Salvinia herzogii* and *Salvinia minima* (water ferns), *Pistia stratiotes* (water lettuce), *Nasturtium officinale* (watercress), *Spirodela intermedia* and *Lemna minor* (duckweeds) and *Azolla pinnata* (water velvet), possess potential to scavenge heavy metals and have been used in abatement of heavy metals. Submerged species including *Potamogeton crispus* (pondweed), *Potamogeton pectinatus* (American pondweed), *Ceratophyllum demersum* (coontail or hornwort), *Vallisneria spiralis*, *Mentha aquatica* (water mint) and *Myriophyllum spicatum* (Eurasian watermilfoil) also bear the potential for extraction of metals from water as well as sediments. Semiaquatic/emergent plant species such as *Typha latifolia* (cattail), *Phragmites* (common reed) and S*cirpus* spp. (bulrush) also possess metal-removing abilities (Dhir et al. 2009; Dhir 2010).

2.1.1.2 Explosives

Submerged and emergent aquatic plant species including *Elodea Michx*. (elodea), *Phalaris* sp. (canary grass), *Ceratophyllum demersum*, *Potamogeton nodosus* and *Sagittaria latifolia* (arrowhead) have demonstrated the capacity to remove explosives such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) from contaminated groundwater (Dhir et al. 2009) (Table 2.4).

2.1.1.3 Radionuclides

Removal of radionuclides such as ^{137}Cs, ^{60}Co and ^{54}Mn by submerged and emergent aquatic plant species including *Potamogeton lucens*, *Potamogeton perfoliatus*, *Nuphar lutea*, *Nitellopsis obtusa*, *Phragmites australis*, *Typha*

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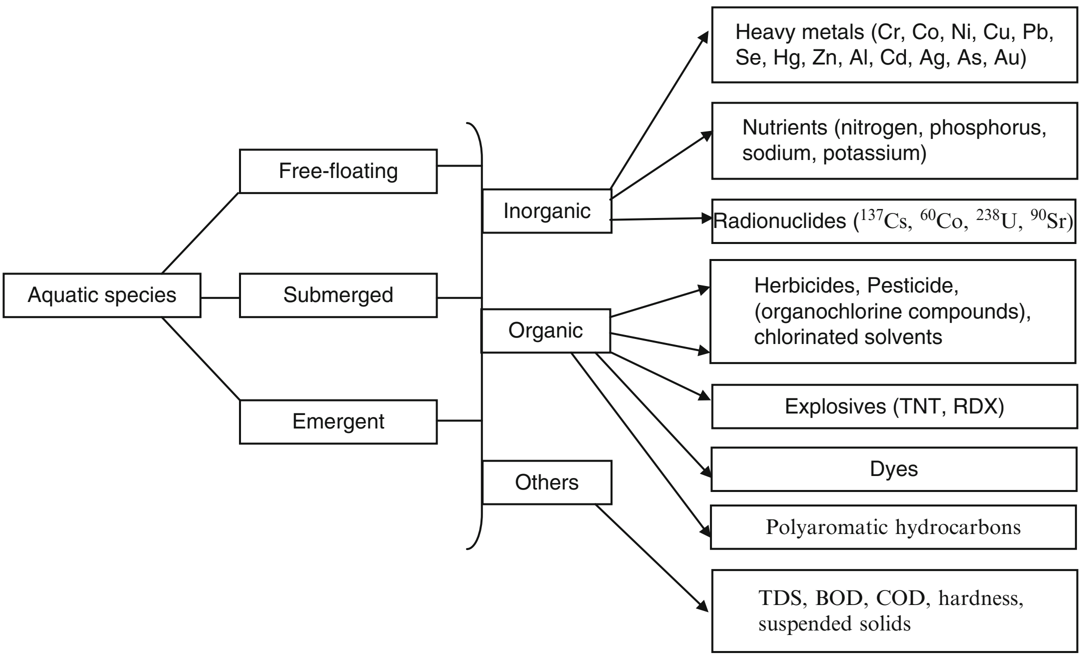

Fig. 2.1 Major categories of contaminants removed by aquatic plants species

Table 2.1 Free-floating aquatic macrophytes with heavy metal accumulation potential

Plant species	Heavy metals	Accumulation	References
Azolla filiculoides	Pb	228 mg kg^{-1} dry wt.	Zayed et al. (1998)
	Cd	2,600–9,000 mg kg^{-1} dry wt.	Benaroya et al. (2004)
	Cu	62 mg kg^{-1} dry wt.	Arora et al. (2006)
	Zn	48–1,200 mg kg^{-1} dry wt.	Taghi Ganji et al. (2005)
	Ni	1,000 mg kg^{-1} dry wt.	
Azolla caroliniana	Hg	578 mg kg^{-1} dry wt.	Bennicelli et al. (2004)
	Cr	356 mg kg^{-1} dry wt.	Rahman and Hasegawa (2011)
	As	284 mg kg^{-1} dry wt.	
Pistia stratiotes	Hg	156 ng kg^{-1} dry wt.	Maine et al. (2004)
	Cr	800–1,600 mg kg^{-1} dry wt.	Miretzky et al. (2004)
	Cu	~1,000 mg kg^{-1} dry wt.	Molisani et al. (2006)
Salvinia cucullata	Cd	1,636.1 μg g^{-1} dry wt.	Phetsombat et al. (2006)
	Pb	14,305.6 μg g^{-1} dry wt.	
Salvinia natans	Cr	10.6 mg kg^{-1} dry wt.	Dhir et al. (2008)
	Zn	4.8 mg kg^{-1} dry wt.	
Spirodela polyrhiza	As	400–900 mg kg^{-1} dry wt.	Zhang et al. (2011)
	Cr		
Eichhornia crassipes	Cr	4,000–6,000 mg kg^{-1} dry wt.	Hu et al. (2007)
	Cu	6,000–7,000 mg kg^{-1} dry wt.	Molisani et al. (2006)
	Cd	2,200 μg kg^{-1} dry wt.	Zhu et al. (1999)
	Arsenite	909.58 mg kg^{-1} dry wt.	Delgado et al. (1993)
	Arsenate	805.20 mg kg^{-1} dry wt.	Low et al. (1994)
	Ni	1,200 mg kg^{-1} dry wt.	
	Zn	10,000 mg kg^{-1} dry wt.	
	Hg	1,000 ng kg^{-1} dry wt.	
Lemna gibba	As	1,021 mg As kg^{-1} dry wt.	Mkandawire and Dudel (2005)
	Cd	14,000 mg Cd kg^{-1}dry wt.	Mkandawire et al. (2004a, b)
	Ni	1,790 μg Ni kg^{-1} dry wt.	

Table 2.2 Submerged aquatic macrophytes with heavy metal accumulation potential

Plant species	Heavy metals	Accumulation	References
Ceratophyllum submersum	Ni	489–774 mg kg^{-1} dry wt.	Kara (2010)
Ceratophyllum demersum L.	Arsenate	862 μg As g^{-1} dry wt.	Xue et al. (2012)
	Arsenite	963 μg As g^{-1} dry wt.	Saygideger et al. (2004)
	Pb	1,143 μg g^{-1} dry wt.	Osmolovskaya and Kurilenko (2005)
	Cr	149 mg kg^{-1} dry wt.	
Myriophyllum spicatum	Co	1,675 mg kg^{-1} dry wt.	Wang et al. (1996)
	Ni	1,529 mg kg^{-1} dry wt.	Sivaci et al. (2004)
	Cu	766 mg kg^{-1} dry wt.	Lesage et al. (2008)
	Zn	2,883 mg kg^{-1} dry wt.	
Potamogeton pectinatus	Cd	596 mg kg^{-1} dry wt.	Rai et al. (2003)
	Pb	318 mg kg^{-1} dry wt.	Tripathi et al. (2003)
	Cu	62.4 mg kg^{-1} dry wt.	Singh et al. (2005)
	Zn	6,590 mg kg^{-1} dry wt.	
	Mn	16,000 mg kg^{-1} dry wt.	
Hydrilla verticillata	Cu	770–3,0830 mg kg^{-1} dry wt.	Srivastava et al. (2011)
	As	121–231 mg kg^{-1} dry wt.	

Table 2.3 Emergent species with heavy metal accumulation potential

Plant species	Heavy metals	Accumulation	References
Typha latifolia	As	1,120 μg g^{-1} dry wt.	Ye et al. (1997)
	Zn	1,231.7 mg kg^{-1} dry wt.	Qian et al. (1999)
	Cu	1,156.7 mg kg^{-1} dry wt.	Nguyen et al. (2009)
	Ni	296.7 mg kg^{-1} dry wt.	Manios et al. (2003) and Afrous et al. (2011)
Typha angustifolia	Pb	7,492.6 mg Pb kg^{-1} dry wt.	Panich-pat et al. (2005)
Elodea densa	Hg	82–177 ng Hg g^{-1} dry wt.	Molisani et al. (2006)
Phragmites australis	As	119.55 mg kg^{-1} dry wt.	Windham et al. (2001, 2003)
	Hg	6.23 mg kg^{-1} dry wt.	Afrous et al. (2011)
Scirpus maritimus	As	65.25 mg/kg	Afrous et al. (2011)
	Hg	2.23 mg/kg	
Spartina alterniflora	As, Hg, Cu, Pb Al, Fe, Zn, Cr, Se	0.3–7.2 mg As kg^{-1} dry wt.	Carbonell et al. (1998)
			Ansede et al. (1999)
			Windham et al. (2001, 2003)
Spartina patens	Cd, As	250 mg Cd g^{-1} dry wt.	Zayed et al. (2000)
			Carbonell et al. (1998)

latifolia, *Elodea canadensis*, *Ceratophyllum demersum* and *Myriophyllum spicatum* have been noted (Dhir et al. 2009) (Table 2.5).

2.1.1.4 Ions/Nutrients

Aquatic plant species such as *Ceratophyllum demersum*, *Potamogeton crispus*, *Eichhornia cras-sipes*, *Elodea nuttallii* and *Elodea canadensis* showed potential for effective removal of excess of inorganic nutrients such as nitrogen and phosphorus from hydroponic systems and microcosm (Dhir et al. 2009).

2.1.2 Organic Contaminants

Aquatic plant species possess potential to remove, sequester and transform organic contaminants. Uptake and accumulation of organophosphorus and organochlorine compounds, chlorinated

Table 2.4 Aquatic plant species with potential for removing explosives

Plant species	Contaminants	References
Myriophyllum aquaticum	TNT, RDX, HMX	Best et al. (1997, 1999a, b)
		Hughes et al. (1997)
		Rivera et al. (1998)
		Pavlostathis et al. (1998)
		Bhadra et al. (1999, 2001)
Myriophyllum spicatum	TNT	Hughes et al. (1997)
Potamogeton nodosus	TNT, RDX	Best et al. (1997, 1999b)
		Bhadra et al. (1999)
Ceratophyllum demersum	TNT, RDX	Best et al. (1997, 1999b)
		Bhadra et al. (2001)
Elodea canadensis	RDX, HMX	Rivera et al. (1998)
		Best et al. (1999a, b)
Phalaris arundinacea	TNT, RDX	Best et al. (1999a, b)
Typha angustifolia	TNT, RDX	Best et al. (1999a, b)
Sagittaria latifolia	TNT, RDX	Best et al. (1997)
		Bhadra et al. (2001)
Scirpus cyperinus	TNT, RDX	Best et al. (1997, 1999a, b)

Table 2.5 Aquatic plant species with the potential for accumulating radionuclides

Plant species	Contaminant	References
Lemna minor	^{140}La, ^{99}Tc, ^{60}Co	Hattink et al. (2000)
		Hattink and Wolterbeek (2001)
		Weltje et al. (2002)
		Popa et al. (2006)
Lemna gibba	^{60}Co, ^{32}P, ^{134}Cs	El-Shinawy and Abdel-Malik (1980)
Azolla caroliniana	^{137}Cs, ^{60}Co	Popa et al. (2004)
Ceratophyllum demersum	^{137}Cs, ^{60}Co, ^{32}P, ^{60}Co, ^{134}Cs, ^{89}Sr	El-Shinawy and Abdel-Malik (1980)
		Abdelmalik et al. (1980)
		Shokod'Ko et al. (1992)
		Bolsunovskiˇ et al. (2002)
Potamogeton pectinatus	^{238}U, ^{137}Cs, ^{90}Sr	Kondo et al. (2003)
Potamogeton lucens	^{90}Sr	Bolsunovskiˇ et al. (2002)
Elodea canadensis	^{137}Cs, ^{90}Sr, ^{241}Am	Shokod'Ko et al. (1992)
		Bolsunovskiˇ et al. (2002)
		Bolsunovsky et al. (2005)

solvents, hydrocarbons, explosives and pharmaceuticals by aquatic plants have been reported (Dhir et al. 2009) (Table 2.6).

2.2 Major Plant Species

2.2.1 Free-Floating Species

Some of the species well studied for their phytoremediation potential have been listed below (Fig. 2.2).

2.2.1.1 Duckweeds

Duckweeds are small (1–15 cm), free-floating aquatic angiosperms. They are monocotyledons belonging to the family *Lemnaceae*. They have worldwide distribution in nutrient-rich waters of temperate and tropic zones.

Duckweed consists of four genera:

Lemna
Spirodela
Wolffia
Wolffiella

Table 2.6 Aquatic plant species with the potential for removing/accumulating various organic contaminants

Plant species	Contaminant	References
Eichhornia crassipes	Ethion, dicofol, cyhalothrin, pentachlorophenol	Roy and Hanninen (1994) and Xia et al. (2002a, b)
Lemna gibba	Phenol, 2,4,5-trichlorophenol (TCP)	Hafez et al. (1998), Ensley et al. (1994), Sharma et al. (1997) and Tront and Saunders (2006)
Lemna minor	2,4,5-trichlorophenol (TCP), halogenated phenols	Day and Saunders (2004), Tront and Saunders (2006), Tront et al. (2007)
Spirodela oligorrhiza	Organophosphorus and organochlorine compounds (o,p′-DDT, p,p′-DDT), chlorobenzenes	Gobas et al. (1991), Rice et al. (1997) and Gao et al. (2000a, b)
Myriophyllum aquaticum	Simazine, o,p-2 DDT, p,p-2 DDT, hexachloroethane (HCA), perchlorate	Knuteson et al. (2002), Nzengung et al. (1999) and Gao et al. (2000a)
Potamogeton crispus	Phenol	Barber et al. (1995)
Ceratophyllum demersum	Organophosphorus and organochlorine compounds, chlorobenzenes	Gobas et al. (1991), Wolf et al. (1991), Rice et al. (1997) and Gao et al. (2000a, b)
Elodea canadensis	Phenanthracene, organophosphorus and organochlorine compounds, chlorobenzenes Hexachloroethane (HCA), DDT, Carbon tetrachloride	Gobas et al. (1991), Wolf et al. (1991), Rice et al. (1997), Machate et al. (1997), Gao et al. (2000a, b), Nzengung et al. (1999), Gao et al. (2000a) and Garrison et al. (2000)
Pontederia cordata	Oryzalin (herbicide)	Fernandez et al. (1999)
Scirpus lacustris	Phenanthracene	Machate et al. (1997)

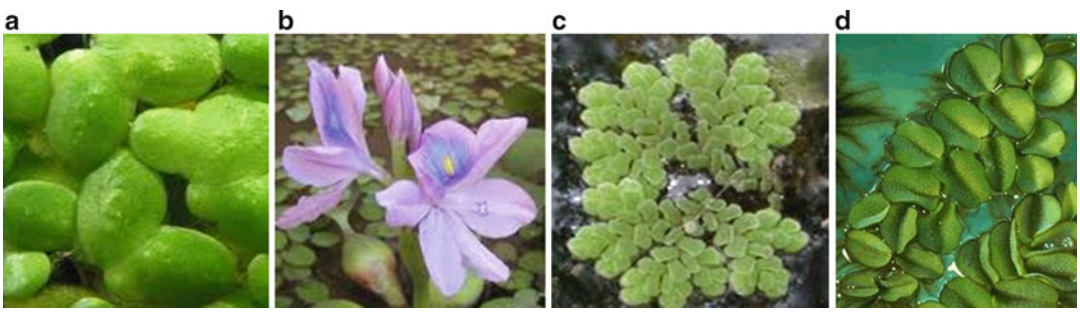

Fig. 2.2 Free-floating aquatic plant species: (**a**) *Lemna*, (**b**) *Eichhornia*, (**c**) *Azolla* and (**d**) *Salvinia*

Lemna is the largest genera among all duckweed species. They are small ubiquitous plants and whole plant body is reduced to form a flat small leaf-like structure called frond which consists of leaflets and root-like structure. The ideal growth conditions are water temperatures between 6 and 33 °C and pH ranging from 5.5 to 7.5 (Mkandawire and Dudel 2007). They reproduce asexually. These are easy to culture in laboratory and hence are material of choice for ecotoxicological investigations (Prasad et al. 2001).

Unique properties of the species which establish them as ideal phytoremediation agents mainly include:

- Fast growth and multiplication (doubling biomass between 0.2 and 7 days)
- High bioaccumulation potential.
- Ability to transform or degrade contaminants.
- Regulate chemical speciation.
- Capacity to treat variable contaminants (both organic and inorganic).
- Some species have been commercially exploited to recover valuable metals like Au

and Ag from wastewater and mining wastes (Obek and Sasmaz 2011).

Average yield of *Lemna* in uncontaminated waters corresponds to 20–50 g m^{-2} d^{-1} dry biomass, while 200 $g^{-2}d^{-1}$ dry biomass has been reported under laboratory conditions and tropical regions. In *Lemna* species, particularly *L. minor* and *L. gibba*, growth rate of 0.6 d^{-1} has been noted under ideal media and nutrient conditions. High biomass production rate contributes to high bioaccumulation potential (Mkandawire and Dudel 2007). Duckweeds possess capacity to remove wide range of inorganic and organic contaminants such as heavy metals, radionuclides, nutrients, pesticides and explosives from domestic, municipal and industrial wastewaters.

Inorganic Contaminants

Lemna species, *L. minor*, *L. gibba* and *L. trisulca*, showed removal of heavy metals, namely, Hg, Pb, Cr, Cu, Zn, Al, Cd, Ag, As and Au, from wastewaters (Kara and Kara 2005; El-Kheir et al. 2007; Kara 2010; Rahman and Hasegawa 2011; Arenas et al. 2011; Obek and Sasmaz 2011; Uysal and Taner 2011; Parra et al. 2012; Sasmaza and Obek 2012; Singh et al. 2012a, b). The removal efficiency varies from 3 to 30 % depending on the element. Nutrient enrichment (P, NO_3^-–N and SO_4^{2-}) of the medium negatively affects the metal accumulation potential, but enhances the metal tolerance capacity of duckweeds and hence growth (Leblebici and Aksoy 2011). Studies with *Lemna gibba* indicated reduction in metal accumulation after addition of PO_4^{3-}. This can be attributed to strong interaction among chemical components and competition among ions in natural aquatic environment. Arsenic (As(V)) is an analog of phosphate and competes for the same uptake carriers in the plasmalemma. Studies indicate competitive inhibition of As(V) by phosphate (Mkandawire et al. 2004a, b; Mkandawire and Dudel 2005).

The tolerance capacity of the plant varied for each metal. *Lemna gibba* tolerated Cu and Ni at concentrations 0.3 and ≤0.5 mg L^{-1}, while *L. minor* tolerated Cd, Cu, Ni and Zn at concentrations of 0.4, 0.4, 3 and 15 mg L^{-1}, respectively (Khellaf and Zerdaoui 2010a, b). *Lemna gibba* showed efficiency for removing boron (B) from polluted and desalinated waters and showed tolerance upto concentrations of 2 mg L^{-1} without any adverse effects on biomass production (Del-Campo Marı´n and Oron 2007). Exposures to higher concentrations of most of these metals (Cu, Cd, Ni, Zn) inhibited growth (around 50 %) measured in terms of biomass production and physiological changes such as photosynthetic and respiration rate (Khellaf and Zerdaoui 2010a, b).

Lemna minor has been studied extensively and studies have demonstrated its potential for treatment of wastewater from oil refinery, sewage water systems and municipal outlets (Azeez and Sabbar 2012). The improvement in water quality has been achieved by reducing heavy metals, turbidity, biochemical oxygen demand (BOD), total soluble solids (TSS), total alkalinity, total suspended solids, phosphate (PO_4^{3-}-P), sulphide, sulphate, nitrates and phenols (El-Kheir et al. 2007). *Lemna minor* and *L. gibba* have also shown capacity to treat rare earth elements (REE) such as lanthanum and radioactive elements such as uranium (U) (Cheng et al. 2002).

Lemna sp. also showed an efficient antioxidant machinery to curtail oxidative stress caused by abiotic stresses including heavy metal exposure. This includes increased level of antioxidant molecules—ascorbate and glutathione—as well as activities of antioxidant enzymes, namely, ascorbate peroxidase, dehydroascorbate reductase and ascorbate free radical (AFR) reductase (Paola et al. 2007). Some studies in *L. minor* suggested that callose acts as a barrier to prevent metal penetration and hence stress, though it is not well accepted. Lead-induced synthesis and deposition of callose was noted in roots of *L. minor*. Though continuous callose bands, small clusters or incomplete bands in the newly formed and anticlinal cell walls (CWs) could form an efficient barrier for Pb penetration, it is noted that such callose arrangement within root CWs inefficiently protect the protoplast from Pb penetration and might not be enough for a successful blockade of the stress factor penetration (Samardakiewicz et al. 2012). Biosynthesis of the cytoplasmic Hsp70 protein, a nonspecific and sensitive detector of stress in fronds exposed to lower doses of stressors including Cd have been detected in *L. minor* (Tukaj et al. 2011).

Organic Contaminants

L. minor accumulates trace-organic contaminants and ultimately served as a sink for these materials in the natural environment. Uptake rate (pH values 6–9) and plant activity showed a positive correlation. Plant showed capacity for removing and tolerating herbicides, namely, isoproturon and glyphosate, 2,4,5-trichlorophenol (TCP) and organic residues including commercial solvent and resin such as phenol, pyridine and formaldehyde present in industrial wastewaters (Tront et al. 2001; Tilaki 2010; Dosnon-Olette et al. 2011). Uptake rates were linearly correlated to fraction of contaminant in protonated form. *Lemna minor* showed efficient uptake capacity for pesticides—copper sulphate (fungicide), flazasulfuron (herbicide) and dimethomorph (fungicide). Duckweed demonstrated the greatest potential to transform and hence degrade (50–66 %) DDT isomers o,p′-DDT and p,p′-DDT. The decay profile of DDT followed first-order kinetics. Reduction of the aliphatic chlorine atoms of DDT was noted as the major pathway for transformation. In contrast, *L. minor* showed susceptibility to hydrophobic organic compounds such as synthetic antifungal drug ketoconazole. Exposure to ketoconazole (0.3–0.6 mg L^{-1}) for 168 h affected growth rate, dry weight and root length (Haeba and Bláha 2011). *Lemna minor* showed capacity to remediate explosives, mainly TNT (Feuillebois et al. 2006; Tront and Saunders 2006).

Other Duckweeds

Spirodela (greater duckweed) and *Wolffia* species have been reported to accumulate and hence treat metal-contaminated waters (Mkandawire et al. 2004a, b; Mkandawire and Dudel 2005; Rahman et al. 2007, 2008; Alvarado et al. 2008; Leblebici and Aksoy 2011; Zhang et al. 2011). *S. polyrhiza*, *S. intermedia* and *Wolffia* showed As, Pb and Cd accumulation and tolerance efficiency (Mkandawire et al. 2004a, b; Mkandawire and Dudel 2005; Rahman et al. 2007, 2008; Alvarado et al. 2008; Zhang et al. 2011). The adsorption process followed first-order kinetics. Biosorption mechanism causes ion exchange between monovalent metal ions present in macrophyte biomass and heavy metal ions and protons present in water. *S. polyrhiza* showed potential for degrading nitrophenols. The bacteria isolated from the roots or rhizosphere region of *S. polyrhiza* contributed to the accelerated degradation of the three NPs, namely, 2-nitrophenol (2-NP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP) (Kristanti et al. 2012).

2.2.1.2 *Eichhornia crassipes* (Water Hyacinth)

Commonly referred as the ‘world’s most noxious/troublesome aquatic weed’. It is a native to tropical and subtropical South America and is now widespread in all tropic climates. It is a free-floating, perennial aquatic fern belonging to family Pontederiaceae. It forms dense mats in the water and mud. It is also referred as ‘bull hyacinths’. It flourishes and reproduces floating freely on the surface of water or it can also be anchored in mud. It grows in ponds, canals, freshwater and coastal marshes and lakes. It multiplies by vegetative reproduction, which allows the plant to quickly colonize large areas in relatively short periods of time (Wolverton and McDonald 1979). The plant can double its population in 6 days. The genus *Eichhornia* comprises seven species, among which *E. crassipes* is the most common.

Management of this weed is an issue of serious concern all over the world plant because of its huge vegetative reproduction and high growth rate (Jafari 2010). Therefore, studies suggested some potential uses of the plant. These mainly include its utilization as follows:

(a) Phytoremediation agent
(b) Biosorbent for toxic metals
(c) Resource for power generation and biogas production
(d) Compost
(e) Animal fodder/fish feed
(f) Pulp material for paper production
(g) Production of fibreboards, low cost roofing material, indoor partitioning, etc.
(h) Formulations of medicines
(i) Biomass can be used for metal recovery

Use of water hyacinth in wastewater treatment is recommended because of its

1. Enormous biomass production rate
2. High tolerance to pollution
3. Absorption capacity for variable contaminants like heavy metal and nutrients

Inorganic Contaminants

E. crassipes attracted considerable attention because of its ability to grow well in polluted water together with its capacity of accumulating heavy metal ions (Maine et al. 2001; So et al. 2003; Lu et al. 2004; Ghabbour et al. 2004; Odjegba and Fasidi 2006). Plants absorb depending upon their affinity towards the particular metal. Based on absorption and accumulation mechanisms, *E. crassipes* render services of cleaning of water body, sewage and sludge ponds from heavy metal and nutrient contamination. *E. crassipes* possess capacity to treat industrial and municipal waters contaminated with Pb, As, Hg, Zn, Se, Cr, Cd, Ni and Cu (Win et al. 2002, 2003; Dixit and Tiwari 2007; Hussain et al. 2010; Mahamadi 2011; Mane et al. 2011; Mokhtar et al. 2011; Rahman and Hasegawa 2011; Murithi et al. 2012). High rate of metal accumulation safely places it in the category of metal hyperaccumulator. Roots tend to accumulate a higher amount of metal than shoots due to translocation process. At lower concentrations, metal accumulation was observed in the roots and leaves, while at higher concentrations, metal translocation from roots and leaves drained into the metallic ions and deposits them in different parts of the plant body petiole. It was deduced that the carboxylate group on the surface of the biomass facilitate metal adsorption (Dixit et al. 2010). Sorption of metal ions depends on contact time, pH and concentration. The sorption data fitted well with the Langmuir and Freundlich models. Acid and base treatment affected metal uptake. Acidic treatment increased the uptake capacity of water hyacinth roots for Cr^{6+}, whereas the removal of Cr^{3+} was lower (Narain et al. 2011).

Activated carbon and ash derived from water hyacinth possess potential for removing metal ions (Kadirvelu et al. 2005). Mahmood et al. (2010) reported that ash of water hyacinth also showed capacity for hyperaccumulation of Pb, Zn, Cr, Zn, Cu and Ni. Plant-derived ash offers several advantages including cost-effectiveness, high efficiency, minimization of chemical/biological sludge and regeneration of biosorbent with possibility of metal recovery.

Exposure to high concentrations of heavy metals such as Cu (1 mg L^{-1}) and Se (5 and 10 mg L^{-1}) caused marked changes in physiology of the plant (Hu et al. 2007; Buta et al. 2011). Higher concentrations of heavy metals adversely affected pigment production (chlorophyll a, chlorophyll b, total chlorophyll), protein, starch, soluble protein and free amino acids. Oxidative stress in chloroplasts brings damage to membranes by impacting the normal physiological function of proteins and lipids. The loss in pigment concentrations results from heavy-metal-mediated peroxidation of chloroplast membranes. The decrease in the total starch contents could result from poor performance of photosystems and inhibition of the Calvin cycle enzymes (Clijsters et al. 1999). The poor protein formation could be related to disruption of nitrogen metabolism from high doses of metals. Since nitrogen is one of the primary essential nutrients involved as a constituent of biomolecules such as nucleic acids, nitrogen bases, coenzymes and proteins, any deviation in these constituents would inhibit the growth and yield of plants (Vitória et al. 2011).

It is considered as the most efficient aquatic plant for wastewater purification since it bears potential for removing vast range of pollutants such as heavy metals, organic substances, nutrients (nitrate, ammonium, phosphorus), total suspended solids (TSS), total dissolved solids (TDS), turbidity from municipal and industrial (textile, metallurgical, pharmaceutical, paper) wastewater, sewage effluents and domestic wastewater (Kutty et al. 2009; Muthunarayanan et al. 2011; Yadav et al. 2011; Ajayi and Ogunbayo 2012; Kumar et al. 2012).

Water hyacinth remediates aquatic environments contaminated with the lanthanide metal, europium (Eu(III)). Highest concentration of Eu(III) is adsorbed onto the surface of the roots. NMR and IR spectroscopy established that carboxylate groups are the dominant functional groups responsible for binding Eu(III) to the roots of water hyacinth.

Organic Contaminants

Dyes are major pollutants present in the effluents of the textile, leather, food processing, dyeing, cosmetics, paper and dye-manufacturing industries. They are synthetic aromatic compounds which are embodied with various functional groups. Dye-containing wastewater causes serious water pollution problems by hindering light penetration. Most of the dyes resist biological oxidation, are stable against light and oxidizing agents, and require tertiary treatment; hence, their removal by conventional treatment procedures is not easy. *Eichhornia crassipes* showed efficiency for removing dyes and degrading ~90 % of red RB, black B and malachite green. The roots of water hyacinth have shown biosorption/accumulation of ethion and reactive dyes (Xia and Ma 2006; Gopinath et al. 2012; Shah et al. 2010). Promising attributes of water hyacinth include its tolerance to dye and dye absorption along with good root development, low maintenance and ready availability in contaminated regions. The sorption process followed first-order kinetics. The negative value of the free energy change indicated the spontaneous nature of the sorption and confirms the affinity between the sorbent and the dye cations.

Water hyacinth significantly reduced naphthalene (a polyaromatic hydrocarbon) (~45 %) present in wastewater and wetlands. Microbial activity of rhizospheric bacteria enhanced removal of naphthalene. Uptake by water hyacinth revealed a biphasic behaviour: a rapid first phase completed after 2.5 h and a second, considerably slower rate, phase (2.5–225 h) (Nesterenko-Malkovskaya et al. 2012).

2.2.1.3 *Azolla* (Water Fern)

Azolla (Azollaceae) is a small, free-floating water fern commonly found in tropical and temperate freshwater ecosystems. It is widely distributed in paddy fields, rivers, ponds and lakes. Plant body is composed of fronds which are triangular or polygonal and float on the water surface individually or in mats. Frond consists of a main stem growing at the surface of the water, with alternate leaves and adventitious roots at regular intervals along the stem. *Anabaena azollae* that lives in the dorsal lobe cavity of its leaf helps in nitrogen fixation. The biomass is also used as a biofertilizer or as a feed supplement for aquatic and terrestrial animals (Costa et al. 1999).

Inorganic Contaminants

Azolla species, namely, *A. caroliniana*, *A. filiculoides and A. pinnata*, possess high capacity to accumulate toxic elements such as Hg, Cd, Cr, Cu, Ni, Zn, Pb and As (Bennicelli et al. 2004; Zhang et al. 2008a, b; Rai and Tripathi 2009; Rahman and Hasegawa 2011; Taghi ganji et al. 2012) and can be used to remove contaminants from wastewater/industrial effluents, domestic wastewater and precious metals such as gold (Au) from aqueous solution (Bennicelli et al. 2004; Rakhshaee et al. 2006; Smadar et al. 2011). The initial binding and exchange of heavy metal ions to insoluble constituents in the *Azolla* matrix most probably involves cell wall charged groups (such as carboxyl and phosphate). Pectin and cellulose are important polysaccharides constituent of plant cell walls, made of fragments of polygalacturonic acid chains, which interact with Ca^{2+} and Mg^{2+} (exchange ions with heavy metals) to form a three-dimensional polymer by $(\text{–COO})_2Ca$ and or $(\text{–COO})_2Mg$ binding as the ion exchanging bases (Sood et al. 2004; Taghi ganji et al. 2005). A correlation between metal adsorption and the availability of carboxyl groups of galacturonic acid, the principal constituent of pectin, have been reported. Methylation, demethylation of carboxyl groups and pectinase treatment demonstrated that pectin of the *Azolla* cell wall is the major metal binding site.

Azolla caroliniana and *Azolla pinnata* showed capacity to purify polluted waters and ameliorate industrial effluents (thermal power, chlor-alkali and coal mine effluent). This is achieved by reducing significant levels of electrical conductivity (EC), TDS, BOD, chemical oxygen demand (COD), hardness, acidity and sodium and potassium content. Native biomass and chemically modified biosorbent, i.e. hydrogen peroxide *Azolla* sorbent (HAS), showed good sorption capacities for Cs and Sr (pH 8 and 9). Microwave reaction showed complete removal of metallic Ag and Pb nanoparticles from the polluted solution using

A. filiculoides. Adsorption and reduction combined using microwave radiation can be applied for removing and recycling metallic ions from contaminated water and industrial wastewater. Reduction of the metallic ions was accomplished by the plant matrix without the need of an external reducing agent. The proteins or sugar alcohols in the plant matrix serve as the reducing agents.

Exposure to high metal concentrations present in the wastewaters particularly Zn plating industrial effluent affected root growth and other biochemical parameters such as chlorophyll, carotenoid, polyphenol, protein, RNA, DNA and nutrient (NO_3^- and PO_4^{3-}) content in the fronds of *Azolla caroliniana* (Deval et al. 2012). Exposure to high Cd and Cu (0.2, 1 and 2 mM) concentrations affected photosystem II activity and altered photochemical yields (Fv/Fm) in *A. filiculoides* and *A. caroliniana* (Sánchez-viveros et al. 2010; Gonzalez-Mendoza et al. 2011).

Organic Contaminants

Azolla filiculoides showed capacity for removal of hydrocarbons from aquatic environment (Cohen et al. 2002). The presence of aromatic hydrocarbons such as benzene, toluene, ethylbenzene and xylene, which are together termed as BTEX, contribute to toxicity of diesel (Lohi et al. 2008). Biodegradation of diesel compounds depends on factors such as the accessibility to microbes, the capacity of the microbial community for hydrocarbon utilization and the inorganic nutrient composition of the environment. *Azolla pinnata* showed ability to degrade hydrocarbon from diesel. Concentrations of xylenes and ethylbenzene were 50–100 times lower. *Azolla* plants release a consortium of bacteria capable of significantly lowering levels of diesel fuel pollution. Enhancement of diesel degradation in the plant-added plots was due to the release of bacteria (bioaugmentation) and physiochemical improvement of the plot conditions (biostimulation) (Al-Baldawi et al. 2012). Plants synthesize a variety of enzymes that help in degradation of petroleum aliphatic and aromatic hydrocarbons. Some microbial degradative enzymes induced by plant compounds can co-oxidize compounds. Phosphate supplementation appeared to stimulate degradation of BTEX. Aquatic plants increase the surface area of the water/nonaqueous phase interface, making more of the petroleum hydrocarbons susceptible to attack by microbes. Photolysis by plant generates free radicals, such as the alkylperoxyl radical, that can oxidize aromatic rings and side chain structures of petroleum hydrocarbons. The solubility of non-volatile hydrocarbons increases at higher temperatures making them more available to microbes. Supplementation with inorganic nutrients can greatly increase the rate of diesel degradation in soil.

Pesticides such as monocrotophos accelerate the formation of reactive oxygen species, i.e. O_2^- and H_2O_2 in cells, via lipid peroxidation in *A. filiculoides*. This results in physiological and biochemical alterations in growth and defence system such as chlorophyll and carotenoid content. Oxidative stress induced proline accumulation and activity of superoxide dismutase (SOD) and peroxidase (POD) (Chris et al. 2011).

Olive mill wastewater (OMWW) contains high amounts of organic compounds (sugars, polyphenols, tannins, polyalcohols, pectins and lipids). The toxicity of OMWW is also due to its high phenolic content. *Azolla* showed capacity to remove polyphenols and chemical oxygen demand (COD) from olive mill wastewater (OMWW) collected from the traditional (TS) and continuous (CS) extraction systems (Ena et al. 2007).

Azolla filiculoides Lam. was able to survive in drug-contaminated waters. Plants showed active removal of drug sulphadimethoxine (S), a persistent antibiotic from the medium (Fornia et al. 2002). This caused alteration in growth (biomass yield) and N_2-fixation in N-free mineral medium. Drug uptake and degradation rates increase with S concentrations in the culture medium. *Azolla caroliniana* showed ability to grow and dissipate phenanthrene (PHE) by using bioaugmentation with hydrocarbonoclastic microorganisms (*Bacillus stearothermophilus* and *Oscillatoria* sp.) (Castro-Carrillo et al. 2008).

2.2.1.4 *Pistia stratiotes* (Water Lettuce)

Pistia is a genus belonging to family Araceae and comprises of a single species, *P. stratiotes*.

It floats on the surface of the water with its roots hanging beneath floating leaves. It is a common aquatic weed in the United States. Dense mats degrade water quality by blocking the air–water interface, reducing oxygen levels in the water and thus threatening aquatic life.

Inorganic Contaminants

Pistia stratoites showed capacity for phytofiltration of toxic heavy metals such as As, Cd, Cu, Ni, Zn, Pb, Cr, Mn and Co from contaminated waters and urban sewage (Maine et al. 2001; Miretzky et al. 2006; Espinoza-Quiñones et al. 2009; Venkatrayulu et al. 2009; Hua et al. 2011; Lu et al. 2011; Rawat et al. 2012; Prajapati et al. 2012). The rate of metal translocation is slow and most of the metal is strongly adsorbed onto root surfaces. Exposure to higher metal concentrations (Mn) (50, 200, 400 mg L^{-1}), Cr (1 and 10 mM) showed a decrease in relative growth rate and reduction in plant biomass (Upadhyay and Panda 2010). The metal sorption data followed Langmuir and Freundlich isotherms. The adsorption process followed first-order kinetics and the mechanism involved in biosorption resulted in ion exchange between monovalent metals as counter ions present in the macrophyte biomass. High metal treatments also affected biochemical parameters such as chlorophylls protein, free amino acid and RNA, DNA content along with enzymic and non-enzymic antioxidants, thus regulating oxidative stress.

Plant species possess capacity for improving water quality of dairy, aquaculture, sewage, industrial wastewater, storm water, drinking and surface water samples by reducing nutrients, COD, pH, turbidity, dissolved oxygen (DO), BOD, phosphate (PO_4^{3-}), nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_3) and total Kjeldahl nitrogen (TKN). Hence, its role in removal of aquatic macrophytes from water bodies is recommended for efficient water purification (Polomski et al. 2009; Lu et al. 2010; Akinbile and Yusoff 2012). Small-scale surface flow constructed wetlands with *Pistia stratoites*, *Phragmites australis*, *Typha orientalis* and *Ipomoea aquatica* exhibited higher nitrate removal efficiencies from groundwater (70–99 %).

Organic Contaminants

Pistia stratiotes L. showed ability to accelerate degradation of aromatic compounds in the rhizosphere. It could promote growth of microbe, retain a large microbial population in the rhizosphere and efficiently transport oxygen to stimulate the rhizospheric microbial activity, leading to phenol, aniline and 2,4-dichlorophenol degradation. It could accelerate removal of compounds through mechanisms such as (1) retaining a large population of the aromatic compound degraders, (2) stimulating bacterial growth and degradation activity and (3) removing aromatic compounds directly. Plant also showed potential to remove chlorpyrifos from water, though higher chlorpyrifos concentrations (0.5 and 1 mg L^{-1}) inhibited relative growth rates (RGR) (Prasertsup and Ariyakanon 2011). Plant showed capability to lower antimicrobial drug concentration, such as sulphonamide (sulphadimethoxine) and a quinolone (flumequine), though plant growth was adversely affected (Forni et al. 2006).

2.2.1.5 *Salvinia* (Water Fern)

Salvinia is a small free-floating aquatic fern belonging to family Salviniaceae. It possesses branched creeping stems bearing two types of leaves—upper green (photosynthetic) and lower submerged (hairy) bearing sori that are surrounded by basifixed membranous indusia (sporocarps). Leaves are present in whorls at each node. The genus *Salvinia* is comprised of 1 genus and 12 species. *Salvinia minima* is the smallest free-floating freshwater fern found in tropical and temperate regions (DeBusk and Reddy 1987). Its wide distribution, faster growth rate and easy handling make it a potential candidate for phytoremediation. Under optimal conditions, populations of *Salvinia* can double in size in approximately 3.5 days.

Heavy metal removal potential of *Salvinia* sp. particularly *S. natans* is well studied (Dhir et al. 2009; Dhir 2010; Dhir and Srivastava 2011). *Salvinia natans* is an established bioaccumulator of metals and has the potential to be used in constructed wetland systems for wastewater treatment as it has a very high growth rate in nutrient-rich and stagnant waters (AbdElnaby and Egorov 2012). Metal accumulation in *Salvinia* was higher in the roots. *Salvinia* demonstrated the ability to withstand Al (concentrations 20 mg L^{-1}), Cr (2.0 mg L^{-1}), As (200 μM) and Pb (20–40 μM) (Gardner and Al-Hamdani 1997; Nichols et al. 2000; Hoffman et al. 2004). Metal accumulation increased with the addition of sulphur to the nutrient solution (Hoffman et al. 2004), while increasing phosphate concentration decreased metal uptake (As) as reported in *S. natans* and *S. minima* (Hoffman et al. 2004).

Higher boron (B) accumulation in *S. natans* induced changes in physiological condition and biomass production. Boron concentration of 1 mg B dm^{-3} had no effect on the tested species, while higher concentrations of 6 and 8 mg B dm^{-3} had negative effects (Holtra et al. 2010). Exposure to higher Cd concentrations proved toxic and showed damage in the leaves of *S. auriculata* (Vestena et al. 2007; Wolff et al. 2012). Necrosis, chlorosis and ultrastructural deformities (chloroplast) such as damage to stomata, trichomes, biomass reduction and deterioration in the cell wall was noted. Lead accumulation caused damage in roots than in leaves as indicated by the decrease in their carotenoid content. *Salvinia minima*, Pb-hyperaccumulator aquatic fern, showed increased accumulation of GSH in both leaves and roots and increased the enzymatic activity of glutathione synthase (GS). Phytochelatins play an important role in protecting leaves from the detrimental effects of Pb perhaps by counteracting the effect of free radicals (Estrella-Gómeza et al. 2012).

Effectiveness of *S. minima* and *S. natans* in accumulating nitrogen (NH_4^+–N, NO_3–N), and phosphorus under different *eutrophic* environments is reported. *Salvinia* growth (fresh and dry weight) significantly declined at NaCl concentrations (3.0, 3.5 and 4.0 g L^{-1}). The reduction in growth coincided with a decline in CO_2 assimilation, while decrease in water potential followed increase in Na accumulation (Al-Hamdani 2008). *Salvinia*'s growth, expressed as frond production and plant biomass (fresh weight), was significantly increased with increasing nitrogen (concentration from 1.0 mg L^{-1} to 100.0 mg L^{-1}) and increasing of P concentration (concentration from 1.0 mg L^{-1} to 100.0 mg L^{-1}) in the growth media. This treatment also resulted in the highest photosynthetic rate, chlorophyll content and anthocyanins concentrations. Nitrogen and phosphorus concentration did not influence carbohydrate and sugar accumulation (Al-Hamdani and Sirna 2008). *Salvinia* shows good potential for use as a bioindicator and it can be used in the biomonitoring of aquatic ecosystems contaminated by metals and could be a good plant for remediation of eutrophic water.

Organic Contaminants

Salvinia molesta showed the ability to resist diesel contaminant (8,700, 17,400, 26,000, 34,800 and 43,500 mg L^{-1}) in synthetic wastewater. 33 % of the aquatic plants withered at the concentration of 8,700 mg L^{-1}, and 100 % withered at higher concentration of 43,500 mg L^{-1}. The withering of plant increased with increase in concentration (Albaldawi et al. 2011).

2.2.2 Submerged Species

Submerged plants such as *Potamogeton crispus* (pondweed), *Potamogeton pectinatus* (American pondweed), *Ceratophyllum demersum*, *Vallisneria spiralis*, *Mentha aquatica* (water mint) and *Myriophyllum spicatum* (parrot feather) have shown potential for accumulating metals from water as well as sediments (Fig. 2.3).

2.2.2.1 *Ceratophyllum* (Coontail or Hornwort)

It is a submerged, rootless, perennial plant and is a cosmopolitan in distribution. It is commonly found in ponds and slow-flowing streams. It has a high capacity for vegetative propagation and biomass production even under low nutritional conditions (Arvind and Prasad 2005).

Inorganic Contaminants

Ceratophyllum demersum and *C. submersum* showed accumulation of Cd, As mainly arsenate and arsenite and Ni from hydroponic cultures (Kumar and Prasad 2004; Kara 2010; Matamoros et al. 2012; Xue et al. 2012). Higher influx of arsenate was noted in plants exposed to As solutions

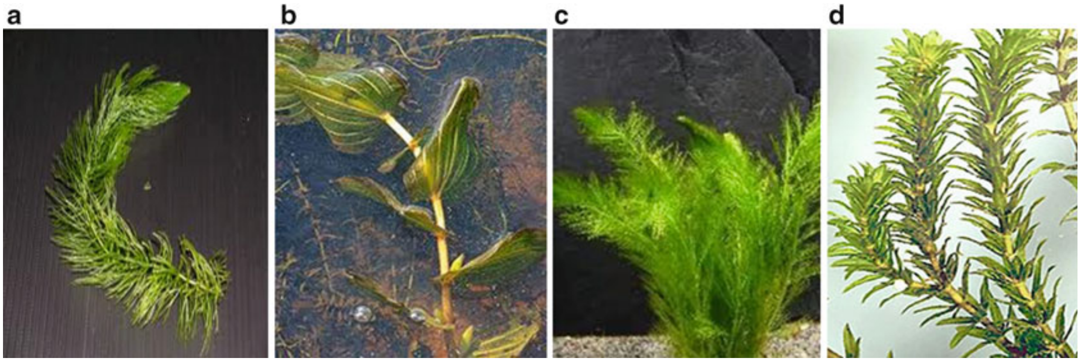

Fig. 2.3 Submerged aquatic plant species: (**a**) *Ceratophyllum*, (**b**) *Potamogeton*, (**c**) *Myriophyllum* and (**d**) *Hydrilla*

without the addition of phosphate (P). Metal accumulation by plant increased with increasing treatment concentration and duration. Exposure to high Pb concentrations (20, 50, 100 μg mL^{-1}) adversely affected total chlorophyll and nitrogen contents (Larson et al. 2002; Saygideger et al. 2004). *Ceratophyllum demersum* could recycle the wastewater mainly raw municipal wastewater (RMW) and treated municipal wastewater (TMW) to be reused for irrigation purpose in agriculture fields. Plant showed good removal efficiency (60–90 %) for Fe, Zn, Mn, Ni, Pb and Cd from TMW and RMW. *C. demersum* showed capabilities to remove trace elements and minerals (Ca, N, P, Na, K) directly from the contaminated water and compost latex (diluted 200 times with distilled water). *C. demersum* showed potential for removing electrical conductivity (EC), COD, ammonium, nitrate and phosphorous (Wang et al. 2005; Foroughi 2011a, b; Foroughi et al. 2010).

C. demersum take up nitrate effectively from hydroponic systems (Toetz 1971). *C. demersum* cultured in mesotrophic, eutrophic and hypertrophic and Hoagland's solutions showed changes of total N (TN) and total P (TP) concentrations in nutrient solutions. The plant from eutrophic solution showed higher SOD and POD activities, showing good survival preferably under eutrophic condition.

Organic Contaminants

Microcosm wetland systems (5-L containers) planted with *C. demersum* along with different aquatic species *S. molesta*, *L. minor* and *E. canadensis* showed potential for removal of diclofenac, triclosan, naproxen, ibuprofen, caffeine and MCPA. Plants contribute to the elimination capacity of microcontaminants in wetland systems through biodegradation and uptake processes (Matamoros et al. 2012). Triclosan, diclofenac and naproxen were removed predominantly by photodegradation, whereas caffeine and naproxen were removed by biodegradation and/or plant uptake. The formation of two major degradation products from ibuprofen, carboxy-ibuprofen and hydroxy-ibuprofen, is reported.

2.2.2.2 *Potamogeton* (Pondweed)

Potamogeton sp. is an aquatic, lightly rooted and partly submerged plant. It is commonly found in slow-moving streams, ponds and lakes. It bears narrow, acute, flat-margined or curly leaves. The biomass production rate can be as high as 100 kg ha^{-1} day^{-1} (Schneider et al. 1999). The species include *P. cripsus* and *P. natans*.

Inorganic Contaminants

Potamogeton pectinatus L. and *Potamogeton malaianus* Miq showed capacity for accumulating Cd, Pb, As, Cu, Zn and Mn (King et al. 2002; Demirezen and Aksoy 2006; Fritioff and Greger 2006; Anawar et al. 2008; Sivaci et al. 2008b; Rahman and Hasegawa 2011). Higher concentrations of metal were found in the leaves of *P. pectinatus*. Dead biomass of the *Potamogeton* sp., particularly *P. natans*, possesses good sorption capacity for Hg and hence removal from aqueous solution. Atomic absorption, electron microscopy and X-ray energy dispersion analyses showed that sorption of Hg(II) took place over the entire biomass surface; bright spots showed high concentrations of Hg which may be due to surface HgO precipitation particularly on active sites. Multilayer sorption of Hg(II) was noted. Sorption process occurs by two different mechanisms. A rapid uptake removing ~ 90 % of metal is followed by a slower passive uptake that involves diffusion into pores on the biomass surface. pH value affects metal uptake capacity and pH value of 9–10 was found to be optimum (Lacher and Smith 2002). It is also suggested that dead biomass might be reducing Hg(II) to Hg(I) and/or HgO.

Submersed plants can be useful in reducing heavy metal concentrations in storm water, since they can accumulate large amounts of heavy metals in their shoots (Fritioff et al. 2005). Storm water comprises rainwater and water draining from hard surfaces such as roads and roofs in urban areas and often contains heavy metals, in particular Cu, Zn, Cd and Pb (Peng et al. 2008). Zn, Cu, Cd and Pb present in storm water were taken up by *P. natans*. Highest accumulation is found in the roots. Cell wall-bound fraction was generally smaller in stems than in leaves. The metal concentrations in the plant tissue increased with increasing temperature and low salinity.

Higher level of metal accumulation results in toxicity. Chlorophyll levels decreased, while anthocyanin and total phenolic concentrations increased with exposure to high Cd concentrations (8, 16, 32 and 64 mg L^{-1}). Abscisic acid content was found to increase with increased in Cd concentration and exposure time (Sivaci et al. 2008a).

Organic Contaminants

Potamogeton spp. showed capacity for removing organochlorine compounds including PCBs. It also showed capacity of treating groundwater contaminated with explosives at army ammunition plants located at Milan. Both lagoon system and gravel-bed system were designed. The lagoons were planted with sago pondweed, water stargrass, elodea and parrot feather. The gravel-bed wetlands were planted with canary grass, wool grass, sweet flag and parrot feather. The gravel-bed wetland effectively reduced 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (HMX), 2,4,6-trinitrobenzene (TNB) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (RDX) in the groundwater. The rate of explosives removal in the wetlands followed first-order kinetics. The lagoon was very ineffective at removing RDX and HMX in the contaminated groundwater. TNT is believed to be degraded by submergent plant species via production of nitroreductase enzymes which should have yielded amino derivatives in the aqueous phase with a decrease in TNT concentrations (Best et al. 1998). In a similar study, plant could treat explosives-contaminated groundwater from the Iowa Army Ammunition Plant (IAAP), Middletown. Species evaluated were *C. demersum* L. and *P. nodosus* Poir. Plants were rooted in local, IAAP, sediment under continuous-flow conditions. Unplanted sediment served as control. Aqueous TNT and RDX concentrations decreased exponentially (first-order kinetics).

Wetland mesocosms planted with *Potamogeton* spp. and *Typha* sp. (*Typha latifolia* and *T. augustifolia*) showed degradation of two commonly used herbicides, atrazine and alachlor. Atrazine mass loss was more rapid in the emergent mesocosms than in the open or submergent mesocosms. Alachlor dissipated more rapidly than atrazine under all treatments. More than 50 % of the alachlor concentration and mass were lost within 21 days under all treatments (dissipation half-life of alachlor mass ~ 10–20 days). Deethylatrazine (DEA), a metabolite of atrazine, was detected in all mesocosms (Lee et al. 1995; Lovett-Doust et al. 1997).

2.2.2.3 *Myriophyllum* (Water Milfoil)

It is a submerged plant commonly found in freshwater lakes, ponds, streams and canals and appears to be adapted to high nutrient environments. It belongs to family Holoragaceae. *Myriophyllum aquaticum* (parrot feather) has both submersed and emergent leaves, with the submersed form being easily mistaken for *Myriophyllum spicatum* (*Eurasian watermilfoil*), a close relative. Leaves are arranged around the stem in whorls of four to six. The submersed leaves are 1.5–3.5-cm long and emergent leaves are 2–5-cm long. The bright-green emergent leaves are stiffer and darker green than the submersed leaves.

Inorganic Contaminants

Myriophyllum spicatum (parrot feather) is an efficient plant species for the treatment of metal-contaminated industrial wastewater as it showed capacity to remove Co, Ni, Cu and Zn from industrial effluents (Wang et al. 1996; Sánchez et al. 2007; Lesage et al. 2008). *Myriophyllum heterophyllum* showed high Cd biosorption and high metal exposures resulted in loss in production of photosynthetic pigments and total phenolic compounds. Abscisic acid content increased with increase in Cd concentration in *Myriophyllum heterophyllum* Michx. and exposure time (Sivaci et al. 2008b).

Organic Contaminants

Myriophyllum spicatum and *Myriophyllum aquaticum* showed ability to take up and transform 2,4,6-trinitrotoluene (TNT). Low concentrations of aminated nitrotoluenes (2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene) were observed in the extracellular medium and tissue extracts (Hughes et al. 1997). Alkylphenols (APs), such as nonylphenol (NP) and octylphenol (OP), are the biodegradation products of ethoxylates, nonionic surfactants which have been widely used as detergents, emulsifiers, wetting agents, plasticizers and UV stabilizers as well as in other agricultural and industrial applications. *M. verticillatum* could accumulate high amounts of NP and OP in their tissues (Zhang et al. 2008a, b). Plant also showed capacity to tolerate organic chemicals such as trichloroacetic acid (TCA) (Hanson et al. 2002).

2.2.2.4 *Hydrilla* (Esthwaite Waterweed)

It is native to the cool and warm waters in Asia, Europe, Africa and Australia, with a sparse, scattered distribution in Europe. The plant genus consists of one species, *H. verticillata*. *Hydrilla* is an invasive, non-native submerged plant with long slender stems that branch out profusely when they reach the water surface. The leaves are 5/8-in. long, strap shaped with pointed tips and a distinct midrib. The green leaves are arranged in whorls of 4–8 and are attached directly to the stem. The leaf margins have distinct saw-toothed edges that are visible to the naked eye and rough to the touch. The female flowers are single, white, with six petals, and float on the surface. The male flowers are greenish and develop close to the leaf axils near the tip of the stem.

Inorganic Contaminants

H. verticillata has been tested for the uptake and remediation of As, Cu, Pb, Zn, Se and Cr from water (Carvalho and Martin 2001; Srivastava et al. 2006; Bunluesin et al. 2007; Begum and HariKrishna 2010; Dixit and Dhote 2010; Xue et al. 2010; Rahman and Hasegawa 2011). Metal uptake and accumulation in *H. verticillata* is dependant on both concentration of the metalloid in water and duration of exposure (Srivastava et al. 2010), as uptake is inhibited at high phosphate concentration. This might be due to the competitive uptake of phosphate and its chemical analog As(V). Results showed that As accumulation was about twofold higher upon exposure to either As(V) or As(III) in S-excess plants compared to that in S-sufficient and S-deficient plants (Srivastava et al. 2007). As accumulation did not induce any toxic effects in terms of lipid peroxidation which could be attributed to the enhanced level of thiol metabolites (cysteine, glutathione) and enzymatic antioxidants (guaiacol peroxidase, catalase, ascorbate peroxidase). *Hydrilla verticillata* are capable of accumulating Hg effectively, though higher exposures (5.0 μM) reduced chlorophyll, protein, cysteine and NPK content.

Hydrilla verticillata have the capacity to absorb heavy metals Cr, Cd, Mn, Hg, Ni, Pb, Fe, Cu, Zn and Cr from contaminated water, thereby reducing pollution level of water (Samdani et al. 2008; Shaikh and Bhosle 2011). Absorption kinetics followed Langmuir model. Ligand exchange mechanism was found to be responsible for high Cr adsorption capacity. Both roots and shoots accumulate metals such as Cu and metals are mainly accumulated in cell

Fig. 2.4 Emergent aquatic plant species: (**a**) *Elodea*, (**b**) *Scirpus*, (**c**) *Typha* and (**d**) *Phragmites*

wall fractions. Potential of *H. verticillata* for bioamelioration of wastewater containing the toxic metals has been demonstrated (Gupta and Chandra 1994, 1996; Rai et al. 1995). Exposure to high Pb and Cd reduced fresh biomass, chlorophyll content, protein, NR activity and glutathione levels due to toxic effect created by metals. In contrast, increase in carotenoid, cysteine and proline content was observed. The increase in cysteine level under Cd stress may be due to enhanced levels of ATP sulfurylase and adenosine 5′-phosphosuphfate sulphotransferase (Singh et al. 2012a). Various Cd concentrations resulted in the induction of phytochelatins at both concentrations that exhibited positive thiol reactions. *H. verticillata* has a cellular mechanism for Pb detoxification (Gupta et al. 1995; Tripathi et al. 1996).

Organic Contaminants

Hydrilla verticillata showed capacity for accumulation and hence removal of hydrophobic organochlorine contaminants such as cis- and trans-chlordane, dieldrin and polychlorinated biphenyls (PCBs) and hexachlorocyclohexane (HCH), an organochloride insecticide (Hopple and Foster 1996; Sinha 2002). HCH toxicity was reduced in plants treated with high Fe concentrations, though HCH accumulation was reduced in presence of high Fe. HCH exposure reduced chlorophyll content, but increased malonaldehyde content, cysteine level, thiol content and activity of antioxidative enzymes such as superoxide dismutase (SOD) (Sinha 2002). The plant showed lindane degradation capacity (Ortega-Clementea and Luna-Pabellob 2012).

2.2.3 Emergent Species

Typha latifolia (cattail), *Phragmites* (common reed) and S*cirpus* spp. (bulrush) are semiaquatic/emergent plant species that possess high metal-removing abilities. Emergent plants bioconcentrate metals from water and sediments, though the site where the metals are localized varies from species to species. Most of the plants retain more of the metal burden in belowground parts (roots), in contrast to a few other species that redistribute a greater proportion in aboveground tissues, especially leaves. The metal uptake by plants results in the transport of metals across the plasma membrane of root cells, xylem loading and translocation, and detoxification and sequestration of metals at cellular level (Fig. 2.4).

2.2.3.1 *Elodea* (Waterweed)

It is a herbaceous freshwater plant. It is commonly reported in parts of *Europe*, *Australia*, *Africa*, *Asia* and *New Zealand*. *Elodea canadensis* (American or Canadian waterweed) is the most common species. It is a rooted multi-branched perennial plant. The dark-green blade-like leaves (3/5-in. long and 1/5-in. wide) are in whorls of three with finely toothed margins. It lives entirely underwater with the exception of small white *flowers* which bloom at the surface and are attached to the plant by delicate stalks.

Inorganic Contaminants

Elodea canadensis (Elodea) showed capacity for removing Fe, Cu, Zn, Cd, Pb and Ni from wastewater and storm water (Fritioff et al. 2005; Begum and HariKrishna 2010; Hansen et al. 2011; Matamoros et al. 2012). *Elodea canadensis* also showed possibility of cleaning U from contaminated waters. *E. nuttallii* showed Fe accumulation (Pratas et al. 2010). Growth of *E. nuttallii* was promoted by low iron concentration, but growth inhibition was observed on exposure to high concentration (beyond 10 mg L^{-1}). The synthesis of protein, pigments, PSII maximal quantum yield, electron transport rate and activities of antioxidant enzymes, namely, superoxide dismutase (SOD), catalase (CAT), peroxidase (POD) and glutathione S-transferase (GST) increased at low concentrations of Fe, Pb, while high concentration inhibited the synthesis of protein and pigments as well as activities of antioxidative enzymes (Dogan et al. 2009; Xing et al. 2010; Sun et al. 2011). Induction of non-protein thiol (SH) groups and ascorbate suggested their role in metal detoxification. Cd induced the production of phytochelatins (PCs) in *E. canadensis*. PCs were produced in a concentration and species dependent manner (Sun et al. 2011).

Elodea nuttallii absorbed phosphorus via both roots and shoots in eutrophic lakes. The phosphorus uptake via shoots significantly exceeded the phosphorus uptake via roots. The absorbed phosphorus was equally translocated via acripetal or basipetal movements and was incorporated in all parts of the plants (Susanne and Hendrik 2008; Wang et al. 2010).

Organic Contaminants

E. canadensis showed uptake and elimination capacity for microcontaminants in wetland systems through biodegradation and uptake processes. This includes pesticides such as copper sulphate (fungicide), flazasulfuron (herbicide), and dimethomorph (fungicide), diclofenac, triclosan, naproxen, ibuprofen, caffeine, clofibric acid and MCPA. The findings suggested that most of these contaminants are removed predominantly by biodegradation.

Elodea canadensis removed or transformed DDT from the medium. The decay profile of DDT from the aqueous culture medium followed first-order kinetics (Olette et al. 2008). DDT was degraded or bound to the elodea plant material. o,p′-DDD and p,p′-DDD are the major metabolites in these plants (Gao et al. 2000a, b). Apparently, reduction of the aliphatic chlorine atoms of DDT is the major pathway for this transformation. It also showed capacity to remove explosives 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in groundwater using constructed wetlands at Milan Army Ammunition Plant. It was demonstrated that TNT disappeared completely from groundwater incubated with plants. Emergent plants reduced in groundwater amended to contain RDX. Highest specific RDX removal rates were found in submersed plants in elodea and in emergent plants in reed canary grass (Best et al. 1999b).

2.2.3.2 *Typha* (Cattail)

It is a cosmopolitan species found in variety of *wetland* habitats in North America, Mexico, Great Britain, Eurasia, India, Africa, New Zealand and Australia. It is a *genus* of about 11 *species* of *monocotyledonous* flowering plants in the family *Typhaceae*. Leaves are alternate and mostly basal to a simple stem that bears the flowering spikes. Plants are *monoecious* and bear *unisexual*, wind-pollinated flowers, developing in dense *spikes*.

Inorganic Contaminants

Typha latifolia exhibited Zn, Pb, As and Cd tolerance and exclusion potential (Ye et al. 2001; Abdel-Ghani et al. 2009; Alonso-Castro et al. 2009; Adhikari et al. 2010; Hadad et al. 2010; Hegazy et al. 2011). *Plant* removed Cd and Pb effectively from solutions and was able to accumulate these metals in the roots and, to a lesser extent, in the leaves. This may be related to its oxygen transport capability, radial oxygen loss from the roots and the capability to modify its rhizosphere. Plants showed presence of inorganic arsenite, arsenate, dimethylarsinic acid and monomethylarsonic acid. Plaque (Fe and Mn) affected Cu accumulation in *Typha latifolia* L. (Ye et al. 2001; Saulais et al. 2011). Plants adsorbed more

Cu and a higher proportion of Cu was observed in roots. *Typha domingensis* leaf powder showed removal of Al, Fe, Zn and Pb from aqueous solution. The infrared spectra of *Typha* leaf powder confirmed ions–biomass interactions responsible for sorption. FTIR investigation revealed that metal binding takes place on the surface of *Typha* biomass. X-ray fluorescence (XRF) spectroscopy and micro-proton-induced X-ray emission (micro-PIXE) depicted that Pb accumulated in root cells around vacuoles and slowly get transported to leaves (*T. angustifolia* and *T. latifolia*). Lead was deposited in the rhizome near the cell wall. Most of the Pb accumulated in leaf cells, especially in chloroplasts, and vacuoles (Abdel-Ghani et al. 2009; Sharain-Liew et al. 2011). However, in the rhizome and leaf, lead granules accumulated near the cell wall and in the chloroplasts. Increase in K, Ca, Fe and Zn concentration in roots, rhizomes and leaves was noted at higher Pb treatments. Micro-PIXE analysis demonstrated Pb accumulation and localization in epidermal and cortical tissues of treated roots and rhizomes (Panich-pat et al. 2005). Cell wall immobilization of Pb is one of the tolerance mechanisms in *Typha latifolia* (Gallardo-Williams et al. 2002; Panich-pat et al. 2005; Ramamoorthy and Kalaivani 2011). Results indicate that Pb may form complexes with phosphorus and sulphur compounds in roots and rhizomes, which may also represent attraction sites for binding Zn. Higher doses of Pb altered rate of photosynthesis, chlorophyll content and POD and SOD activities in *Typha* plants.

Wetlands planted with *Typha domingensis* could treat effluent from metallurgical operations. The root and stele cross-sectional areas, number of vessels and biomass registered in inlet plants promoted the uptake, transport and accumulation of contaminants Cr, Ni, Zn and total phosphorus in tissues. The modifications recorded accounted for the adaptability of *T. domingensis* to the conditions prevailing in the constructed wetland, which allowed this plant to become the dominant species and enabled the wetland to maintain a high contaminant retention capacity (Aslam et al. 2010). *Typha angustata* showed capacity to treat domestic sewage. The lower levels of BOD and total dissolved solids (TDS) and lower concentration of heavy metals such as Pb, Mn, Zn and Cu and higher level of dissolved oxygen (DO) were noticed in the reed (*Typha angustata*) root zone compared to non-reed root zone. The numbers of colonies of bacterial species and fungal populations were found to increase in reed zone than non-reed root zone. Rhizosphere of *Typha angustata* has a direct influence on the composition and density of soil microbial community. Exudates of reed plant caused an increase in the metabolic activity of microbes of the rhizosphere and transformed the organic and inorganic pollutants into harmless compounds. It is concluded that *Typha* root zone with its myriad of microbes served as a bio-bed which has the potential to reduce the BOD and TDS levels of sewage water, decrease the concentration of heavy metals and increase dissolved oxygen. *Typha domingensis* also showed phytoremediation of heavy metals from urban domestic and municipal wastewater. The concentrations in the root and shoot tissues were found in the order of Fe > Mn > Zn > Ni > Cd. Small-scale wetland mesocosms vegetated with *Typha* showed efficacy for treatment of wastewater as significant reduction in total suspended solids (TSS), 5-day biochemical oxygen demand (BOD5) and total Kjeldahl nitrogen (TKN) was noted (Calheiros et al. 2009; Borkar and Mahatme 2011; Mojiri 2012). *Typha domingensis* also showed capacity to absorb and accumulate Al, Fe, Zn and Pb from industrial wastewater ponds in El-Sadat City, Egypt. Maximum metal removal was achieved by rhizofiltration.

The wetland microcosms significantly reduced the concentrations of Se, As, B and cyanide (CN) in the wastewater. The primary sink for the retention of contaminants within the microcosms was the sediment, which accounted for 40–50 % removal, while accumulation in plant tissues accounted for only 2–4 % and while 3 % of the Se was removed by biological volatilization to the atmosphere. Cattail, Thalia and rabbitfoot grass were highly tolerant of the contaminants and exhibited no growth retardation. The data from the wetland microcosms support the view that constructed wetlands could be used to successfully reduce the toxicity of aqueous effluent contaminated with extremely high concentrations of $SeCN^-$, As and B, but pilot-scale studies need to be carried out to validate the results (Manios et al. 2003; Lu et al. 2009).

Organic Contaminants

Horizontal subsurface flow CWs planted with *Phragmites australis* (UP series) and *Typha latifolia* provided high removal of organics BOD and COD (80–90 %) from tannery wastewater and other contaminants, such as nitrogen. The plant also showed capacity to remove parathion, trichloroethylene, pesticide residues and pharmaceuticals such as ibuprofen and clofibric acid (Wilson et al. 2000; Bankstona et al. 2002; Amaya-Chávez et al. 2006; Dordio et al. 2007, 2009, 2011). Cattails also showed potential for decolorizing and remediating textile wastewater (Nilratnisakorn et al. 2009).

2.2.3.3 *Phragmites* (Reed)

It is a large *perennial grass* found in *wetlands* throughout temperate and tropical regions of the world. *Phragmites australis* is sometimes regarded as the sole species of the genus, though some *botanists* divide *Phragmites australis* into three or four species: *Phragmites australis* (Cav.) *Trin*. ex *Steud*., *Phragmites communis* Trin., *Arundo phragmites* L. (the *basionym*) and *Phragmites altissimus*. The perennial has alternately spaced spear-shaped leaves, rootstalks, called rhizomes and flowers, and spikelets with tufts of silky hair.

Reed bed systems showed stable removal efficacy of organics of a similar rate to the conventional technologies and also have higher ability of removing nutrients, so beneficial against eutrophication.

Inorganic Contaminants

Phragmites australis is effective for removing heavy metals from the industrial wastewater under arid and semi-arid conditions. Hg and As accumulations in belowground tissues were higher than those for the aboveground tissues (Afrous et al. 2011). Hydroponic experiments with Cd exposure did not affect root and shoot growth and mineral composition (N, P, K, Fe, Zn and Mn), while combined treatments of Cd, Cu and Zn significantly decreased shoot length, root number, plant fresh weight and tissue concentrations of N, P and K. Pilot subsurface horizontal flow constructed wetland with *Phragmites australis* and *Phragmites mauritianus* showed domestic wastewater treatment by reducing BOD, COD, suspended solids, TDS, conductivity, nitrate nitrogen, total phosphorus (TP) and total nitrogen (TN) (Alia et al. 2004; Todorovics et al. 2005; Yang et al. 2007; Chale 2012). The results obtained show that *P. mauritianus* may not be a suitable plant for use in constructed wetlands (Weis and Weis 2004) since it sheds a lot of litter which introduces nutrients into the system. *Phragmites communis* demonstrates an efficient approach to remove various liquid-phase pollutants such as Zn, COD, colour and NH_3–N from wastewater by using both free water surface flow and submerged surface flow constructed wetland (CW) systems (Weis and Weis 2004). Growth of *Phragmites communis* enables well-developed root network in CW system, thus leading to a higher adsorption capacity. The presence of bio-membrane on the plant root not only enhances but also stabilizes the efficiencies for removing various contaminations from the wastewater. In a similar study, subsurface horizontal flow constructed wetlands receiving tannery wastewater vegetated with *Typha latifolia* and *Phragmites australis* showed reduced organic load by decreasing COD and BOD (Calheiros et al. 2007; Kalipci 2011; Ong et al. 2011; Cortes-Esquive et al. 2012; Ramprasad 2012).

Organic Contaminants

Constructed wetland planted with *Phragmites australis* treated azo dye Acid Orange 7 (AO7). Toxic signs were observed at the *Phragmites australis* after the addition of AO7 into the wetland reactors, but it adapted to the wastewater with passage of time. The presence of *Phragmites australis* had a significant impact on the removal of organic matters, AO7, aromatic amines and NH_4–N (Davies et al. 2005).

2.2.3.4 *Scirpus* (Bulrush)

The genus has a cosmopolitan distribution. It belongs to family Cyperaceae. Many species are common in wetlands and can produce dense stands of vegetation, along rivers, coastal deltas and ponds. It is a perennial herb with short, tough rhizomes, forming dense tussocks ~2-m tall. Most species have leaves reduced to tiny sheathing structures. The flowers or inflorescences of these plants are found on the tip of the growing stems and resemble tight clusters of grass-like flowers.

Inorganic Contaminants

Efficacy of small-scale wetland mesocosms planted with vegetation (a mixture of *Typha*, *Scirpus* and *Juncus* species) showed efficacy for treatment of domestic wastewater by reducing total suspended solids (TSS), BOD, total Kjeldahl nitrogen (TKN) and conductivity. Increased DO and reduction in faecal coliform, *Enterococcus*, *Salmonella*, *Shigella*, *Yersinia* and coliphage populations also were observed in vegetated wetlands (Hench et al. 2003). Horizontal subsurface flow constructed wetland planted with *Limnocharis flava* and *Scirpus atrovirens* showed efficacy for removing nutrients (NH_3–N and PO_4–P) from landfill leachate (Kamarudzaman et al. 2011). *Phragmites australis*, *Typha latifolia and Scirpus* also showed capacity for uptake of As and Hg from industrial wastewater. Higher metal accumulation was noted in belowground tissues. Lab-scale horizontal subsurface flow constructed wetland (CW) planted with *Phragmites australis* and *Scirpus maritimus* treated moderate strength wastewater (Afrous et al. 2011). The physicochemical characteristics of the wastewater changed significantly as the wastewater flowed through the respective wetland cells. CW unit with zeolite achieved significantly higher removal for COD, ammonium, TSS and total nitrogen at 4- and 3-day HRT (Gross et al. 2007; Shuib et al. 2011; Sharif et al. 2013).

Organic Contaminants

Estrogenic hormones 17b-estradiol (E2) and 17a-ethinyl estradiol (EE2) have been detected in municipal wastewater effluent and surface waters at concentrations toxic to aquatic fauna. An engineered treatment wetland with E2, and EE2 showed that 36 % of the E2 and 41 % of the EE2 were removed during the cell's 84-h hydraulic retention time (HRT). The attenuation was most likely the result of sorption to hydrophobic surfaces in the wetland coupled with biotransformation. Sorption was indicated by the retardation of the hormones relative to the conservative tracer (Gray and Sedlak 2005). Biotransformation was indicated by elevated concentrations of the E2 metabolite, estrone. It was also suggested that removal efficiency can be increased by increasing HRT or the density of plant materials. *Scirpus mucronatus* showed growth in diesel fuel-contaminated soil and could survive high concentrations of hydrocarbons. 33.3 % of plants were withered in 5 and 10 g kg^{-1}, 66.6 % on 15, 20, and 50 g kg^{-1}, 100 % withered on 100 and 200 g kg^{-1} of contaminant concentration after 30 days of exposure (Purwanti et al. 2012).

2.2.4 Other Plant Species

Ipomoea aquatica (water spinach) showed capacity to grow in Cd-contaminated surface water and remediate Cd-contaminated wastewater. Root length and root biomass were negatively correlated with the total soluble Cd ions. High Cd bioconcentration factors of *I. aquatica* (375–2,227 L kg^{-1} for roots, 45–144 L kg^{-1} for shoots) imply that it is a potential aquatic plant to remediate Cd-contaminated wastewater (Wang et al. 2008). Lotus (*Nelumbo nucifera*) showed the best removal efficiency for wastewater (domestic) treatment. Plant showed removal of SS, BOD5, TKN, NH_3–N, NO_2–N, NO_3–N, TP and coliform bacteria (Kanabkaew and Puetpaiboon 2004). *Vetiveria zizanioides* (vetiver grass) showed capacity to tolerate very high levels of heavy metals Al, Mn, Mg, As, Cd, Cr, Ni, Cu, Pb, Hg, Se, Zn and the herbicides and pesticides in soils and water. It could also resist very high acidity, alkalinity and salinity conditions (pH from 3.0 to 10.5; EC = 8 dScm). Vetiver also has high capacity to absorb and remove agro-chemicals like carbofuran, monocrotophos and anachlor from soil, thus preventing them from contaminating and accumulating in the crop plants. It also showed an ability to tolerate very high acidity, alkalinity (pH from 3.0 to 10.5); soil salinity (EC = 8 dScm), sodicity (ESP = 33 %), magnesium and very high levels of heavy metals Al, Mn, Mg, As, Cd, Cr, Ni, Cu, Pb, Hg, Se, Zn and the herbicides and pesticides in soils. Vetiver roots can absorb and accumulate several times of some of the heavy metals present in the soil and water. Less of the As, Cd, Cr, Hg and moderate amount of (16–33 %) of Cu, Pb, Ni and Se absorbed were translocated to the shoots. Vetiver also has high capacity to absorb and remove agro-chemicals like carbofuran, monocrotophos and anachlor from soil, thus preventing them from contaminating and accumulating in the crop plants.

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Literature Cited

Abdel-Ghani NT, Hegazy AK, El-Chaghaby GA (2009) *Typha domingensis* leaf powder for decontamination of aluminium, iron, zinc and lead: biosorption kinetics and equilibrium modeling. Int J Environ Sci Technol 6(2):243–248

Abdelmalik WEY, El-Shinawy RMK, Ishak MM, Mahmoud KA (1980) Uptake of radionuclides by some aquatic macrophytes of Ismailia Canal, Egypt. Hydrobiology 69:3

AbdElnaby AM, Egorov MA (2012) Efficiency of different particle sizes of dried *Salvinia natans* in the removing of Cu(II) and oil pollutions from water. J Water Chem Technol 34:143–146

Adhikari T, Kumar R, Singh MV, Rao AS (2010) Phytoaccumulation of lead by selected wetland plant species. Commun Soil Sci Plant Anal 41:2623–2632

Afrous A, Manshouri M, Liaghat A, Pazira E, Sedghi H (2011) Mercury and arsenic accumulation by three species of aquatic plants in Dezful, Iran. Afr J Agric Res 6(24):5391–5397

Ajayi TO, Ogunbayo AO (2012) Achieving environmental sustainability in wastewater treatment by phytore-mediation with water hyacinth (*Eichhornia crassipes*). J Sustain Dev 5:80–90

Akinbile CO, Yusoff MS (2012) Assessing water hyacinth (*Eichhornia crassipes*), (*Pistia stratiotes*) effectiveness in aquaculture wastewater treatment. Int J Phytoremediation 14(3):201–211

Albaldawi IA, Suja' F, Abdullah SRS, Idris M (2011) Preliminary test of hydrocarbon exposure on *Salvinia molesta* in phytoremediation process. Revelation Sci 01:52–56

Al-Baldawi IA, Abdullah SRS, Suja F, Anuar N, Idris M (2012) Preliminary test of hydrocarbon exposure on *Azolla pinnata* in phytoremediation process. In: International conference on environment, Energy and biotechnology IPCBEE, vol 33. IACSIT Press, Singapore, pp 244–247

Al-Hamdani S (2008) Influence of different sodium chloride concentrations on selected physiological responses of *Salvinia*. J Aquat Plant Manage 46: 172–175

Al-Hamdani SH, Sirna CB (2008) Physiological responses of *Salvinia minima* to different phosphorus and nitrogen concentrations. Am Fern J 98:71–82

Alia NA, Bernal MP, Ater M (2004) Tolerance and bioaccumulation of cadmium by *Phragmites australis* grown in the presence of elevated concentrations of cadmium, copper, and zinc. Aquat Bot 80:163–176

Alonso-Castro AJ, Carranza-Álvarez C, la Torre MCA, Chávez-Guerrero L, García-De la Cruz RF (2009) Removal and accumulation of cadmium and lead by *Typha latifolia* exposed to single and mixed metal solutions. Arch Environ Contam Toxicol 57:688–696

Alvarado S, Gu'edez M, Lu'e-Mer'u MP, Nelson G, Alvaro A, Jes'us AC et al (2008) Arsenic removal from waters by bioremediation with the aquatic plants water hyacinth (*Eichhornia crassipes*) and Lesser Duckweed (*Lemna minor*). Bioresour Technol 99:8436–8440

Amaya-Chávez A, Martínez-Tabche L, López-López E, Galar-Martínez M (2006) Methyl parathion toxicity to and removal efficiency by *Typha latifolia* in water and artificial sediments. Chemosphere 63(7):1124–1129

Anawar HM, Garcia-Sanchez A, Alam MT, Majibur RM (2008) Phytofiltration of water polluted with arsenic and heavy metals. Int J Environ Pollut 33:292–312

Ansede JH, Pellechia PJ, Yoch DC (1999) Selenium biotransformation by the salt marsh cordgrass *Spartina alterniflora*: evidence for dimethylseleniopropionate formation. Environ Sci Technol 33:2064

Arenas A, Marcó D, Torres G (2011) Evaluation of the plant *Lemna minor* for the bioremediation of water contaminated with mercury. Avances en ciencias e ingeniería 2:1–11

Arora A, Saxena S, Sharma DK (2006) Tolerance and phytoaccumulation of chromium by three *Azolla* species. World J Microbiol Biotechnol 22:97

Arvind P, Prasad MNV (2005) Cadmium-zinc interactions in a hydroponic system using *Ceratophyllum demersum*: adaptive ecophysiology, biochemistry and molecular toxicology. Braz J Plant Physiol 17:3–20

Aslam MM, Hassan S, Baig MA (2010) Removal of metals from the refinery wastewater through vertical flow constructed wetlands. Int J Agric Biol 12:796–798

Azeez NM, Sabbar AA (2012) Efficiency of duckweed (*Lemna minor*) in phytotreatment of wastewater pollutants from basrah oil refinery. J Appl Phytotechnol Environ Sanit 1:163–172

Bankstona JL, Solab DL, Komora AT, Dwyera DF (2002) Degradation of trichloroethylene in wetland microcosms containing broad-leaved cattail and eastern cottonwood. Water Res 36:1539–1546

Barber JT, Sharma HA, Ensley HE (1995) Detoxification of phenol by the aquatic angiosperm, *Lemna gibba*. Chemosphere 31:3567

Begum A, HariKrishna S (2010) Bioaccumulation of trace metals by aquatic plants. Int J Chem Technol Res 2:250–254

Benaroya RO, Tzin V, Tel-Or E, Zamski E (2004) Lead accumulation in the aquatic fern *Azolla filiculoides*. Plant Physiol Biochem 42:639

Bennicelli R, Stezpniewska Z, Banach A, Szajnocha K, Ostrowski J (2004) The ability of *Azolla caroliniana* to remove heavy metals (Hg(II), Cr(III), Cr(VI)) from municipal waste water. Chemosphere 55:141–146

Best EPH, Zappi ME, Fredrickson HL, Sprecher SL, Larson SL, Ochman M (1997) Screening of aquatic and wetland plant species for phytoremediation of explosives-contaminated groundwater from the Iowa army ammunition plant. Ann N Y Acad Sci 829:179

Best EP, Miller JL, Fredrickson HL, Larson SL, Zappi ME (1998) Explosives removal from groundwater of the Iowa army ammunition plant in continuous-flow laboratory systems planted with aquatic and wetland plants. Army Engineer Waterways Experiment station Vicksburg ms Environmental Lab, Vicksburg

Best EP, Sprecher SL, Larson SL, Fredrickson HL, Bader DF (1999a) Environmental behavior of explosives in groundwater from the Milan army ammunition plant in aquatic and wetland plant treatments. Removal, mass balances and fate in groundwater of TNT and RDX. Chemosphere 38(14):3383–3396

Best EPH, Sprecher SL, Larson SL, Fredrickson HL, Bader DF (1999b) Environmental behavior of explosives in groundwater from the Milan army ammunition plant in aquatic and wetland plant treatments. Uptake and fate of TNT and RDX in plants. Chemosphere 39:2057

Bhadra R, Spanggord RJ, Wayment DG, Hughes JB, Shanks JV (1999) Characterization of oxidation products of TNT metabolism in aquatic phytoremediation systems of *Myriophyllum aquaticum*. Environ Sci Technol 33:3354

Bhadra R, Wayment DG, Williams RK, Barman SN, Stone MB, Hughes JB, Shanks JV (2001) Studies on plant-mediated fate of the explosives RDX and HMX. Chemosphere 44:1259

Bolsunovskiˇ AI, Ermakov AI, Burger M, Degermendzhi AG, Sobolev AI (2002) Accumulation of industrial radionuclides by the Yenisei River aquatic plants in the area affected by the activity of the mining and chemical plant. Radiat Biol Radioecol 42:194

Bolsunovsky A, Zotina T, Bondareva L (2005) Accumulation and release of 241Am by a macrophyte of the Yenisei River (*Elodea canadensis*). J Environ Radioact 81:33

Borkar RP, Mahatme PS (2011) Wastewater treatment with vertical flow constructed wetland. Int J Environ Sci 2:590–603

Bunluesin S, Kruatrachue M, Pokethitiyook P, Upatham S, Lanza GR (2007) Batch and continuous packed column studies of cadmium biosorption by *Hydrilla verticillata* biomass. J Biosci Bioeng 103:509–513

Buta E, Paulette L, Mihaiescu T, Buta M, Cantor M (2011) The influence of heavy metals on growth and development of *Eichhornia crassipes* species, cultivated in contaminated water. Horti Agrobot 39(2):135–141

Calheiros CSC, Rangel AOSS, Castro PML (2007) Constructed wetland systems vegetated with different plants applied to the treatment of tannery wastewater. Water Res 41:1790–1798

Calheiros CSC, Rangel AOSS, Castro PML (2009) Treatment of industrial wastewater with two-stage constructed wetlands planted with *Typha latifolia* and *Phragmites australis*. Int J Environ Sci Technol 6(2):243–248

Carbonell AA, Aarabi MA, Delaune RD, Gambrell RP, Patrick WH Jr (1998) Arsenic in wetland vegetation: availability, phytotoxicity, uptake and effects on plant growth and nutrition. Sci Total Environ 217:189

Carvalho KM, Martin DF (2001) Removal of aqueous selenium by four aquatic plants. J Aquat Plant Manag 39:33–36

Castro-Carrillo LA, Delgadillo-Martínez J, Ferrera-Cerrato R, Alarcón A (2008) Phenanthrene dissipation by *Azolla caroliniana* utilizing bioaugmentation with hydrocarbonoclastic microorganisms. Interciencia 33:1–7

Chale FMM (2012) Nutrient removal in domestic wastewater using common reed (*Phragmites mauritianus*) in horizontal subsurface flow constructed wetlands. Tanzania J Nat Appl Sci 3:495–499, Online ISSN 1821–7249 2012

Cheng J, Landesman I, Bergmann A, Classen JJ, Howard JW, Yamamoto YT (2002) Nutrient removal from swine lagoon liquid by *Lemna minor* 8627. Trans Asae 45(4):1003–1010

Chris A, Masih J, Abraham G (2011) Growth, photosynthetic pigments and antioxidant responses of *Azolla filiculoides* to monocrotophos toxicity. J Chem Pharm Res 3(3):381–388

Clijsters H, Cuypers A, Vangronsveld J (1999) Physiological response to heavy metals in higher plants, defence against oxidative stress. Zeitschrift fur Naturforsch 54c:730–734

Cohen MF, Williams J, Yamasaki H (2002) Biodegradation of diesel fuel by an *Azolla* derived bacterial consortium. J Environ Sci Health Part A Toxic/Hazard Subst Environ Eng A37(9):1593–1606

Cortes-Esquive JA, Giácoman-Vallejos G, Barceló-Quintal ID, Méndez-Novelo R, Ponce-Caballero MC (2012) Heavy metals removal from swine wastewater using constructed wetlands with horizontal subsurface flow. J Environ Prot 3:871–877

Costa ML, Santos MC, Carrapiço F (1999) Biomass characterization of *Azolla filiculoides* grown in natural ecosystems and wastewater. Hydrobiologia 415: 323–327

Davies LC, Carias CC, Novais JM, Martins-Dias S (2005) Phytoremediation of textile effluents containing azo dye by using *Phragmites australis* in a vertical flow intermittent feeding constructed wetland. Ecol Eng 25:594–605

Day JA, Saunders FM (2004) Glycoside formation from chlorophenols in *Lemna minor*. Environ Toxicol Chem 25:613
DeBusk TA, Reddy KR (1987) Density requirements to maximise the productivity of water hyacinth (*Eichhornia crassipes* [Mart] Solms). In: Reddy KR, Smith WH (eds) Aquatic plants for water treatment and resource recovery. Magnolia Publishing Inc, Orlando, FL, pp 673–680, 1032 p
Del-Campo Marıń CM, Oron G (2007) Boron removal by the duckweed *Lemna gibba*: a potential method for the remediation of boron-polluted waters. Water Res 41:4579–4584
Delgado M, Bigeriego M, Guardiola E (1993) Uptake of Zn, Cr and Cd by water hyacinth. Water Res 27:269
Demirezen D, Aksoy A (2006) Common hydrophytes as bioindicators of iron and manganese pollution. Ecol Indicators 6:388–393
Deval CG, Mane AV, Joshi NP, Saratale GD (2012) Phytoremediation potential of aquatic macrophyte *Azolla caroliniana* with references to zinc plating effluent. Emir J Food Agric 24(3):208–223
Dhir B (2010) Use of aquatic plants in removing heavy metals from wastewater. Int J Environ Eng 2(1/2/3): 185–201
Dhir B, Srivastava S (2011) Heavy metal removal from a multi-metal solution and wastewater by *Salvinia natans*. Ecol Eng 37:893–896
Dhir B, Sharmila P, Saradhi PP (2008) Photosynthetic performance of *Salvinia natans* exposed to chromium and zinc rich wastewater. Braz J Plant Physiol 20:61–70
Dhir B, Sharmila P, Saradhi PP (2009) Potential of aquatic macrophytes for removing contaminants from the environment. Crit Rev Environ Sci Technol 39: 754–781
Dixit S, Dhote S (2010) Evaluation of uptake rate of heavy metals by *Eichhornia crassipes* and *Hydrilla verticillata*. Environ Monit Assess 169(1–4):367–374
Dixit S, Tiwari S (2007) Effective utilization of an aquatic weed in an eco-friendly treatment of polluted water bodies. J Appl Sci Environ Manage 11(3):41–44
Dixit S, Dhote S, Dubey R, Vaidya HM, Das RJ (2010) Sorption characteristics of heavy metal ions by aquatic weed. Desalination Water Treat 20:307–312
Dogan M, Saygideger SD, Colak U (2009) Effect of lead toxicity on aquatic macrophyte *Elodea canadensis* Michx. Bull Environ Contam Toxicol 83:249–254
Dordio AV, Carvalho PAJ, Estêvão CAJ, Pinto AP, Cristina C (2007) Removal of pharmaceuticals in constructed wetlands using Typha and LECA. A pilot study. http://dspace.uevora.pt/rdpc/bitstream/10174/1290/1/AnaDordio_Wetpol2007-2.pdf
Dordio AV, Duarte C, Barreiros M, Carvalho AJ, Pinto AP, da Costa CT (2009) Toxicity and removal efficiency of pharmaceutical metabolite clofibric acid by Typha spp.potential use for phytoremediation. Bioresour Technol 100(3):1156–1161
Dordio AV, Ferroa R, Teixeiraab D, Palaceac AJ, Pintoab AP, Diasac CMB (2011) Study on the use of Typha spp. for the phytotreatment of water contaminated with ibuprofen. Int J Environ Anal Chem 91:654–667
Dosnon-olette R, Couderchet M, Oturan MA, Oturan N, Eullaffroy P (2011) Potential use of *Lemna minor* for the phytoremediation of isoproturon and glyphosate. Int J Phytoremediation 13(6):601–612
El-Kheir WA, Ismail G, El-nour FA, Tawfik T, Hammad D (2007) Assessment of the efficiency of duckweed (*Lemna gibba*) in wastewater treatment. Int J Agric Biol 9:681–687
El-Shinawy RMK, Abdel-Malik WEY (1980) Retention of radionuclides by some aquatic fresh water plants. Hydrobiology 69:125
Ena A, Carlozzi P, Pushparaj B, Paperi R, Carnevale S, Sacchi A (2007) Ability of the aquatic fern *Azolla* to remove chemical oxygen demand and polyphenols from olive mill effluent. Grasas y Aceites 58(1), Enero-Marzo 34–39
Ensley HE, Barber JT, Polita MA, Oliver AI (1994) Toxicity and metabolism of 2, 4-dichlorophenol by aquatic angiosperm *Lemna gibba*. Environ Toxicol Chem 13:325
Espinoza-Quiñones FR, Módenes AN, Costa IL Jr, Palácio SM, Daniela NS, Trigueros EG, Kroumov AD, Silva EA (2009) Kinetics of lead bioaccumulation from a hydroponic medium by aquatic macrophytes *Pistia stratiotes*. Water Air Soil Pollut 203:29–37
Estrella-Gómeza NE, Sauri-Duchb E, Zapata-Pérezc O, Santamaría JM (2012) Glutathione plays a role in protecting leaves of *Salvinia minima* from Pb^{2+} damage associated with changes in the expression of SmGS genes and increased activity of GS. Environ Exp Bot 75:188–194
Fernandez RT, Whitwell T, Riley MB, Bernard CR (1999) Evaluating semiaquatic herbaceous perennials for use in herbicide phytoremediation. J Am Soc Horticult Sci 124:539
Feuillebois R, Gum J, Woodring K, Carvalho-Knighton KM (2006) TNT remediation with *Lemna minor*. Georgia World Congress Center. The 231st ACS national meeting, Atlanta, GA, 26–30 Mar 2006
Forni C, Patrizi C, Migliore L (2006) Floating aquatic macrophytes as a decontamination tool for antimicrobial drugs. In: Twardowska I et al (eds) Soil and water pollution monitoring, protection and remediation. Springer, pp 3–23
Fornia C, Cascone A, Fioric M, Migliorea L (2002) Sulphadimethoxine and *Azolla filiculoides* Lam.: a model for drug remediation. Water Res 36: 3398–3403
Foroughi M (2011a) Investigation of the influence of *Ceratophyllum demersum* to refine diluted compost latex. J Appl Sci Environ Manage 15(2):371–374
Foroughi M (2011b) Role of *Ceratophyllum demersum* in recycling macro elements from wastewater. J Appl Sci Environ Manage 15(2):401–405
Foroughi M, Najafi P, Toghiani S (2010) Trace elements removal from waster water by *Ceratophyllum demersum*. J Appl Sci Environ Manage 15:197–201

Fritioff A, Greger M (2006) Uptake and distribution of Zn, Cu, Cd, and Pb in an aquatic plant *Potamogeton natans*. Chemosphere 63:220–227

Fritioff A, Kautsky L, Greger M (2005) Influence of temperature and salinity on heavy metal. Environ Pollut 133:265–274

Gallardo-Williams MT, Whalen VA, Benson RF, Martin DF (2002) Accumulation and retention of lead by cattail (*Typha domingensis*), hydrilla (*Hydrilla verticillata*), and duckweed (*Lemna obscura*). J Environ Sci Health A Toxic Hazard Subst Environ Eng 37(8):1399–1408

Gao J, Garrison AW, Mazur CS, Wolfe NL, Hoehamer CF (2000a) Uptake and phytotransformation of o, p′-DDT and p, p′-DDT by axenically cultivated aquatic plants. J Agric Food Chem 48(12):6121–6127

Gao J, Garrison AW, Hoehamen C, Mazur CS, Wolfe NL (2000b) Uptake and phytotransformation of organophosphorous pesticide by axenically cultivated aquatic plants. J Agric Food Chem 48:6114

Gardner JL, Al-Hamdani SH (1997) Interactive effects of aluminum and humic substances on *Salvinia*. J Aquat Plant Manage 35:30–34

Garrison AW, Nzengung VA, Avants JK, Ellington JJ, Jones WJ, Rennels D, Wolfe NL (2000) Phytodegradation of p, p′-DDT and the enantiomers of o, p′-DDT. Environ Sci Technol 34:1663

Ghabbour EA, Davies G, Lam YY, Vozzella ME (2004) Metal binding by humic acids isolated from water hyacinth plants (*Eichhornia crassipes*) [Mart.] (SolmLaubach: Pontedericeae) in the Nile Delta, Egypt. J Environ Pollut 131:445–451

Gobas EAPC, McNeil EJ, Lovett-Doust L, Haffner GD (1991) Bioconcentration of chlorinated aromatic hydrocarbons in aquatic macrophytes. Environ Sci Technol 25:924

Gonzalez-Mendoza D, Ramoza-Perez F, Gremaldo-Juarez O, Escoboza-Garcia F, Soto-Ortiz R (2011) Physiological responses of *Azolla caroliniana* exposure to cadmium. World J Agric Sci 7(3):347–350

Gopinath, Karthikeyan, Sivakumar, Magesh, Mohana-Sundaram, Poongodi, Ramesh, Rajamohan (2012) Studies on removal of malachite green from aqueous solution by sorption method sing water hyacinth – *Eichornia crassipes* roots. J Biodivers Environ Sci 2:1–8

Gray JL, Sedlak DL (2005) The fate of estrogenic hormones in an engineered treatment wetland with dense macrophytes. Water Environ Res 77:24

Gross A, Kaplan D, Baker K (2007) Removal of chemical and microbiological contaminants from domestic greywater using a recycled vertical flow bioreactor (RVFB). Ecol Eng 3(1):107–114

Gupta M, Chandra P (1994) Lead contamination in *Vallisnaria spiralis* and *Hydrilla verticillata* (L.f.). Royle J Environ Sci Health A29:503–516

Gupta M, Chandra P (1996) Bioaccumulation and physiological changes in *Hydrilla verticillata* (l.f.) Royle in response to mercury bull. Environ Contam Toxicol 56:319–326

Gupta M, Rai UN, Tripathi RD, Chandra P (1995) Lead induced changes in glutathione and phytochelatin in *Hydrilla verticillate*. Chemosphere 30:2011–2020

Hadad HR, Mufarrege MM, Pinciroli M, Di Luca GA, Maine MA (2010) Morphological response of *Typha domingensis* to an industrial effluent containing heavy metals in a constructed wetland. Arch Environ Contam Toxicol 58(3):666–675

Haeba M, Bláha L (2011) Comparison of different endpoints responses in aquatic plant *Lemna minor* exposed to ketoconazole. Egypt J Nat Toxins 8(1, 2):49–57

Hafez N, Abdalla S, Ramadan YS (1998) Accumulation of phenol by *Potamogeton crispus* from aqueous industrial waste. Bull Environ Contam Toxicol 60:944

Hansen AT, Stark RA, Hondzo M (2011) Uptake of dissolved nickel by *Elodea canadensis* and epiphytes influenced by fluid flow conditions. Hydrobiologia 658:127–138

Hanson ML, Sibley PK, Ellis DA, Fineberg NA, Mabury SA, Solomon KR, Muir DC (2002) Trichloroacetic acid fate and toxicity to the macrophytes *Myriophyllum spicatum* and *Myriophyllum sibiricum* under field conditions. Aquat Toxicol 56:241–255

Hattink J, Wolterbeek HT (2001) Accumulation of ^{99}Tc in duckweed *Lemna minor* L. as a function of growth rate and ^{99}Tc concentration. J Environ Radioact 57:117–138

Hattink J, De Goeij JJM, Wolterbeek HT (2000) Uptake kinetics of ^{99}Tc in common duckweed. Environ Exp Bot 44:9–13

Hegazy AK, Abdel-Ghani NT, El-Chaghaby GA (2011) Phytoremediation of industrial wastewater potentiality by *Typha domingensis*. Int J Environ Sci Technol 8:639–648

Hench KR, Bissonnette GK, Sexstone AJ, Coleman JG, Garbutt K, Skousen JG (2003) Fate of physical, chemical, and microbial contaminants in domestic wastewater following treatment by small constructed wetlands. Water Res 37:921–927

Hoffman T, Kutter C, Santamaria JM (2004) Capacity of *Salvinia minima* Baker to tolerate and accumulate As and Pb. Eng Life Sci 4:61–65

Holtra A, Traczewska TM, Sitarska M, Zamorska-Wojdyla M (2010) Assessment of the phytoremediation efficacy of boron-contaminated waters by *Salvinia natans*. Environ Prot Eng 36:87–94

Hopple JA, Foster GD (1996) Hydrophobic organochlorine compounds sequestered in submersed aquatic macrophytes (*Hydrilla verticillata* (L.F.) Royle) from the tidal Potomac River (USA). Environ Pollut 94:39–46

Hu C, Zhang L, Hamilton D, Zhou W, Yang T, Zhu D (2007) Physiological responses induced by copper bioaccumulation in *Eichhornia crassipes* (Mart.). Hydrobiologia 579:211–218

Hua J, Zhang C, Yin Y, Chen R, Wang X (2011) Phytoremediation potential of three aquatic macrophytes in manganese- contaminated water. Water Environ J 26:335–342

Hughes JB, Shanks JE, Vanderford MY, Lauritzen J, Bhadra R (1997) Transformation of TNT by aquatic plants and plant tissue cultures. Environ Sci Technol 31:266–271

Hussain ST, Mahmood T, Malik SA (2010) Phytoremediation technologies for Ni^{++} by water hyacinth. Afr J Biotechnol 9(50):8648–8660

Jafari N (2010) Ecological and socio-economic utilization of water hyacinth (*Eichhornia crassipes* Mart Solms). J Appl Sci Environ Manage 14(2):43–49

Kadirvelu K, Karthika C, Vennilamani N, Pattabhi S (2005) Activated carbon from industrial solid waste as an adsorbent for the removal of Rhodamine-B from aqueous solution: kinetic and equilibrium studies. Chemosphere 60:1009–1017

Kalipci E (2011) Investigation of decontamination effect of *Phragmites australis* for Konya domestic wastewater treatment. J Med Plants Res 5(29): 6571–6577

Kamarudzaman AN, Ismail NS, Aziz RA, Ab Jalil MF (2011) Removal of nutrients from landfill leachate using subsurface flow constructed wetland planted with *Limnocharis flava* and *Scirpus atrovirens*. In: International conference on environmental and computer science, IPCBEE, vol 19, IACSIT Press, Singapore

Kanabkaew T, Puetpaiboon U (2004) Aquatic plants for domestic wastewater treatment: Lotus (*Nelumbo nucifera*) and Hydrilla (*Hydrilla verticillata*) systems. Songklanakarin J Sci Technol 26(5):749–756

Kara Y (2010) Bioaccumulation of nickel by aquatic macrophytes. Desalination Water Treat 19:325–328

Kara Y, Kara I (2005) Removal of cadmium from water using duckweed (*Lemna trisulca*). Int J Agric Biol 7:660–662

Khellaf N, Zerdaoui M (2010a) Growth response of the duckweed *Lemna gibba* to copper and nickel phytoaccumulation. Ecotoxicology 19:1363–1368

Khellaf N, Zerdaoui M (2010b) Growth, photosynthesis and respiratory response to copper in *Lemna minor*: a potential use of duckweed in biomonitoring. Iran J Environ Health Sci Eng 7:299–306

King JK, Harmon SM, Fu TT, Gladden JB (2002) Mercury removal, methylmercury formation, and sulfate-reducing bacteria profiles in wetland mesocosms. Chemosphere 46:859–870

Knuteson SL, Whitwell T, Klaine SJ (2002) Influence of plant age and size on simazine uptake and toxicity. J Environ Qual 31:2090

Kondo K, Kawabata H, Ueda S, Hasegawa H, Inaba J, Mitamura O, Seike Y, Ohmomo Y (2003) Distribution of aquatic plants and absorption of radionuclides by plants through the leaf surface in brackish Lake Obuchi, Japan, bordered by nuclear fuel cycle facilities. J Radioanalytical Nuclear Chem 257:305

Kristanti RA, Kanbe M, Toyama T, Tanaka Y, Tang Y, Wu X, Mori K (2012) Accelerated biodegradation of nitrophenols in the rhizosphere of *Spirodela polyrrhiza*. J Environ Sci (China) 24(5):800–807

Kumar GP, Prasad MNV (2004) Cadmium adsorption and accumulation by *Ceratophyllum demersum* L.: A fresh water macrophyte. Eur J Miner Process Environ Protect 4:95–101

Kumar PS, Kumar SS, Anuradha K, Sudha B, Ansari S (2012) Phytoremediation as an alternative for treatment of paper industry effluents by using water hyacinth (*Eichhornia crassipes*) – a polishing treatment. Int J Res Chem Environ 2:95–99

Kutty SRM, Ngatenah SNIB, Isa MH, Malakahmad A (2009) Nutrients removal from municipal wastewater treatment plant effluent using *Eichhornia Crassipes*. World Acad Sci Eng Technol 36:828–833

Lacher C, Smith RW (2002) Sorption kinetics of Hg(II) onto *Potamogeton natans* biomass. Eur J MinerProcess Environ Protect 2:220–231

Larson R, Sims G, Marley K, Montez-Ellis M, Paul T, Michelle C (2002) Nitrate management using terrestrial and aquatic plant species. http://igc.siu.edu/proceedings/02/larson.pdf

Leblebici Z, Aksoy A (2011) Growth and lead accumulation capacity of *Lemna minor* and *Spirodela polyrhiza* (lemnaceae): interactions with nutrient enrichment. Water Air Soil Pollut 214:175–184

Lee KE, Huggins DG, Thurman EM (1995) Effects of hydrophyte community structure on Atrazine and Alachlor degradation in wetlands. systematics and ecology. In: Campbell KL (ed) Versatility of wetlands in the agricultural landscape. American Society of Agricultural Engineers, Tampa, pp 525–538

Lesage E, Mundia C, Rousseau DPL, Van de Moortel AMK, Laing GD, Tack FMG, De Pauw N, Verloo MG (2008) Removal of heavy metals from industrial effluents by the submerged aquatic plant *Myriophyllum spicatum* L. In: Vyamazal J (ed) Wastewater Treatment, Plant Dynamics and Management in Constructed and Natural Wetlands. Springer, pp 211–221

Lohi A, Cuenca MA, Anania G, Upreti SR, Wan L (2008) Biodegradation of diesel fuel-contaminated wastewater using a three-phase fluidized bed reactor. J Hazard Mater 154:105–111

Lovett-Doust J, Lovett-Doust L, Biernacki M, Mal TK, Lazar R (1997) Organic contaminants in submersed macrophytes drifting in the Detroit River. Can J Fish Aquat Sci 54(10):2417–2427

Low KS, Lee CK, Tai CH (1994) Biosorption of copper by water hyacinth roots. J Environ Sci Health A29(1):171

Lu X, Kruatrachue M, Pokethitiyook P, Homyok K (2004) Removal of cadmium and zinc by water hyacinth, *Eichhornia crassipes*. Sci Asia 30:93–103

Lu X, Nguyen N, Gabos S, Le XC (2009) Arsenic speciation in cattail (*Typha latifolia*) using chromatography and mass spectrometry. Mol Nutr Food Res 53(5): 566–571

Lu Q, He ZL, Graetz DA, Stoffella PJ, Yang X (2010) Phytoremediation to remove nutrients and improve eutrophic stormwaters using water lettuce (*Pistia stratiotes* L.). Environ Sci Pollut Res 17:84–96

Lu Q, Zhenli LH, Graetz DA, Stoffella PJ, Yang X (2011) Uptake and distribution of metals by water lettuce (*Pistia stra tiotes* L.). Environ Sci Pollut Res 18:978–986

Machate T, Noll H, Behrens H, Kettrup A (1997) Degradation of phenanthracene and hydraulic characteristics in constructed wetland. Water Res 31:554

Mahamadi C (2011) Water hyacinth as a biosorbent: a review. Afr J Environ Sci Technol 5(13):1137–1145

Mahmood T, Malik SA, Hussain ST (2010) Biosorption and recovery of heavy metals from aqueous solutions by *Eichhornia crassipes* (water hyacinth) ash. Bioresource 5(2):1244–1256

Maine MA, Duarte MV, Sun˜ e' NL (2001) Cadmium uptake by floating macrophytes. Water Res 35: 2629–2634

Maine AM, Sune NL, Lagger SC (2004) Bioaccumulation: comparison of the capacity of two aquatic macrophytes. Water Res 38:1494

Mane PC, Bhosle AB, Kulkarni PA (2011) Biosorption and biochemical study on water hyacinth (*Eichhornia crassipes*) with reference to selenium. Arch Appl Sci Res 3(1):222–229

Manios T, Stentiford EI, Millner P (2003) Removal of heavy metals from a metaliferous water solution by *Typha latifolia* plants and sewage sludge compost. Chemosphere 53:487–494

Matamoros V, Nguyen LX, Arias CA, Salvadó V, Brix H (2012) Evaluation of aquatic plants for removing polar microcontaminants: a microcosm experiment. Chemosphere 88(10):1257–1264

Miretzky P, Saralegui A, Cirelli AF (2004) Aquatic macrophytes potential for simultaneous removal of heavy metals (Buenos Aires, Argentine). Chemosphere 57:997

Miretzky P, Saralegui A, Cirelli AF (2006) Simultaneous heavy metal removal mechanism by dead macrophytes. Chemosphere 62:247–254

Mkandawire M, Dudel G (2005) Accumulation of arsenic in *Lemna gibba* (duckweed) in tailing waters of two abandoned uranium mining sites in Saxony, Germany. Sci Total Environ 336:81–89

Mkandawire M, Dudel EG (2007) Are *Lemna* spp. Effective phytoremediation agents ? Bioremediation Biodivers Bioavailab 1:56–71

Mkandawire M, Lyubun YV, Kosterin PV, Dudel EG (2004a) Toxicity of arsenic species to *Lemna gibba* L. and the influence of phosphate on arsenic bioavailability. Environ Toxicol 19:26–35

Mkandawire M, Taubert B, Dudel EG (2004b) Capacity of *Lemna gibba* L. (duckweed) for uranium and arsenic phytoremediation in mine tailing waters. Int J Phytoremediation 6(4):347–362

Mojiri A (2012) Phytoremediation of heavy metals from municipal wastewater by *Typha domingensis*. Afr J Microbiol Res 6(3):643–647

Mokhtar H, Morad N, Fizri FFA (2011) Hyperaccumulation of copper by two species of aquatic plants. In: International conference on environment science and engineering IPCBEE 8. IACSIT Press, Singapore, pp 115–118

Molisani MM, Rocha R, Machado W, Barreto RC, Lacerda ID (2006) Mercury contents in aquatic macrophytes from two Reservoirs in the para'ıba do sul: Guandu river system, Se, Brazil. Braz J Biol 66:101

Murithi G, Onindo CO, Muthakia GK (2012) Kinetic and equilibrium study for the sorption of Pb(II) ions from aqueous phase by water hyacinth (*Eichhornia crassipes*). Bull Chem Soc Ethiopia 26(2):181–193

Muthunarayanan V, Santhiya M, Swabna V, Geetha A (2011) Phytodegradation of textile dyes by water hyacinth (*Eichhornia crassipes*) from aqueous dye solutions. Int J Environ Sci 7:1709–1724

Narain S, Ojha CSP, Mishra SK, Chaube UC, Sharma PK (2011) Cadmium and chromium removal by aquatic plant. Int J Environ Sci 1:1297–1304

Nesterenko-Malkovskaya A, Kirzhner F, Zimmels Y, Armon R (2012) Eichhornia crassipes capability to remove naphthalene from wastewater in the absence of bacteria. Chemosphere 87(10):1186–1191

Nguyen TTT, Davy F B, Rimmer M, De Silva S (2009) Use and exchange of genetic resources of emerging species for aquaculture and other purposes. FAO/NACA expert meeting on the use and exchange of aquatic genetic resources relevant for food and agriculture, 31 March–02 April 2009, Chonburi, Thailand

Nichols PB, Couch JD, Al-Hamdani SH (2000) Selected physiological responses of *Salvinia minima* to different chromium concentrations. Aquat Bot 1439:1–8

Nilratnisakorn S, Thiravetyan P, Nakbanpote W (2009) A constructed wetland model for synthetic reactive dye wastewater treatment by narrow-leaved cattails (*Typha angustifolia* Linn.). Water Sci Technol 60(6):1565–1574, AUTHOR(S)

Nzengung VA, Lee NW, Rennels DE, McCutcheon SC, Wang C (1999) Use of aquatic plants and algae for decontamination of waters polluted with chlorinated alkanes. Int J Phytoremediation 1:203

Obek E, Sasmaz A (2011) Bioaccumulation of aluminum by *Lemna gibba* from secondary treated municipal wastewater effluents. Bull Environ Contam Toxicol 86(2):217–220

Odjegba VJ, Fasidi IO (2006) Effects of heavy metals on some proximate composition of *Eichhornia crassipes*. J Appl Sci Environ Manage 10(1):83–87

Olette R, Couderchet M, Biagianti S, Eullaffroy P (2008) Toxicity and removal of pesticides by selected aquatic plants. Chemosphere 70(8):1414–1421

Ong S, Ho L, Wong Y, Danny LD, Samad H (2011) Semi-batch operated constructed wetlands planted with *Phragmites australis* for treatment of dyeing wastewater. J Eng Sci Technol 6:619–627

Ortega-Clementea LA, Luna-Pabellob VM (2012) Dynamic performance of a constructed wetland to treat lindane-contaminated water. Int Res J Eng Sci Technol Innov 1(2):57–65

Osmolovskaya N, Kurilenko V (2005) Macrophytes in phytoremediation of heavy metal contaminated water and sediments in urban inland ponds. Geophys Res Abstr 7:10510

Panich-pat T, Srinives P, Kruatrachue M, Pokethitiyook P, Upathamd S, Lanzae GR (2005) Electron microscopic studies on localization of lead in organs of *Typha angustifolia* grown on contaminated soil. ScienceAsia 31:49–53

Paola IM, Paciolla C, D'aquino L, Morgana M, Tommasi F (2007) Effect of rare earth elements on growth and antioxidant metabolism in *Lemna minor*. Caryologia 60:125–128

Parra LM, Torres G, Arenas AD, Sánchez E, Rodríguez K (2012) Phytoremediation of low levels of heavy metals using duckweed (*Lemna minor*). In: Ahmad P, Prasad MNV (eds) Abiotic stress responses in plants: metabolism, productivity and sustainability. Springer, pp 451–463

Pavlostathis SG, Comstock KK, Jacobson ME, Saunders FM (1998) Transformation of 2,4,6-trinitrotoluene by the aquatic plant *Myriophyllum aquaticum*. Environ Toxicol Chem 17:2266

Peng K, Luo C, Lou L, Li X, Shen Z (2008) Bioaccumulation of heavy metals by the aquatic plants *Potamogeton pectinatus* L. and *Potamogeton malaianus* Miq. and their potential use for contamination indicators and in wastewater treatment. Sci Total Environ 392(1):22–29

Phetsombat S, Kruatrachue M, Pokethitiyook P, Upatham S (2006) Toxicity and bioaccumulation of cadmium and lead in *Salvinia cucullata*. J Environ Biol 27: 671–678

Polomski RF, Taylor MD, Bielenberg DG, Bridges WC, Klaine SJ, Whitwell T (2009) Nitrogen and phosphorus remediation by three floating aquatic macrophytes in greenhouse-based laboratory-scale subsurface constructed wetlands. Water Air Soil Pollut 197:223–232

Popa K, Cecal A, Humelnicu D, Caraus I, Draghici CL (2004) Removal of $^{60}Co^{2+}$ and $^{137}Cs^{+}$ ions from low radioactive solutions using *Azolla caroliniana* willd. water fern. Cent Eur J Chem 2:434

Popa K, Palamaru MN, Iordan AR, Humelnicu D, Drochioiu G, Cecal A (2006) Laboratory analyses of 60Co2+, 65Zn2+ and (55+59)Fe3+ radioactions uptake by *Lemna minor*. Isot Environ Health Stud 42:87

Prajapati SK, Meravi N, Singh S (2012) Phytoremediation of chromium and cobalt using *Pistia stratiotes*: a sustainable approach. Proc Int Acad Ecol Environ Sci 2(2):136–139

Prasad MNV, Malec P, Waloszek K, Bojko M, Strzalka K (2001) Physiological responses of *Lemna trisulca* to cadmium and copper bioaccumulation. Plant Sci 161:881–889

Prasertsup P, Ariyakanon N (2011) Removal of chlorpyrifos by water lettuce (*Pistia stratiotes* L.) and duckweed (*Lemna minor* L.). Int J Phytoremediation 13(4):383–395

Pratas J, Rodrigues N, Alves F, Patricio J (2010) Uranium removal in artificial wetlands. In: Advances in waste management. ISBN: 978-960-474-190-8 pp 112–117

Purwanti IF, Mukhlisin M, Abdullah SRS, Basri H, Idris M, Hamzah A, Latif MT (2012) Range finding test of hydrocarbon on *Scirpus mucronatus* as preliminary test for phytotoxicity of contaminated soil. Revelation Sci 2:61–65

Qian JH, Zayed A, Zhu ML, Yu M, Terry N (1999) Phytoaccumulation of trace elements by wetland plants, III: uptake and accumulation of ten trace elements by twelve plant species. J Environ Qual 28:1448

Rahman MA, Hasegawa H (2011) Aquatic arsenic: phytoremediation using floating macrophytes. Chemosphere 83:633–646

Rahman MA, Hasegawa KH, Ueda K, Maki T, Okumura C, Rahman MM (2007) Arsenic accumulation in duckweed (*Spirodela polyrhiza* L.): a good option for phytoremediation. Chemosphere 69:493–499

Rahman MA, Hasegawa H, Ueda K, Makia T, Rahman MM (2008) Arsenic uptake by aquatic macrophyte *Spirodela polyrhiza* L: interactions with phosphate and iron. J Hazard Mater 160:356–361

Rai PK, Tripathi BD (2009) Comparative assessment of *Azolla pinnata* and *Vallisneria spiralis* in Hg removal from G.B. Pant Sagar of Singrauli industrial region, India. Environ Monit Assess 148:75–84

Rai UN, Tripathi RD, Sinha S, Chandra P (1995) Chromium and cadmium bioaccumulation and toxicity in Hydrilla verticillata (L.f.) Royle and *Chara corallina* Wildenow. J Environ Sci Health A 30:537–551

Rai UN, Tripathi RD, Vajpayee P, Pandey N, Ali MB, Gupta DK (2003) Cadmium accumulation and its phytotoxicity in *Potamogeton pectinatus* (Potamogetonaceae). Bull Environ Contam Toxicol 70:566

Rakhshaee R, Khosravi M, Ganji MT (2006) Kinetic modeling and thermodynamic study to remove Pb(II), Cd(II), Ni(II) and Zn(II) from aqueous solution using dead and living *Azolla filiculoides*. J Hazard Mater 134:120–129

Ramamoorthy D, Kalaivani S (2011) Studies on the effect of *Typha angustata* (Reed) on the removal of sewage water pollutants. J Phytol 3(6):13–15

Ramprasad C (2012) Experimental study on waste water treatment using lab scale reed bed system using *Phragmitis australis*. Int J Environ Sci 3:297–304

Rawat SK, Rana RKS, Singh P (2012) Remediation of nitrite contamination in ground and surface waters using aquatic macrophytes. J Environ Biol 33:51–56

Rice PJ, Anderson TA, Coats JR (1997) Phytoremediation of herbicide-contaminated surface water with aquatic plants. In: Kruger EL, Anderson TA, Coats JR (eds) Phytoremediation of soil and water contaminants. American Chemical Society, Washington, DC

Rivera R, Medina VF, Larson SL, McCutcheon SC (1998) Phytotreatment of TNT-contaminated groundwater. J Soil Contam 7:511

Roy S, Hanninen O (1994) Pentachlorophenol: uptake/elimination, kinetics and metabolism in an aquatic plant, *Eicchornia crassipes*. Environ Toxicol Chem 13:763

Samardakiewicz S, Krzesłowska M, Bilski H, Bartosiewicz R, Woźny A (2012) Is callose a barrier for lead ions entering *Lemna minor* L. root cells? Protoplasma 249(2):347–351

Samdani S, Attar SJ, Kadam C, Baral SS (2008) Treatment of Cr (VI) contaminated wastewater using biosorbent, *Hydrilla verticillata*. Int J Eng Res Ind Appl 1:271–282, ISSN 0974–1518

Sánchez D, Graça MAS, Canhoto J (2007) Testing the use of the water Milfoil (*Myriophyllum spicatum* L.) in laboratory toxicity assays. Bull Environ Contam Toxicol 78:421–426

Sánchez-viveros G, González-mendoza D, Alarcón A, Ferrera-cerrato R (2010) Copper effects on photosynthetic

activity and membrane leakage of *Azolla filiculoides* and *A. Caroliniana*. Int J Agric Biol 12:365–366
Sasmaza A, Obek E (2012) The accumulation of silver and gold in *Lemna gibba* exposed to secondary effluents. Chem Erde-Geochem 72:149–152
Saulais M, Bedell JP, Delolme C (2011) Cd, Cu and Zn mobility in contaminated sediments from an infiltration basin colonized by wild plants: The case of *Phalaris arundinacea* and *Typha latifolia*. Water Sci Technol 64:255–262
Saygideger S, Dogan M, Keser G (2004) Effect of lead and pH on lead uptake, chlorophyll and nitrogen content of *Typha latifolia* L. and *Ceratophyllum demersum* L. Int J Agric Biol 6:168–172
Schneider IAH, Smith RW, Rubio J (1999) Effect of some mining chemicals on biosorption of Cu(II) by the non living biomass of the fresh water macrophyte *Potamogeton lucens*. Miner Eng 12:255–260
Shah RA, Kumawat DM, Singh N, Wani KA (2010) Water hyacinth (*eichhornia crassipes*) as a remediation tool for dye-effluent pollution. Int J Sci Nat 1(2):172–178
Shaikh PR, Bhosle A (2011) Bioaccumulation of chromium by aquatic macrophytes *Hydrilla* sp. & *Chara* sp. Adv Appl Sci Res 2(1):214–220
Sharain-Liew YL, Joseph CG, How S (2011) Biosorption of lead contaminated wastewater using cattails (*Typha angustifolia*) leaves: kinetic studies. J Serb Chem Soc 76(7):1037–1047
Sharif F, Westerhoff P, Herckes P (2013) Sorption of trace organics and engineered nanomaterials onto wetland plant material. Environ Sci Process Impacts. doi:10.1039/C2EM30613A Advance article
Sharma HA, Barber JT, Ensley HE, Polito MA (1997) Chlorinated phenols and phenols by *Lemna gibba*. Environ Toxicol Chem 16:346
Shokod'Ko TI, Drobot PI, Kuzmenko MI, Shklyar AY (1992) Peculiarities of radionuclides accumulation by higher aquatic plants. Hydrobiol J 28:92
Shuib N, Baskaran K, Davies WR, Muthukumaran S (2011) Effluent quality performance of horizontal subsurface flow constructed wetlands using natural zeolite (escott). In: International conference on environment science and engineering IPCBEE, vol 8. IACSIT Press, Singapore
Singh NK, Pandey GC, Rai UN, Tripathi RD, Singh HB, Gupta DK (2005) Metal accumulation and ecophysiological effects of distillery effluent on *Potamogeton pectinatus* L. Bull Environ Contam Toxicol 74:857
Singh A, Kumar CS, Agarwal A (2012a) Physiological study of combined heavy metal stress on *Hydrilla verticillata* (l.f.) Royle. Int J Environ Sci 2:2234–2242
Singh D, Gupta R, Tiwari A (2012b) Potential of duckweed (*Lemna minor*) for removal of lead from wastewaters by phytoremediation. J Pharm Res 5(3):1578–1582
Sinha S (2002) Oxidative stress induced by HCH in *Hydrilla verticillata* Royle: modulation in uptake and toxicity due to Fe. Chemosphere 46:281–288
Sivaci EK, Sivaci A, Sokman M (2004) Biosorption of cadmium by *Myriophyllum spicatum* and *Myriophyllum triphyllum* orchard. Chemosphere 56:1043
Sivaci A, Elmas E, Gumus F (2008a) Changes in abscisic acid contents of some aquatic plants exposed to cadmium and salinity. Int J Bot 4:104–108
Sivaci A, Fatih E, Gümüş E, Sivaci R (2008b) Removal of Cadmium by *Myriophyllum heterophy Emire llum* Michx. and *Potamogeton crispus* L. and its effect on pigments and total phenolic compounds. Arch Environ Contam Toxicol 54:612–618
Smadar E, Benny C, Tel-Or E, Lorena V, Antonio C, Aharon G (2011) Removal of silver and lead Ions from water wastes using *Azolla filiculoides*, an aquatic plant, which adsorbs and reduces the ions into the corresponding metallic nanoparticles under microwave radiation in 5 min. Water Air Soil Pollut 218:365–370
So LM, Chu LM, Wong PK (2003) Microbial enhancement of Cu^{2+} removal capacity of *Eichhornia crassipes* (Mart.). Chemosphere 52:1499–1503
Sood A, Uniyal PL, Prasanna R, Ahluwalia AS (2004) Biosorption of Pb, Cd, Cu and Zn from the wastewater by treated *Azolla filiculoides* with $H_2O_2/MgCl_2$. Int J Environ Sci Technol 1:265–271
Srivastava S, Mishra S, Tripathi RD, Dwivedi S, Gupta DK (2006) Copper-induced oxidative stress and responses of antioxidants and phytochelatins in *Hydrilla verticillata* (L.f.) Royle. Aquat Toxicol 80:405–415
Srivastava S, Mishra R, Tripathi D, Dwivedi S, Trivedi PK, Tandon PK (2007) Phytochelatins and antioxidant systems respond differentially during arsenite and arsenate stress in *Hydrilla verticillata* (L.f.). Royle Environ Sci Technol 41(8):2930–2936
Srivastava S, Mishra S, Dwivedi S, Tripathi R (2010) Role of thiol metabolism in arsenic detoxification in *Hydrilla verticillata* (L.f.) Royle. Water Air Soil Pollut 212:155–165
Srivastava S, Srivastava M, Suprasanna S, D'Souza F (2011) Phytofiltration of arsenic from simulated contaminated water using *Hydrilla verticillata* in field conditions. Ecol Eng 37:1937–1941
Sun Q, Liu WB, Wang C (2011) Different response of phytochelatins in two aquatic macrophytes exposed to cadmium at environmentally relevant concentrations. Afr J Biotechnol 10(33):6292–6299
Susanne A, Hendrik S (2008) *Elodea nuttallii*: uptake, translocation and release of phosphorus. Aquat Biol 3:209–216
Taghi ganji M, Khosravi M, Rakhshaee R (2005) Biosorption of Pb, Cd, Cu and Zn from the wastewater by treated *Azolla filiculoides* with $H_2O_2/MgCl_2$. Int J Environ Sci Technol 1:265–271
Taghi ganji M, Khosravi M, Rakhshaee R (2012) Phytoremediation potential of aquatic macrophyte, Azolla. Ambio 41:122–137
Tilaki RAD (2010) Effect of glucose and lactose on uptake of phenol by *Lemna minor*. Iran J Environ Health Sci Eng 7:123–128
Todorovics C, Garay TM, Boltán BZ (2005) The use of the reed (*Phragmites australis*) in wastewater treatment on constructed wetlands. Acta Biologica Szegediensis 49(1–2):81–83

Toetz DW (1971) Diurnal uptake of nitrogen trioxide [*sic*] and ammonium by a *Ceratophyllum*-periphyton community. Limnol Oceanogr 16:819–822

Tripathi RD, Rai UN, Gupta M, Chandra P (1996) Induction of phytochelatins in *Hydrilla verticillata* (l.f.) Royle under cadmium stress. Bull Environ Contam Toxicol 56:505–551

Tripathi RD, Rai UN, Vajpayee MB, Ali MB, Khan E, Gupta DK, Mishra S, Shukla MK, Singh SN (2003) Biochemical responses of *Potamogeton pectinatus* L. exposed to higher concentration of zinc. Bull Environ Contam Toxicol 71:255

Tront AM, Saunders FM (2006) Role of plant activity and contaminant speciation in aquatic plant assimilation of 2,4,5-trichlorophenol. Chemosphere 64(3): 400–407

Tront JM, Day JA, Saunders MF (2001) Trichlorophenol removal with *Lemna minor*. In: Proceedings of the water environment federation, vol 40. WEFTEC, San Diego, p 929

Tront JM, Reinhold DM, Bragg AW, Saunders FM (2007) Uptake of halogenated phenols by aquatic plants. J Environ Eng 133:955

Tukaj S, Bisewska J, Roeske K, Tukaj Z (2011) Time and dose dependent induction of HSP70 in *Lemna minor* exposed to different environmental stressors. Bull Environ Contam Toxicol 87(3):226–230

Upadhyay R, Panda SK (2010) Influence of chromium salts on increased lipid peroxidation and differential pattern in antioxidant metabolism in *Pistia stratiotes* L. Braz Arch Biol Technol 53:1137–1144

Uysal Y, Taner F (2011) The evaluation of the Pb(II) removal efficiency of duckweed *Lemna minor* from aquatic mediums at different conditions. In: Gökçekus H, Türker U, LaMoreaux JW (eds) Survival and sustainability environmental earth sciences. Springer, Berlin/Heidelberg, pp 1107–1116

Venkatrayulu C, Rani VK, Reddy DC, Ramamurthi R (2009) Bio-adsorption of copper (II) by aquatic weed plants *Hydrilla* and *Pistia*. Asian J Animal Sci 4:82–85

Vestena S, Cambraia J, Oliva MA, Oliveira JA (2007) Cadmium accumulation by water hyacinth and *Salvinia* under different sulfur concentrations. J Braz Soc Ecotoxicol 2:269–274

Vitória AP, Lage-Pinto F, Campaneli da Silva LB, da Cunha M, de Oliveira JG, Rezende CE, Magalhães de Souza CM, Azevedo RA (2011) Structural and ecophysiological alterations of the water hyacinth [*Eichhornia crassipes* (Mart.) Solms] due to anthropogenic stress in Brazilian Rivers. Braz Arch Biol Technol 54:1059–1068

Wang TC, Weissman JC, Ramesh G, Varadarajan R, Benemann JR (1996) Parameters for removal of toxic heavy metals by water Milfoil (*Myriophyllum spicatum*). Bull Environ Contam Toxicol 57:779–786

Wang J, Gu Y, Zhu Z, Wu B, Yin D (2005) Physiological responses of *Ceratophyllum demersum* under different nutritional conditions. Ying Yong Sheng Tai Xue Bao 16(2):337–340

Wang K, Huang L, Lee H, Chen P, Chang S (2008) Phytoextraction of cadmium by *Ipomoea aquatica* (water spinach) in hydroponic solution: effects of cadmium speciation. Chemosphere 72:666–672

Wang Q, Li Z, Cheng S, Wu Z (2010) Effects of humic acids on phytoextraction of Cu and Cd from sediment by *Elodea nuttallii*. Chemosphere 78:604–608

Weis JS, Weis P (2004) Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration. Environ Int 30:685

Weltje L, Brouwer AH, Verburg TG, Wolterbeek HT, de Goeij JJM (2002) Accumulation and elimination of lanthanum by duckweed (*Lemna minor* L.) As influenced by organism growth and lanthanum sorption to glass. Environ Toxicol Chem 21:1483–1489

Wilson PC, Whitwell T, Klaine SJ (2000) Metalaxyl and simazine toxicity to and uptake by *Typha latifolia*. Arch Environ Contam Toxicol 39:282–288

Win DT, Than MM, Tun S (2002) Iron removal from industrial waters by water hyacinth. Aust J Technol 6(2):55–60

Win DT, Than MM, Tun S (2003) Lead removal from industrial waters by water hyacinth. Aust J Technol 6(4):187–192

Windham L, Weis JS, Weis P (2001) Lead uptake, distribution and effects in two dominant salt marsh macrophytes *Spartina alterniflora* (cordgrass) and *Phragmites australis* (commonreed). Mar Pollut Bull 42:811

Windham L, Weis JS, Weis P (2003) Uptake and distribution of metals in two dominant salt marsh macrophytes, *Spartina alterniflora* (cordgrass) and *Phragmites australis* (common reed). Estuar Coast Shelf Sci 56:63

Wolf SD, Lassiter RR, Wooten SE (1991) Predicting chemical accumulation in shoots of aquatic plants. Environ Toxicol Chem 10:655

Wolff G, Pereira GC, Castro EM, Louzada J, Coelho FF (2012) The use of *Salvinia auriculata* as a bioindicator in aquatic ecosystems: biomass and structure dependent on the cadmium concentration. Braz J Biol 72, doi.org/10.1590/S1519-69842012000100009

Wolverton BC, McDonald R (1979) The water hyacinth: from profilic pest to potential provider. Ambio 8:2–9

Xia H, Ma X (2006) Phytoremediation of ethion by water hyacinth from water. Bioresour Technol 97: 1050–1054

Xia J, Wu L, Tao Q (2002a) Phytoremediation of methyl parathion by water hyacinth (*Eichhornia crassipes* Solm.). Chem Abstr 137:155879

Xia J, Wu L, Tao Q (2002b) Phytoremediation of some pesticides by water hyacinth (*Eichhornia crassipes* Solm.). Chem Abstr 138:390447

Xing W, Li D, Liu G (2010) Antioxidative responses of *Elodea nuttallii* (Planch.) H. St. John to short-term iron exposure. Plant Physiol Biochem 48:873–878

Xue PY, Li GX, Liu WJ, Yan CZ (2010) Copper uptake and translocation in a submerged aquatic plant *Hydrilla verticillata* (L.f.) Royle. Chemosphere 81(9):1098–1103

Xue P, Yan C, Sun G, Luo Z (2012) Arsenic accumulation and speciation in the submerged macrophyte

Ceratophyllum demersum L. Environ Sci Pollut Res Int 19:3969–3976

Yadav SB, Jadhav AS, Chonde SG, Raut PD (2011) Performance evaluation of surface flow constructed wetland system by using *Eichhornia crassipes* for wastewater treatment in an institutional complex. Univ J Environ Res Technol 1:435–444

Yang Q, Chen ZH, Zhao JG, Gu BH (2007) Contaminant removal of domestic wastewater by constructed wetlands: effects of plant species. J Integr Plant Biol 49(4):437–446

Ye ZH, Baker AJM, Wong MH, Willis AJ (1997) Zinc, lead and cadmium tolerance, uptake and accumulation by *Typha latifolia*. New Phytol 136:469

Ye ZH, Cheung KC, Wong MH (2001) Copper uptake in *Typha latifolia* as affected by iron and manganese plaque on the root surface. Can J Bot 79:314–320

Zayed A, Gowthaman S, Terry N (1998) Phytoaccumulation of trace elements by wetland plants, I: Duckweed. J Environ Qual 27:715

Zayed A, Pilon-Smits E, de Souza M, Lin ZQ, Terry N (2000) Remediation of selenium polluted soils and waters by phytovolatilization. In: Terry N, Barnuelos G (eds) Phytoremediation of contaminated soil and water. Lewis, Boca Raton, p 61

Zhang X, Lin AJ, Zhao FJ, Xu GZ, Duan GL, Zhu YG (2008a) Arsenic accumulation by the aquatic fern *Azolla*: comparison of arsenate uptake, speciation and efflux by *Azolla caroliniana* and *Azolla filiculoides*. Environ Pollut 156:1149–1155

Zhang Z, Wu Z, Li H (2008b) The accumulation of alkylphenols in submersed plants in spring in urban lake, China. Chemosphere 73:859–863

Zhang X, Hu Y, Liu Y, Chen B (2011) Arsenic uptake, accumulation and phytofiltration by duckweed (*Spirodela polyrhiza* L.). J Environ Sci (China) 23(4):601–606

Zhu YL, Zayed AM, Qian JH, Souza M, Terry N (1999) Phytoaccumulation of trace elements by wetland plants. II water hyacinth (*Eichhornia crassipes*). J Environ Qual 28:339

3 Mechanism of Removal of Contaminants by Aquatic Plants

Plants possess highly specific and efficient mechanisms to acquire essential micronutrients from the environment. Uptake and removal of contaminant varies for each category of aquatic macrophyte i.e. free-floating, submerged and emergent. The mode of uptake by plants is also different for organic and inorganic contaminant. Uptake of inorganic compounds (ionic or complexed form) is mediated by active or passive uptake mechanisms within the plant, whereas uptake of organic compounds is generally governed by hydrophobicity (log k_{ow}) and polarity. Uptake of pollutants by plant roots is different for organic and inorganic compounds. Uptake of inorganic contaminants is facilitated by membrane transporters, while uptake of organic contaminants is driven by simple diffusion based on their chemical properties. Assimilated and absorbed contaminant is then transformed and detoxified by a variety of biochemical reactions in the plant system using versatile enzymatic machineries.

3.1 Inorganic Contaminants

Uptake of inorganic contaminants, mainly nutrients, heavy metals and radionuclides in aquatic plants, takes place by roots and foliar absorption. The primary role of roots is expected to be nutrient assimilation, and the main role of foliage is inorganic carbon fixation. In floating macrophytes, uptake takes place predominantly by foliar absorption only. The uptake is followed by their transport and entrance into the vascular cylinder. Contaminants move through epidermis, Casparian strip and endodermis from where they are sorbed, bound or metabolized (Shimp et al. 1993). The organic–metal complex (soluble, less toxic) is transported to cell compartments with low metabolic activity, i.e. cell wall and vacuole, where it is stored in the form of a stable organic or inorganic compound. Extraordinary high levels of contaminants (thousands of ppm) taken up from the environment are generally concentrated in roots, shoots and/or leaves. Uptake, transport and storage mechanism vary for each category of contaminant removed by aquatic plants.

3.1.1 Heavy Metals

Aquatic plants accumulate/remove metals and other toxic elements from water by phytosorption phytofiltration, phytostabilization and phytoextraction mechanisms (Tangahu et al. 2011).

The metal bioremoval in aquatic plants include:

(a) Bioaccumulation—A slow, irreversible ion sequestration process. It is a passive process of metal uptake and primarily involves adsorption when plants are in direct contact with the medium and results in the accumulation of metals mainly in aerial parts of the plants.
(b) Biosorption—An initial, fast, reversible metal-binding process. The active (rapid) uptake of metal occurs mainly by roots from where it is translocated to other plant parts.

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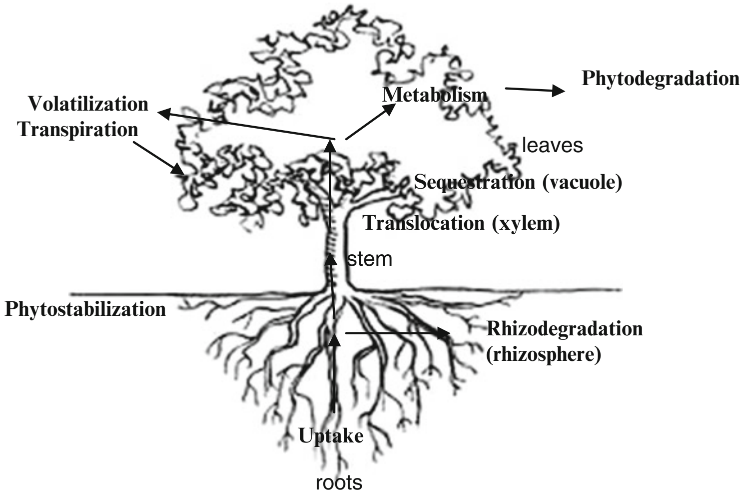

Fig. 3.1 Possible mechanisms of contaminant removal by plants

Removal of metal ions occurs via interactions with functional groups that are found in the proteins, lipids and carbohydrates present in the cell walls. The kinetics for metal adsorption by aquatic plants fit well in Langmuir and Freundlich isotherms and follows first-order kinetics (Fig. 3.1).

In free-floating aquatic plant species, the active (rapid) uptake of metal occurs mainly by roots, from where it is translocated to other plant parts. In submerged plant species, leaves are the main site of mineral uptake. The foliar absorption of heavy metals occurs by passive movement through the cuticle, where the negative charges of the pectin and cutin polymers of the thin cuticle and polygalacturonic acids of the cell walls create a suck inward (Dhir 2010). Due to an increase in charge density inward, the transport of positive metal ions takes place.

The mechanism of metal removal in submerged plants involves:

- Passive penetration of ions in apparent free space (AFS)
- Active uptake of ions into cytoplasm
- Active storage of ions into vacuoles from the cytoplasm

Emergent plants absorb, translocate and bioconcentrate metals from water and sediments. Most of the metal is immobilized in soils in rhizosphere zone from where it is reduced to sulphite or metallic form. Most of the plants retain metal burden in below-ground parts (roots), in contrast to a few other species that redistribute a greater proportion in above-ground tissues, especially leaves (Dhir 2010). The removal of metal from water depends on factors such as:

- Sediment geochemistry
- Water physico-chemistry
- Plant physiology
- Plant genotype

The metal uptake in emergent plants is facilitated by specialized structures called metal-rich rhizoconcretions or iron plaque present on root surface. These structures are mainly composed of iron hydroxides and metal such as Mn that are immobilized and precipitated on root surface. Plaque restricts metal uptake at low pH but facilitates uptake at higher pH. The anaerobic environment in bottom water and sediments promote metal uptake as metals are present in more soluble less oxidized forms.

The rate of absorption, accumulation and translocation of metal in plants depends on plant species and is further regulated by environmental factors like temperature, pH, redox potential, time, dose, temperature, agitation speed and salinity. The rate of heavy metal removal is concentration and time dependent. pH regulates the availability of metals to macrophytes through speciation of metals. The redox potential also regulates heavy metal uptake in plants. Low redox potential supports the metal binding to sulphides in sediments, thus immobilizing them. Salinity decreases the uptake of metals in plants due to the formation of chloride complexes. Chelators such as siderophores, organic acids and phenolics released by plants, and bacteria enhance bioavailability of metals and hence promoting uptake.

The metal uptake by plants results in accumulation in the root itself or their transport (translocation) across the plasma membrane of root cells, xylem loading, detoxification and sequestration of metals at cellular level. The heavy metals are incorporated in plant tissues or stored in bound form. Uptake–translocation mechanisms are likely to be closely regulated. In general, the heavy metal removal mechanisms in plants include three steps: uptake, translocation and storage.

(a) Uptake

Plant roots solubilize and take up micronutrients from very low ppb levels to very high ppm levels in the soil. Ion uptake is facilitated by (1) proton pumps such as ATPases, (2) co- and antitransporters and (3) channels. Uptake efficiency depends on physicochemical properties of the contaminant, chemical speciation and the plant's capacity. Inorganic contaminants are taken up predominantly *via* membrane transporter proteins. Arsenic (as arsenate) might be taken up by plants due to the similarities to the plant nutrient phosphate, while Se replaces the nutrient sulphur in compounds taken up by a plant (Brooks 1998; Abedin et al. 2002).

(b) Translocation

Metal transport is assisted by specialized proteins embedded in the plant cell plasma membrane. Transport proteins besides facilitating metal uptake in plants also play an important role in homeostasis. Some of these proteins include ATPases, Nramps, cation diffusion facilitator (CDF) proteins and zinc ion permeases (ZIP). Cation diffusion facilitators (CDF type), the ABC transporters for phytochelatins and the metal chaperones are commonly reported in hyperaccumulator species. Uptake of inorganic ions is saturable following Michaelis–Menten kinetics (Marschner 1995).

(c) Storage

The translocation is followed by compartmentalization, i.e. metal deposition in vacuoles driven by ATP-dependent Cd/H^+ antiport or ABC proteins or excretion by specific glands. The metal toxicity in plants induces oxidative stress that induces alterations in membrane structures. This is curtailed by various tolerance mechanisms that include:

- Chelation binding of metal ions by high-affinity ligands, which reduce the concentration of free metal ions in the solution. These mainly include binding of metal ions via thiol-rich peptides such as phytochelatin (PC) and metallothionein (MT) synthesis, amino acids and organic acids. Phytochelatins (PC) have high affinity for binding heavy metals such as Cd, Hg, Cu or As.
- Synthesis of stress metabolites and/or proteins.
- Efficient antioxidant machinery.
- Biotransformation, the toxicity of the metal can be reduced by plants by the chemical reduction of the element and/or incorporation into organic compounds or enzymatic degradation.
- Reduced uptake or efflux pumping of metals at plasma membrane.
- Binding to cell wall.
- Cytoplasmic Ni seems to be detoxified by binding to histidine, while vacuolar storage of Ni is probably in the form of citrate (Dhir et al. 2009).

Strong chelators efficiently bind the metals in a non-toxic form, thereby allowing flux through the xylem up to the leaves. The metal hyperaccumulator contains constitutively high organic acid and phenolic levels, which form strong complexes with the metal thus maintaining cation/anion homeostasis. According to malate shuttle hypothesis, in Zn-resistant plants, excess Zn is bound to malate in the cytoplasm, and after transport to the vacuole, a ligand exchange occurs. Zn forms more stable complexes with citrate, oxalate or other ligands, while malate returns to the cytoplasm.

Heavy metal toxicity increases cellular reactive oxygen species, such as superoxide anion, hydroxyl anion and hydrogen peroxide which causes oxidative stress. The reactive oxygen species are deactivated by enzymatic (superoxide dismutase, catalase, ascorbate peroxidase, guaiacol peroxidase and glutathione reductase) and nonenzymatic (glutathione, ascorbic acid, phenolic compounds and tocopherol) antioxidant systems (Parvaiz et al. 2008; Azqueta et al. 2009).

The mechanism of uptake and transport for some heavy metals such as As has been studied in detail.

1. Uptake

   Arsenate, arsenite, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are the common forms of As present in soil available for plant uptake. Plant roots take up arsenite mainly as the neutral molecule $As(OH)_3$. Arsenate is taken up phosphate transporters. Arsenate is taken up by plant roots via phosphate transporters and reduced to arsenite in root cells.

2. Transport

   In higher plants, arsenite, methylated As, enters plant root cells via nodulin 26-like intrinsic proteins (NIPs) that are the structural and functional equivalents of the microbial and mammalian aquaglyceroporins (Wallace et al. 2006). NIPs are a subfamily of the plant major intrinsic proteins (MIPs), collectively known as aquaporins or water channels (Maurel et al. 2008). Aquaporins also facilitate the transport of methylated forms. In most plant species, arsenite is the main form loaded into the xylem sap. The dominance of trivalent As in plant tissues when arsenate is the form supplied to plants indicates a high capacity of arsenate reduction.

3. Storage

   It is detoxified by complexation with thiol-rich peptides and sequestrated in the vacuoles in As non-hyperaccumulating plants. Arsenic is a strong inducer of PC synthesis. A number of genes or enzymes involved in glutathione synthesis, metabolism and transport are upregulated on exposure to arsenate, probably reflecting a higher demand for GSH under As stress. The PC–arsenite complexes are likely to be stored in vacuoles. ATP-binding cassette (ABC) proteins confer arsenite resistance by transporting the glutathione *S*-conjugated arsenite into the vacuole. The PC-arsenite complexes are also likely to be transported into vacuoles by an ABC protein (Zhao et al. 2010).

3.1.2 Radionuclides

Aquatic plant species exhibit an equally high potential to accumulate radionuclides. The uptake and reduction of radionuclides by aquatic plants is rapid as they are actively transported across the plasma membrane. In aquatic plants, the major mode of entrance of radionuclides is foliar absorption where it is photoreduced (chloroplast), followed by complexation with ligands present in the cell including proteins, cysteine and glutathione. Kinetic studies indicate that radionuclide absorption by plants is time and concentration dependent and depicts first-order uptake rate (Popa et al. 2006; Dhir et al. 2009).

In general, the uptake of radionuclides in plants involves two steps:

1. *Passive*: a rapid binding of ions to negatively charged groups on the cell surface and transport through the cell wall within a short duration
2. *Active*: metabolically dependent penetration of ions through cell membrane, movement inside cytoplasm and the bioaccumulation of the metal ions onto the protoplasts

In aquatic plants, the major mode of entrance for Tc is foliar absorption of TcO_4–. Technetium (TcO_4^-) taken up by plants is actively transported across the plasma membrane or transported to leaves, where it is photoreduced (chloroplast), followed by complexation with ligands present in the cell including proteins, cysteine and glutathione. The total amount of Tc present in plants is the sum of both the pertechnetate and reduced Tc form (Hattink et al. 2000, 2003). The fractions of polysaccharides and lipids present on the cell surface are actively involved in the accumulation of radionuclides. The uptake of radionuclides is also facilitated by the presence of carbonate groups present on the surface of the plant (Dhir et al. 2009). The mechanism of uptake and translocation of some radionuclides have been studied in detail.

3.1.2.1 Caesium (Cs) Transport in Plants

Uptake

Caesium uptake in plants takes place through roots and is facilitated by two transport systems located on plant root cell membranes, namely, the K^+ transporter and the K^+ channel pathway (Zhu and Smolders 2000). Caesium absorption by plant roots is rapid and this is followed by translocation to the above-ground plant parts. Lower K concentrations in solution promote Cs uptake. At low K concentrations, Cs^+ is absorbed by the K^+ uptake system of the root. Higher concentrations of K^+ strongly suppresses Cs^+ uptake. Cs^+ is efficiently transported by high-affinity K^+ uptake transporter. Increasing concentrations of NH_4^+ reduce uptake of Cs, while increasing concentrations of divalent cations Ca^{2+} and Mg^{2+} slightly reduce the uptake of Cs. This is because divalent cations compete with Cs uptake through competition in the apoplast.

Transport

Carrier and channel modes have been proposed as possible mechanisms with a molecular basis for the transport of K^+ across cell membranes of plant roots. Carrier-mediated transport is facilitated by a high-affinity system (transporter) within cell membranes operating predominantly at low external K concentration (<0.3 mM). Potassium is transported across the plasma membrane against the electrochemical gradient via this system. This transporter (HKT1) is probably a K^+H^+ cotransporter. It has been suggested that multiple high-affinity K^+ transport systems may be involved in K^+ uptake. Channel-mediated transport is a low-affinity system operating at high external K concentrations (above 0.5–1 mM) (Zhu et al. 2000). The high-affinity transport system follows the Michaelis–Menten equation (i.e. saturation kinetics) and is believed to be carrier-mediated (H^+ cotransporter), whereas the low-affinity one exhibits linear kinetics and is expected to be channel-mediated. Another hypothesis states that Cs influx occurs through the K channels but that the ratio of Cs to K in the efflux part varies with K supply. Potassium starvation induces the expression of K^+ transporters, such as HKT1 (high-affinity K^+ transporter) which may increase Cs^+ uptake.

3.1.3 Nitrogen and Phosphorus

The uptake of nitrogen in the forms of NH_4^+ and NO_3^- has been reported for aquatic species (Henriksen et al. 1992; Lazof et al. 1992; Rao et al. 1993; Reidenbach and Horst 1997; Gessler et al. 1998; Cedergreen and Madsen 2002). *Lemna minor* has shown the capacity to take up significant amounts of inorganic N through both roots and fronds. High nutrient uptake capabilities of leaves have also been reported for the submerged macrophytes *Ruppia maritima* and *Zostera marina*, where weight-specific uptake rates of PO_4^{3-} and NH_4^+ by leaves are noted. *Eichhornia crassipes, Salvinia auriculata, Phragmites australis* and *Phalaris arundinacea* exhibited removal capacity for nitrogen and phosphorus such as of NO_3–N, NH_4–N and PO_4–P (Petrucio and Esteves 2000). The removal of nitrate nitrogen (NO_3–N) in natural and constructed wetland systems occurs via three interacting processes: plant uptake, microbial assimilation/immobilization and denitrification. Most denitrifying bacteria require anoxic conditions and a labile organic carbon source to biologically reduce nitrate to nitrogen gas (N2) (Zhu and Sikora 1994; Vymazal and Kropfelova 2008). Nitrogen and P removal are temperature dependent as higher removal is noted in summer than winter. Phosphorus is taken up in the form of phosphate and uptake is facilitated by ion channels or proton pumps.

3.2 Organic Contaminants

Aquatic plant species possess the potential to remove, sequester and transform organic contaminants. The capacity of aquatic plants for uptake and accumulation of organophosphorus, organochlorine compounds, and chlorobenzenes has been studied extensively (Gobas et al. 1991; Rice et al. 1997; Macek et al. 2000). Uptake of organic contaminants is driven by simple diffusion based on their chemical properties. In order to penetrate into a leaf, the organic contaminant should pass through the stomata or traverse the epidermis, which is covered by film-like wax cuticle. The majority of toxic compounds penetrate into a leaf as solutions (pesticides, liquid aerosols, etc.). Plants absorb xenobiotics primarily through roots and leaves (Wang and Liu 2007). Leaf absorption is often a consequence of agricultural spraying with organochemicals, while volatile compounds are taken up directly (Burken et al. 2005). Organic pollutants pass the membrane between root symplast and xylem apoplast via simple diffusion. Entry of organic pollutants into the xylem depends on similar passive movement over membranes as their uptake into the plants (Nwoko 2010). Penetration into roots occurs mainly by simple diffusion through unsuberized cell walls, from which xenobiotics reach the xylem stream. There are no specific transporters in plants for these man-made compounds, so the movement rate of xenobiotics into and through the plant depends largely on their physicochemical properties.

Removal of organic contaminants involves two major mechanisms:

1. Direct uptake of contaminants followed by metabolization and subsequent accumulation of non-phytotoxic metabolites into the plant tissue
2. Release of exudates and enzymes that stimulate microbial activity and the resulting enhancement of microbial transformations in the rhizosphere (the root zone)

The potential of aquatic plants to sequester organic contaminants depends upon the plants lipid rich cuticle, which helps in the sequestration of lipophilic organic compounds (Dhir et al. 2009).

The amount of organic compound sequestered by aquatic plants depends on:

- The plant species
- Biochemical composition of the plant tissues
- Physicochemical properties such as:
  (a) Polarity (D_{ow})
  (b) Aqueous solubility
  (c) Hydrophobicity (K_{ow})
  (d) Volatility of the contaminant
  (e) Molecular weight of organic compounds

The inherent ability of the roots to take up organic compounds depends upon hydrophobicity (or lipophilicity) of the target compounds (Schnoor et al. 1995). This parameter is often expressed as the log of the octanol–water partitioning coefficient, K_{ow}. Generally the higher the log K_{ow}, the greater the root uptake of compound. An optimum log K_{ow} value is required for a compound to be a good candidate for phytoremediation. Burken and Schnoor (1997) predicted a model that showed that uptake of organic pollutants by plants was based on log K_{ow}. Moderately hydrophobic compounds ($0.5 < \log K_{ow} < 4.5$) would be significantly taken up and translocated inside plant tissues. More hydrophobic compounds are more strongly bound to root surfaces or partition into root solids, resulting in less translocation within the plant (Cunningham et al. 1996). In contrast, highly soluble organic compounds can be readily taken up by plants. Organic compounds cover a wide range of polarity (log D_{ow} from −2 to 6), biodegradability and photodegradability (Calderón-Preciado et al. 2011; Murray et al. 2012). The passive uptake of contaminant is driven by availability of the contaminant in its protonated form. The protonated form of the contaminant is considered as the species available for biotic partitioning in plants, which further gets coupled to enzymatic transformation and compartmentalization in vacuoles. Kinetics revealed the first-order rate equations for the uptake and elimination of organic contaminants by aquatic plants.

Plant uptake of organic compounds depends on the type of plant, contaminant and many other physical and chemical characteristics of the soil. A typical microbial population in the rhizosphere comprises bacteria, actinomycetes and fungi. The roots of the plants exude a wide spectrum of compounds including sugars, amino acids, carbohydrates and essential vitamins that may act as growth and energy-yielding substrates for the microbial consortia in the root zone. Exudates may also include compounds such as acetates, esters, benzene derivatives and enzymes.

Plant root exudates can change metals speciation (i.e. form of the metal) and the uptake of metal ions and simultaneous release of protons, which acidifies the soil and promotes metal transport and bioavailability. Plants provide exudates that provide an excellent habitat for increased microbial populations and pump oxygen to roots, a process that ensures aerobic transformations near the root that otherwise may not occur in the bulk soil. Exudates stimulate bacterial transformations and build up the organic carbon in the rhizosphere. Microbial populations present in the rhizosphere enhance degradation of organics by the provision of appropriate beneficial primary substrates for co-metabolic transformations of the target contaminants. Enzymes such as dehalogenase, nitroreductase, peroxidase, laccase, nitrilase and oxygenase help in significant transformation of contaminants. The organic compounds in the root exudates can stimulate microbial growth in the rhizosphere (the region immediately surrounding plant roots). Fungi associated with some plant roots (i.e. mycorrhizae) can also influence the chemical conditions within the soil. Decaying roots and above-ground plant material that is incorporated into the soil will increase the organic matter content of the soil, potentially leading to increased sorption of contaminants and humification (the incorporation of a compound into organic matter). Mycorrhizal fungi, growing in symbiotic association with the plant, have unique enzymatic pathways that help to degrade organics (Kvesitadze et al. 2009).

The metabolic pathways for the transformation of organic contaminants by aquatic plant species have been identified. The exposure of aquatic plants to organic chemicals results in:

(a) Rapid uptake or sequestration followed by
(b) Transformation or degradation, either reductive or oxidative
(c) Assimilation of metabolites by covalent binding to plants

Since the metabolic capacities tend to be enzymatically and chemically similar to those processes that occur in mammalian livers, this is referred as ‘green livers’. The three sequential steps/phases of the *green liver* model involved in metabolization of organics are:

Phase I conversion/activation

Organic compound undergoes hydrolysis, reduction and oxidation. This facilitates its uptake and assimilation (Eapen et al. 2007; Komives and Gullner 2005). Introduction of functional groups to the organic compounds results in the formation of more polar, chemically active and water-soluble compounds (Komives and Gullner 2005). In plants, oxidative metabolism is mediated mainly by cytochrome P450 monooxygenase (Sandermann 1994). These enzymes are very crucial during the oxidative process of bioactivation, to emulsify highly hydrophobic pollutants and make them chemically reactive electrophilic compounds which form conjugates (Morant et al. 2003).

Phase II conjugation

Activated organic metabolite gets conjugated or bounded with sugar, amino acids and glutathione or sulphydryl (–SH) group of glutathione resulting in hydrophilic forms. Conjugation results in the formation of high-molecular-weight, more polar and less toxic compounds as compared to the original compound. Glutathione *S*-transferases catalyze the nucleophilic attack of sulphur atom glutathione on electrophilic group of variety of hydrophobic organic substrates. Conjugation takes place in the cytosol. Transformation of organochlorine pesticides is the hydroxylation of 2,4-D followed by conjugation with glucose and malonyl and deposition in vacuoles.

Every enzyme that participates in detoxification process has specific functions (Table 3.1). Dehalogenase dehalogenates chlorinated solvents and is specifically noted in hybrid poplar (*Populus* spp.) parrot feather (*Myriophyllum aquaticum*). Laccase cleaves aromatic ring after TNT is reduced to triaminotoluene and has been reported in stonewort (*Nitella* spp.) and parrot feather (*Myriophyllum aquaticum).* Nitrilase cleaves cyanide groups from aromatic ring and has been reported in willow (*Salix* spp.). Nitroreductase reported in hybrid poplar (*Populus* spp.), Stonewort (*Nitella* spp.) and parrot feather (*Myriophyllum aquaticum)* reduces nitro groups on explosives and other aromatic compounds.

Table 3.1 Enzymes participating in various processes of contaminant transformation

S. no.	Type of enzyme	Function
Step I		
1.	Oxidases	Hydroxylation, dehydrogenation, demethylation, other oxidative reactions (cytochrome P450-containing monooxygenases, peroxidases, phenol oxidases, ascorbate oxidase, catalase)
2.	Reductases	Reduction of nitro groups (nitroreductase)
3.	Dehalogenases	Splitting atoms of halogens from halogenated and polyhalogenated xenobiotics
4.	Esterases	Hydrolyzing ester bonds in pesticides and other organic contaminants
Step II		
5.	Transferases	Transfers one group or moiety from one molecule to another (glutathione *S*-transferase (GST), glucuronozyl-*O*-transferase, malonyl-*O*-transferase, glucosyl-*O*-transferase)
Step III		
6.	Transferases	Transfers one group or moiety from one molecule to another (glutathione *S*-transferases)
Others		
	Nitrilase	Cleaves cyanide groups on explosives and other aromatic compounds
	Peroxidase	Degradation of phenols
	Laccase	Cleaves aromatic ring after TNT is reduced to triaminotoluene
	Phosphatase	Cleaves phosphate groups from organophosphate pesticides

Peroxidase that helps in degradation of phenols has been noted in horseradish (*Armoracia rusticana*), while phosphatase that cleaves phosphate groups from organophosphate pesticides has been reported in giant duckweed (*Spirodela polyrhiza*) (Susarla et al. 2002).

Phase III, sequestration/compartmentation

During compartmentation, organic compounds are conjugated and segregated into vacuoles or bound to the cell wall material (hemicellulose or lignin). The sequestration of organic compounds such as halogenated organic compounds by plants includes rapid physical (adsorption, absorption, partitioning) and chemical processes (complexation and reaction with cuticular and membrane components). Kinetics revealed the first-order rate equations for the uptake and elimination of organic contaminants by aquatic plants. The potential of aquatic plants to sequester organic contaminants depends upon the plants lipid rich cuticle, which helps in the sequestration of lipophilic organic compounds. The xenobiotic conjugates can also be incorporated into biopolymers such as lignin where they are characterized as nonextractable/bound residues, whereas in aquatic/wetland plants they can be excreted for storage outside the plant. Once an organic chemical is taken up by plant, it can be transformed via lignification, volatilization, metabolization or mineralization to carbon dioxide, water and chlorides. Deto-xification mechanisms may transform the parent chemical to non-phytotoxic metabolites, including lignin, that are stored in various places in plant cells (Coleman et al. 1997; Dietz and Schnoor 2001). Cytosolic metabolites are transported to the vacuoles or apoplast by tonoplast membrane-bound transporters. Vacuolar compartmentalization is a major step in detoxification of organics (Coleman et al. 2002). ATPase is the main enzymes involved in this transport (Martinois et al. 1993). Cytochrome P450, peroxygenases and peroxidases are involved in plant oxidations of xenobiotics. Other enzyme classes like glutathione *S*-transferases, carboxylesterases, *O*-glucosyltransferases, *O*-malonyltransferases, *N*-glucosyltransferases and *N*-malonyltransferases are associated with xenobiotic metabolism in plant cells, transport of intermediates and compartmentation processes (Sandermann 1992, 1994) (Fig. 3.2).

The mechanism of removal of some organic contaminants has been studied in detail.

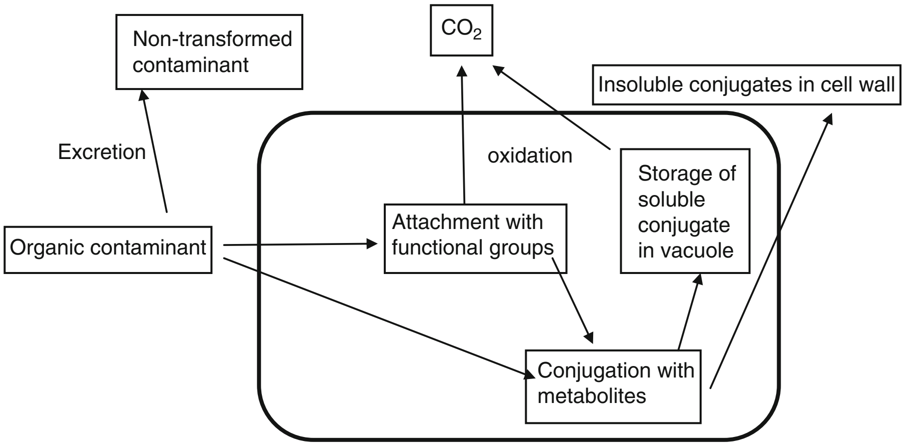

Fig. 3.2 Fate of organic contaminant in plant cells (Modified from Kvesitadze et al. 2009)

3.2.1 Halogenated Compounds

The mechanisms involved in the removal of halogenated organic compounds from water by aquatic plant species include:

- Rapid sequestration by partitioning to the lipophilic plant cuticles
- Phytoreduction to less halogenated metabolites and phytooxidation
- Assimilation into plant tissues as non-toxic products, presumably formed by covalent binding with the plant tissues

The sequestration of organic compounds such as halogenated organic compounds by plants includes rapid physical (adsorption, absorption, partitioning) and chemical processes such as complexation and reaction with cuticular and membrane components. Absorbed contaminant is transformed by a variety of biochemical reactions and versatile enzymatic machineries in the plant system. Phytoreduction reactions in plants are catalyzed by enzymes like dehalogenases, such as glutathione S-transferase and Fe–S clusters in chloroplast ferredoxin, while phytooxidation and covalent binding (phytoassimilation process) are reactions mediated by oxidative enzymes (possibly cytochrome P450 with monooxygenase activity, glutathione or laccase). The phytoreduction reactions mainly include dehalogenation reactions, which have been reported specifically for halogenated compounds such as hexachloroethane (HCA) and dichlorodiphenyltrichloroethane (DDT) (Nzengung et al. 1999; Nzengung and Jeffers 2001). The phytoreduction products either get oxidized into polar compounds or are covalently bound to plant tissues (assimilated), though the concentration of reduction products is always higher for any plant species than the oxidation products. Garrison et al. (2000) reported enzyme-mediated reductive transformation processes in plants. A dehalogenase activity from *Elodea* that reductively transformed HCA to form perchloroethylene (PCE) is also reported. Studies with *Elodea* also established the reduction of DDT to corresponding DDD analogs, plant-bound fractions and other unknown products (Gao et al. 2000a, b). Another plant-derived enzyme, dehalogenase, helps reduce chlorinated solvents such as trichloroethylene (TCE) to chloride ion, carbon dioxide and water.

A dehalogenase activity from *Elodea* reductively transformed hexachloroethane (HCA) to form perchloroethylene (PCE). Studies with *Elodea* also established the reduction of DDT to corresponding DDD analogs, plant-bound fractions and other unknown products.

3.2.1.1 Polychlorinated Biphenyls (PCBs)

PCBs are xenobiotic chlorinated aromatic compounds categorized as persistent organic pollutants (POPs) detected in virtually every compartment of the ecosystem, including air, water, soil, sediment and living organics. PCBs are highly hydrophobic, leading to their bioaccumulation in living organisms (biomagnification). Processes involved in phytoremediation of PCBs include rhizoremediation, phytoextraction and phytotransformation. Due to their high hydrophobicity, PCBs bind strongly to soil particles and are only poorly taken up inside plant tissues (Aken et al. 2010; Das and Chandran 2011). Therefore, microbes in the rhizosphere play a dominant role in their biodegradation. There are many processes by which vegetation can stimulate microbial activity in soil and enhance biodegradation of recalcitrant PCBs:

(a) Plant roots release organic compounds, such as sugar, amino acids and organic acids, that can be used as electron donors to support aerobic co-metabolism or anaerobic dehalogenation of chlorinated compounds. In some instances, microbial aerobic metabolism consumes oxygen, resulting in anaerobic conditions favourable to PCB dehalogenation.
(b) Plants secrete extracellular enzymes that can initiate transformation of PCBs and facilitate further microbial metabolism.
(c) Plants release inducers that enhance microbial degradation. Plant phenolic exudates enhance the activity of the PCB degrader, *B. xenovorans* LB400.
(d) Plants increase soil permeability and oxygen diffusion in the rhizosphere, which potentially enhances microbial oxidative transformation by oxygenases.
(e) Plant roots are also known to secrete diverse microbial growth factors.
(f) Plant roots release organic acids and molecules that can act as surfactants, therefore mobilizing PCBs and rendering them more susceptible to be absorbed inside plant tissues.
(g) Plant root exudates, including phenolic compounds, flavonoids and terpenes, increase microbial activity in soil and hence biodegradation of PCBs.

Uptake

The efficiency of plant uptake of PCBs—with log K_{ow} ranging from 4.5 (2-monochlorobiphenyl) to 8.2 (decachlorobiphenyl)—is expected to decrease fast with the degree of chlorination. At low log K_{ow}, higher-chlorinated compounds would not be taken up inside plant tissues, mono- to tetrachlorinated PCBs can be adsorbed to plant roots, but only lower-chlorinated PCBs were translocated to aerial parts (mono-, di- and trichlorinated PCBs to upper stems and mono- and dichlorinated PCBs to shoots) (Van Aken et al. 2010).

Metabolism

Metabolism of PCBs varies according to the plant species and degree of chlorination and substitution pattern. Metabolism of xenobiotic compounds including PCB is a three-phase process. *Phase I* involves oxidation of PCBs to produce various hydroxylated products, characterized by a higher solubility and reactivity. This step serves to increase water solubility and provides an opportunity for conjugation via glycosidic bond formation. *Phase II* involves *conjugation* of activated compounds with molecules of plant origin (e.g. glutathione or amino acids) forming adducts less toxic and more soluble than parent PCBs. *Phase III* involves *sequestration* of the conjugates in plant organelles (e.g. vacuole) or incorporation into plant structures (e.g. cell wall).

Transformation

Metabolism of PCBs in plants involves enzyme oxygenases including cytochrome P450 monooxygenases and peroxidases. Studies suggest the role of three enzymes including peroxidases, Remazol Brilliant Blue R (RBBR) oxidases and cytochrome P450s in PCB metabolism in plants (Aken et al. 2010). Conjugative enzymes involved in PCB metabolism involve the role of various transferases, such as glutathione *S*-transferases (e.g. conjugation of glutathione with several pesticides) and glycosyltransferases (e.g. conjugation of glucose with chlorophenols and DDT). These are likely to be involved in the conjugation and compartmentation of PCB adducts in plant tissues. Plant tolerance to several chlorinated pollutants, such as atrazine, metolachlor and 1-chloro-2,4-dinitrobenzene (CDNB), can be enhanced by the overexpression of enzymes involved in glutathione synthesis, including γ-glutamylcysteine synthetase (ECS) and glutathione synthetase (GS), further suggesting the potential implication of glutathione in PCB metabolism.

3.2.2 Hydrocarbons

Plant uptake of hydrocarbons varies according to hydrophobicity. Hydrophilic compounds (log $K_{ow} < 1$) have little affinity for root membranes, moderately hydrophobic hydrocarbons (log $K_{ow} = 1.0–3.0$) such as BTEX show high uptake efficiency from soil and groundwater, while PAHs (log $K_{ow} > 4$) depict poor uptake as they are strongly sorbed to soil and are therefore not bioavailable. The degradation of hydrocarbons can be via direct or indirect pathway. Direct route involves uptake by a plant, while indirect pathway involves rhizospheric effect where root exudates enhance metabolic degradation and the release of root-associated enzymes transforms organic pollutants. The complete degradation of hydrocarbons is brought under aerobic conditions. The degradation of petroleum hydrocarbons is mediated by specific enzyme system (Kvesitadze et al. 2009). The oxidative process is catalyzed by enzymes oxygenases and peroxidases. Monooxygenases and cytochrome P450 enzyme systems play an important role in the microbial degradation of oil, chlorinated hydrocarbons, fuel additives and many other compounds. Plant enzymes such as dehalogenase, nitroreductase, peroxidase, laccase and nitrilase have been shown to play role in degradation of petroleum hydrocarbons.

Plants volatilize contaminants (such as petroleum hydrocarbons) that have been taken up through its roots to the atmosphere (phytovolatilization). It is also applicable to contaminants such as BTEX, TCE, vinyl chloride and carbon tetrachloride (Ndimele 2010).

3.2.3 Herbicides

Stomata play an important role in absorption of toxic compounds. The abaxial side of a leaf, generally rich in stomata, absorbs the organic substances particularly herbicides (α-naphthylacetic acid, 2,4-D, picloram and derivatives of urea). The contaminant's penetration into the roots essentially differs from the leaves. Substances pass into roots only through cuticle-free unsuberized cell walls. Roots absorb environmental contaminants in two phases:

- Fast phase: substances diffuse from the surrounding medium into the root.
- Slow phase: gradually distribute and accumulate in the tissues.

The intensity of the contaminants absorption depends on solubility, concentration, molecular mass, polarity and pH. The fate of contaminant depends on its chemical nature, external temperature, variety of plants and vegetation, etc. Excretion is the simplest way of getting rid of any organic contaminant entered the plant cell. The toxicant molecule does not undergo chemical transformation and, being translocated through the apoplast, is excreted from the plant. This pathway of xenobiotic (contaminant) elimination is rather rare and takes place at high concentrations of highly mobile (phloem mobile or ambimobile) xenobiotics. Contaminants being absorbed and penetrated into plant cell undergo enzymatic transformations leading to the increase of their hydrophilicity process simultaneously accompanied by decreasing of toxicity. Plant cytochrome P450-containing monooxygenases play an important role in the hydroxylation. Cytochrome P450-containing monooxygenases use NADPH and/or NADH reductive equivalents for the activation of molecular oxygen and incorporation of one of its atoms into lipophilic organic compounds (XH) that results in formation of hydroxylated products (XOH). Glutathione *S*-transferases are the main group of enzymes involved in the detoxification of herbicides by conjugating them with tripeptide glutathione. Knuteson et al. (2002) suggested dealkylation as the probable mechanism for metabolism of simazine (herbicide) into 2-chloro-4-amino-6-isopropylamino-*s*-triazine or hydroxysimazine followed by storage of end products in vacuoles.

3.2.4 Explosives

Studies with *Myriophyllum aquaticum* demonstrated aquatic macrophytes possess potential for oxidative and reductive metabolism of TNT (Pavlostathis et al. 1998; Jacobson et al. 2003). The rapid sorption/sequestration of explosives such as TNT is followed by:

(a) Reduction, resulting in the formation of primary reduction products, namely, 2-amino-4,6-dinitrotoluene (2ADNT) and 4-amino-2,6-dinitroluene (4ADNT) conjugates (Bhadra et al. 1999; Best et al. 1999a, b; McCutcheon and Schnoor 2003), or
(b) Oxidation of TNT facilitated by plausible enzymes such as oxygenases, which are the cytochrome P450 group of enzymes localized in microsomes (endoplasmic reticulum) of plant cells

Nitroreductase and laccase enzymes break down ammunition wastes (2,4,6-trinitrotoluene or TNT) and incorporate the broken ring structures into new plant material or organic detritus that becomes a part of sediment organic matter. The major oxidation products reported so far include 2,4-dinitro- 6-hydoxy-benzyl alcohol, 2-amino-4,6-dinitrobenzoic acid and 2,4-dinitro-6-hydroxytoluene (Medina et al. 2000). The site of localization of TNT and metabolites varies from submerged to emergent plant species. In submerged species, leaves are reported as the major site of compartmentalization, whereas in emergent species, roots are the major site followed by stem and leaves. The rate of removal of TNT by plant is rapid and varies with treatment conditions, such as plant density, contaminant concentration and temperature. Studies revealed that the decline in TNT concentration from the aqueous medium is exponential and follows first-order kinetics as assessed by the Michaelis–Menten model, while the uptake of TNT by aquatic plants including *Myriophyllum aquaticum* is a mixed, second-order rate that is a function of the mass of the plant (Medina et al. 2000). Mass balances and pathway analyses have shown that nitroreductase and laccase enzymes present in the root zone break down ammunition wastes specifically 2,4,6-trinitrotoluene or TNT and incorporate the broken ring structures into new plant material or organic detritus that becomes a part of sediment organic matter. During TNT breakdown, plants such as hornwort increased pH from 3 to 7, sorbed high concentrations of metals that would usually inhibit bacteria and remained healthy and viable.

Literature Cited

Abedin MJ, Feldmann J, Medarg AA (2002) Uptake kinetics of arsenic species in rice plants. Plant Physiol 128:1120–1128

Aken BV, Correa PA, Schnoor JL (2010) Phytoremediation of polychlorinated biphenyls. New Trends Promis Environ Sci Technol 44(8):2767–2776

Azqueta A, Shaposhnikov S, Collins AR (2009) DNA oxidation: investigating its key role in environmental mutagenesis with the comet assay. Mutat Res Genet Toxicol Environ Mutagen 674:101–108

Best EPH, Sprecher SL, Larson SL, Fredrickson HL, Bader DF (1999a) Environmental behavior of explosives in groundwater from the Milan army ammunition plant in aquatic and wetland plant treatments. Uptake and fate of TNT and RDX in plants. Chemosphere 39:2057

Best EPH, Sprecher SL, Larson SL, Fredrickson HL, Bader DF (1999b) Environmental behavior of explosives in groundwater from the Milan army ammunition plant in aquatic and wetland plant treatments. Removal, mass balances and fate in groundwater of TNT and RDX. Chemosphere 38:3383

Bhadra R, Spanggord RJ, Wayment DG, Hughes JB, Shanks JV (1999) Characterization of oxidation products of TNT metabolism in aquatic phytoremediation systems of *Myriophyllum aquaticum*. Environ Sci Technol 33:3354

Brooks RR (1998) Plants that hyperaccumulate heavy metals. CAB International, Wallingford, 384

Burken JG, Schnoor JL (1997) Uptake and metabolism of atrazine by poplar trees. Environ Sci Technol 31:1399–1406

Burken JG, Ma XM, Struckhoff GC, Gilbertson AW (2005) Volatile organic compound fate in phytoremediation applications: natural and engineered systems. J Biosci 60:208–215

Calderón-Preciado D, Matamoros V, Bayona JM (2011) Occurrence and potential crop uptake of emerging contaminants and related compounds in an agricultural irrigation network. Sci Total Environ 412–413: 14–19

Cedergreen N, Madsen TV (2002) Nitrogen uptake by the floating macrophyte *Lemna minor*. New Phytol 155:285–292

Coleman JOD, Blake-Kalff MMA, Davies TGE (1997) Detoxification of xenobiotics by plants: chemical modification and vacuolar compartmentation. Trends Plant Sci 2:144–151

Coleman JO, Frova C, Schroder P, Tussut M (2002) Exploiting plant metabolism for phytoremediation of persistent herbicides. Environ Sci Pollut Res Int 9:18–28

Cunningham SD, Anderson TA, Schwab P, Hsu FC (1996) Phytoremediation of soils contaminated with organic pollutants. Adv Agron 56:55–114

Das N, Chandran P (2011) Microbial degradation of petroleum hydrocarbon contaminants: an overview. Biotechnol Res Int 2011:941810. doi:10.4061/2011/941810, 13 p

Dhir B (2010) Use of aquatic plants *in* removing heavy metals from wastewater. Int J Environ Eng 2(1/2/3):185–201

Dhir B, Sharmila P, Saradhi PP (2009) Potential of aquatic macrophytes for removing contaminants from the environment. Crit Rev Environ Sci Technol 39:754–781

Dietz AC, Schnoor JL (2001) Advances in phytoremediation. Environ Health Perspect 109:63–168

Eapen S, Singh S, D'Souza SF (2007) Advances in development of transgenic plants for remediation of xenobiotic pollutants. Biotechnol Adv 25:442–451

Gao J, Garrison AW, Hoehamen C, Mazur CS, Wolfe NL (2000a) Uptake and phytotransformation of o, p DDT and p, p DDT by axenically cultivated aquatic plants. J Agric Food Chem 48:6121

Gao J, Garrison AW, Hoehamen C, Mazur CS, Wolfe NL (2000b) Uptake and phytotransformation of organophosphorous pesticide by axenically cultivated aquatic plants. J Agric Food Chem 48:6114

Garrison AW, Nzengung VA, Avants JK, Ellington JJ, Jones WJ, Rennels D, Wolfe NL (2000) Phytodegradation of p, p′-DDT and the enantiomers of o, p′-DDT. Environ Sci Technol 34:1663

Gessler A, Schneider S, von Sengbusch D, Werber P, Hanemann U, Huber C, Rothe A, Kreutzer K, Rennenberg H (1998) Field and laboratory experiments on net uptake of nitrate and ammonium by the roots of spruce (*Picea abies*) and beech (*Fagus sylvatica*) trees. New Phytol 138:275–285

Gobas EAPC, McNeil EJ, Lovett-Doust L, Haffner GD (1991) Bioconcentration of chlorinated aromatic hydrocarbons in aquatic macrophytes. Environ Sci Technol 25:924

Hattink J, Goeij JJM, Wolterbeek HT (2000) Uptake kinetics of ^{99}Tc in common duckweed. Environ Exp Bot 44:9

Hattink J, Harns AV, Goeij JJM (2003) Uptake, biotransformation and elimination of ^{99}Tc in duckweed. Sci Total Environ 312:59

Henriksen GH, Raman DR, Walker LP, Spanswick RM (1992) Measurement of net fluxes of ammonium and nitrate at the surface of barley roots using ion-sensitive microelectrodes. Plant Physiol 99:734–747

Jacobson ME, Chiang SY, Gueriguian L, Weshtholm LR, Pierson J (2003) Transformation kinetics of trinitrotoluene conversion in aquatic plants. In: McCutcheon SC, Schnoor JL (eds) Phytoremediation: transformation and control of contaminants. Wiley, New York, pp 409–427

Knuteson SL, Whitwell T, Klaine SJ (2002) Influence of plant age and size on simazine uptake and toxicity. J Environ Qual 31:2090

Komives T, Gullner G (2005) Phase 1 xenobiotic metabolic systems in plants. Z Naturforsch C 60:179–185

Kvesitadze E, Sadunishvili T, Kvesitadze G (2009) Mechanisms of organic contaminants uptake and degradation in plants. World Acad Sci Eng Technol 31:454–464

Lazof DB, Rufty TW, Redinbaugh MG (1992) Localization of nitrate absorption and translocation within morphological regions of the corn root. Plant Physiol 100:1251–1258

Macek T, Mackova M, Ká J (2000) Exploitation of plants for the removal of organics in environmental remediation. Biotechnol Adv 18:23–34

Marschner H (1995) Mineral nutrition of higher plants. Academic, San Diego, p 889

Martinois E, Grill E, Tommasini R, Kreuz K, Amrehin N (1993) ATP dependent glutathione S-conjugate 'export' pump in the vacuolar membrane of plants. Nature 364:247–249

Maurel C, Verdoucq L, Luu DT, Santoni V (2008) Plant aquaporins: membrane channels with multiple integrated functions. Annu Rev Plant Biol 59:595–624

McCutcheon SC, Schnoor JL (2003) Overview of phytotransformation and control of wastes. In: McCutcheon SC, Schnoor JL (eds) Phytoremediation: transformation and control of contaminants. Wiley, New York, pp 53–58

Medina VF, Larson SL, Bergstedt AE, McCutcheon SC (2000) Phytoremoval of trinitrotoluene from water with batch kinetic studies. Water Res 34:2713

Morant M, Bak S, Moller BL, Werck-Reichhart D (2003) Plant cytochromes P450: tools for pharmacology, plant protection and phytoremediation. Curr Opin Biotechnol 2:151–162

Murray BJ, Haddrell AE, Peppe S, Davies JF, Reid JP, O'Sullivan D, Price HC, Kumar R, Saunders RW, Plane JMC, Umo NS, Wilson TW (2012) Glass formation and unusual hygroscopic growth of iodic acid solution droplets with relevance for iodine mediated particle formation in the marine boundary layer. Atmos Chem Phys 12:8575–8587

Ndimele PE (2010) A review on the phytoremediation of petroleum hydrocarbon. Pak J Biol Sci 13:715–722

Nwoko CO (2010) Trends in phytoremediation of toxic elemental and organic pollutants. Afr J Biotechnol 9(37):6010–6016

Nzengung VA, Jeffers P (2001) Sequestration, phytoreduction and phytooxidation of halogenated organic chemicals by aquatic and terrestrial plants. Int J Phytoremediation 3:13

Nzengung VA, Lee NW, Rennels DE, McCutcheon SC, Wang C (1999) Use of aquatic plants and algae for decontamination of waters polluted with chlorinated alkanes. Int J Phytoremediation 1:203

Parvaiz A, Maryam S, Satyawati S (2008) Reactive oxygen species, antioxidants and signaling in plants. J Plant Biol 51:167–173

Pavlostathis SG, Comstock KK, Jacobson ME, Saunders FM (1998) Transformation of 2,4,6-trinitrotoluene by

the aquatic plant *Myriophyllum aquaticum*. Environ Toxicol Chem 17:2266
Petrucio MM, Esteves FA (2000) Uptake rates of nitrogen and phosphorus in water by *Eichhornia crassipes* and *Salvinia auriculata*. Rev Braz Biol 10:229–236
Popa K, Palamaru MN, Iordan AR, Humelnicu D, Drochioiu G, Cecal A (2006) Laboratory analyses of $^{60}Co^{2+}$, $^{65}Zn^{2+}$ and $^{(55+59)}Fe^{3+}$ radioactions uptake by *Lemna minor*. Isotopes Environ Health Stud 42:87
Rao TP, Ito O, Matsunga R (1993) Differences in uptake kinetics of ammonium and nitrate in legumes and cereals. Plant Soil 154:67–72
Reidenbach G, Horst WJ (1997) Nitrate-uptake capacity of different root zones of *Zea mays* (L.) *in vitro* and *in situ*. Plant Soil 196:295–300
Rice PJ, Anderson TA, Coats JR (1997) Phytoremediation of herbicide-contaminated surface water with aquatic plants. In: Kruger EL, Anderson TA, Coats JR (eds) Phytoremediation of soil and water contaminants. American Chemical Society, Washington, DC
Sandermann H (1992) Plant metabolism of xenobiotics. Trends Biochem Sci 17:82–84
Sandermann H (1994) Higher plant metabolism of xenobiotics: the green liver concept. Pharmacogenetics 4:225–241
Schnoor JL, Licht LA, McCutcheon SC, Wolfe NL, Carreira LH (1995) Phytoremediation of organic and nutrient contaminants. Environ Sci Technol 29:318–323
Shimp JF, Tracy JC, Davis LC, Lee E, Huang W, Erickson LE, Schnoor JL (1993) Beneficial effects of plants in the remediation of soil and groundwater contaminated with organic materials. Crit Rev Environ Sci Technol 23:41–77
Susarla S, Medina VF, McCutcheon SC (2002) Phytoremediation: an ecological solution to organic chemical contamination. Ecol Eng 18:647–658
Tangahu BV, Abdullah SRS, Basri H, Idris M, Anuar N, Mukhlisin M (2011) A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. Int J Chem Eng 2011:939161. doi:10.1155/2011/939161, 31 p
Van Aken B, Correa PA, Schnoor JL (2010) Phytoremediation of polychlorinated biphenyls: new trends and promises. Environ Sci Technol 44(8):2767–2776
Vymazal J, Kropfelova L (2008) Wastewater treatment in constructed wetlands with horizontal sub-surface flow, vol 14, Environmental pollution. Springer, Dordrecht
Wallace IS, Choi WG, Roberts DM (2006) The structure, function and regulation of the nodulin 26-like intrinsic protein family of plant aquaglyceroporins. Biochimica Biophyica Acta 1758:1165–1175
Wang C, Liu ZQ (2007) Foliar uptake of pesticides: present status and future challenge. Pest Biochem Physiol 87:1–8
Zhao F, McGrath SP, Meharg AA (2010) Arsenic as a food chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. Ann Rev Plant Biol 61:535–559
Zhu T, Sikora FJ (1994) Ammonium and nitrate removal in vegetated and unvegetated gravel bed microcosm wetlands. In: Proceedings of 4th international conference on wetland systems for water pollution control, ICWS'94, Secretariat, Guangzhou, People's Republic of China, pp 355–366
Zhu YG, Smolders E (2000) Plant uptake of radiocaesium: a review of mechanisms, regulation and application. J Exp Bot 51(351):1635–1645
Zhu YG, Shaw G, Nisbet AF, Wilkins BT (2000) Effect of potassium starvation on the uptake of radiocaesium by spring wheat (*Triticum aestivum* cv. Tonic). Plant Soil 220:27–34

4 Role of Wetlands

Land areas which are wet during part or all of the year are referred as wetlands. They are of two types: natural and artificial/constructed/man-made. Vegetation, soil and hydrology form the major components of wetlands. Aquatic plant species form a major part of both natural and constructed wetlands. Aquatic plant species play an important role in oxygen production, nutrient cycling, water quality improvement and sediment stabilization (Mohan and Hosetti 1999).

Aquatic plants are preferred over other biological agents due to their low cost, frequent abundance in aquatic ecosystems and easy handling. The microbial-rich rhizosphere of wetland plants is involved in degradation. Wetland technology gained importance because of its low operation and maintenance costs, low greenhouse effects and energy efficiency. These advantages make constructed wetlands a cheaper alternative to conventional treatment methods. Besides simplicity of operation and maintenance, treatment effectiveness, tolerance to fluctuations in hydraulic and constituent loading rates, and potential aesthetic attributes including increased green space, new wildlife habitat and additional recreational and educational areas also add to this. They have developed a strong potential for application in developing countries, particularly small rural communities.

Wetlands gained attention in recent years due to their inherent capacity for removing pesticides, surfactant, PCPs, pharmaceuticals and other microcontaminants (Knight et al. 1993a; Boreen et al. 2003; Gross et al. 2004; Conkle et al. 2008, 2012; Matamoros et al. 2008; Pal et al. 2010) and are believed to be natural sinks for many contaminants. Wetlands offer important ecological benefits complying with the good chemical status demands by the EU framework directive.

4.1 Constructed Wetlands (Man-Made, Artificial or Engineered Wetlands)

Constructed wetlands (CW/CTWs) are designed to improve water quality and the efficiency is dependent on plant processes (Kurzbaum et al. 2012; Anning et al. 2013). They are formed by the interaction of biological and physical components of the ecosystem capable of removing different types of contaminants from water. They mimic the functions of natural wetlands. Constructed wetlands have been used for removing a wide range of inorganic contaminants, including heavy metals, perchlorate, cyanide, nitrate and phosphate, as well as certain organic contaminants, including explosives and herbicides, and emerging contaminants such as pharmaceuticals, fragrances, antiseptics, fire retardants, herbicides and plasticizers (Haber et al. 2003; Birch et al. 2004; Braeckevelt et al. 2011; Budd et al. 2011; Bustamante et al. 2011; Haarstad et al. 2012). These have been successfully used to treat a wide variety of wastewaters including petroleum effluents, pulp and paper wastewater, refinery, and chlor-alkali effluent, landfill leachates, domestic

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Table 4.1 Constructed wetlands implemented successfully at different contaminated sites

Site	Contaminants	Medium	References
Lake Drainage District of San Joaquin Valley, Corcoran, California, USA	Se	Agricultural subsurface drainage	Gao et al. (2003)
Savannah River Site, Aiken, South Carolina, USA	Fe, Mn	Industrial effluent	Knox et al. (2006)
Lead–zinc mining facility (Tara Mines), Ireland	Pb, Zn, Fe	Mine wastewater	O'Sullivan et al. (2004)
Widows Creek electric utility, Alabama, USA; electrical power station at Springdale, Pennsylvania, USA	Co, Ni, Fe, Mn, Cd	Coal combustion by-product ash leachate	Ye et al. (1997a, b, c)
Iowa Army Ammunition Plant, Iowa, USA	TNT	Explosives-contaminated groundwater	Best et al. (1997)
Milan Army Ammunition Plant, Tennessee, USA	TNT, RDX	Explosives-contaminated groundwater	Best et al. (1999) and Sikora et al. (1995)
San Joaquin Valley, California, USA	Se	Effluents from oil refineries	Hansen et al. (1998)

wastewater, municipal wastewater, domestic sewage, agricultural wastewater, dairy wastewater and mine and drainage (DeBusk et al. 1996a; Kadlec and Knight 1996; DeBusk 1998; Kadlec 1998; Sobolewski 1999; Yang et al. 2007; Choudhary et al. 2011; Comino et al. 2011; Gustavsson, and Engwall 2012; Gunes et al. 2012; Idris et al. 2012; Lin and Han 2012; Sudarsan et al. 2012; Yu et al. 2012) (Table 4.1). Constructed wetlands have been found to be effective in treating domestic and municipal wastewater by reducing suspended solids, organic matter, phosphorus, nitrogen and pathogens (Hencha et al. 2003). During the last two decades, extensive literature in form of books has been published on various (technical and scientific) aspects of constructed wetlands (Jackson 1989; Livingston 1989; Knight et al. 1993b; Kadlec and Knight 1996; Vymazal et al. 1998; Kadlec and Wallace 2008; Matamoros and Bayona 2008).

Constructed wastewater treatment wetlands can be used to treat wastewater from different sources like:

- Sewage
- Municipal wastewater
- Septic tanks
- Storm water
- Agricultural wastewater (including livestock waste, runoff and drainage water)
- Landfill leachate
- Partially treated industrial wastewater
- Drainage water from mines
- Runoff from highways

4.1.1 Composition of Wetlands

Vegetation, soil and hydrology are the major components of all wetlands. Due to complex interaction in plants, microorganisms, soil matrix and substances in the wastewater, constructed wetlands have been considered 'black box' systems. Constructed wetlands are of different basic designs featuring different flow characteristics and consist of saturated substrates, vegetation and microbes. Root zone (or rhizosphere) is the active reaction zone of CWs where physicochemical and biological processes take place by the interaction of plants, microorganisms, the soil and pollutants. The rhizosphere of wetland plants provides an enriched culture zone for the microbes involved in degradation. The wetland sediment zone provides reducing conditions that are conducive to the metal removal pathway. The soil is the main supporting material for plant growth and microbial films. Hydraulic processes are influenced by soil matrix. Mixture of sand and gravel produces the best results in terms of both hydraulic conditions and the removal of contaminants. Soil physical parameters such as interstitial pore spaces and effective grain sizes considerably influence the flow of wastewater in constructed wetlands—and ultimately the removal of contaminants.

The removal of contaminants occurs via several mechanisms, including sedimentation, filtration, sorption, plant uptake and microbial breakdown. Inorganic and organic constituents present in wastewaters are treated in wetlands through various ways:

- Physically removed through filtration
- Biologically degraded to non-toxic forms
- Absorbed by wetland plants
- Adsorbed to media surfaces
- Chemically transformed and stored within the wetland matrix

Complex biological and physical environments of CWs collectively alter the chemical nature of contaminants. They detoxify wastewater by immobilizing and/or transforming pollutants to less toxic forms. The pollutants may be taken up into the plant tissues, where they are accumulated and biotransformed to less toxic or immobile states and/or volatilized to the atmosphere (Hansen et al. 1998; Qian et al. 1999; Zhu et al. 1999). In CWs treating domestic wastewaters, emerging contaminants are reported to be eliminated by photodegradation, biodegradation, sedimentation, plant uptake and/or adsorption (Matamoros and Bayona 2008). Apart from this, natural, restored and created wetlands that are fed with natural waters are also impacted by urban and agricultural runoff. Metalloids like Se and As can be transformed by both biological and chemical processes to a variety of forms that differ in mobility and toxicity (Terry et al. 2000).

4.1.2 Types of Wetlands

Treatment wetlands are generally classified as either free water surface (FWS) or subsurface flow (SSF) systems. Free water surface wetland (FWS) encompasses shallow water flowing over plant media mainly mineral (sandy) or organic (peat) soils underneath vegetation. Vegetation mainly consists of marsh plants, such as *Typha* and *Scirpus*, but may also include floating and submerged aquatic vegetation and wetland shrubs and trees. Free water surface wetlands vary dramatically in size, from less than 1 ha to greater than 1,000 ha. Free water surface wetlands offer ecological and engineering benefit. Free water surface wetlands are used for treating agricultural and urban runoff.

Subsurface flow (SSF) constructed wetlands (CWs) are one of the most common types of systems used throughout the world. Subsurface flow wetlands differ from FWS wetlands in that they incorporate a rock or gravel matrix so that the wastewater is passed through in a horizontal or vertical fashion. They consist of beds that are usually dug into the ground, lined, filled with a granular medium and planted with emergent macrophytes. Wastewater flows through the granular medium and comes into contact with biofilms and plant roots and rhizomes. SSF CWs are mainly designed to treat primary settled wastewater, although they are also commonly used to improve the quality of secondary effluents. Subsurface flow wetlands continue to provide effective treatment of most wastewater constituents through the winter in temperate climates. Contaminants are removed from wastewater in SSF CWs by physical, chemical and biological processes (García et al. 2010). Redox conditions prevailing in SSF CWs are linked to contaminant removal mechanisms. The main biological processes linked to organic matter transformation—aerobic respiration, denitrification, acid fermentation, sulphate reduction and methanogenesis. They are mainly involved in removal of surfactants, pesticides and herbicides, emergent contaminants, nutrients and heavy metals. Subsurface flow wetlands are the common system design implemented in Europe for domestic wastewater treatment, while in the United States (North America), the FWS type is more common (DeBusk and DeBusk 2001). FWS wetlands can commonly occur in communities with 1,000 or fewer people to a population greater than 1 million in cities.

Subsurface flow constructed wetlands are further subdivided into two types:

(a) Horizontal surface flow systems (HSF)—Wastewater is maintained at a constant depth and flows horizontally below the surface of the granular medium (Vymazal 2006).

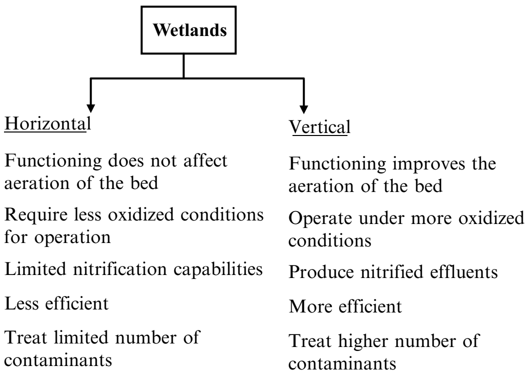

Fig. 4.1 Difference between horizontal and vertical wetlands

(b) Vertical flow systems (VFS)—Wastewater is distributed over the surface of the wetland and trickles downwards through the granular medium (Fig. 4.1).

Vertical systems can further be sorted in four types depending on the hydraulic regimes: unsaturated flow, permanently saturated flow, intermittent unsaturated flow and flood and drain wetlands. Concerns over matrix clogging and the potential high cost of renovation also limit the deployment of extremely large SSF wetlands.

4.1.2.1 Hybrid Treatment Wetlands

Two or more different types of wetlands are often combined to form hybrid wetlands to get higher removal efficiency. It is comprised of VF and HF beds that are arranged in a two-stage pattern to achieve higher treatment efficiency and is most widely used in Europe (Vymazal 2005; Kadlec and Wallace 2009). FWS wetlands have recently been hybridized with other VF and/or HF wetlands to improve nutrient and bacteria removal efficiency, to reduce the acreage necessary for target pollutant removal and/or to enhance habitat quality and ancillary benefits such as wildlife conservation and recreation (Vymazal 2005; Fleming-Singer and Horne 2006; Rousseau et al. 2008). A hybrid wetland also incorporates FWS wetlands dominated by free-floating aquatic vegetation (FFAV), emergent aquatic vegetation (EAV) or submerged aquatic vegetation (SAV) communities to achieve higher treatment efficiency, particularly for P removal. For example, the large-scale treatment wetlands in south Florida, collectively known as the Stormwater Treatment Areas, have been constructed to reduce P levels in agricultural runoff. A front-end treatment cell (dominated by *T. domingensis* and/or *T. latifolia* with other EAV and FFAV species) is used initially to treat runoff, and a back-end treatment cell (dominated by *C. demersum*, *N. guadalupensis*, *Chara* sp. and/or *Hydrilla verticillata*) is expected to reduce further P concentration of the effluent from the front-end cell.

Some treatment wetlands have been constructed that combine different wetland types. These include 134-ha Eastern Service Area wetland in Orlando, FL, which consists of constructed FWS wetlands that are followed by natural forested wetlands. Hybrid systems are based on need of specific contaminant removal. Enhanced nitrogen removal in SSF wetlands create an oxygenated environment that enhances nitrification in the rock or gravel matrix. Many subsurface wetlands accomplish this by sequencing horizontal flow beds with vertical flow beds to enhance nitrification (DeBusk and DeBusk 2001). Vertical flow beds have been combined to get enhanced removal of COD and nitrogen (Fig. 4.2).

4.1.3 Major Wetland Species

Macrophytes play an important role in wetlands. Emergent, submerged and/or free-floating aquatic species form a part of both natural and constructed wetlands (Brix 1994, 1997). The common species include *Scirpus maritimus*, *Scirpus cyperinus*, *Scirpus robustus* (salt marsh bulrushes), *Polypogon monspeliensis* (rabbitfoot grass), *Typha angustifolia, Typha latifolia* (cattail), *Typha orientalis*, *Typha minima*, *Juncus xiphioides* (Irish-leaved rush), *Phragmites australis* (Cav.) Trin., *Myriophyllum spicatum*, *Elodea* sp., *Pontederia cordata* L., *Cyperus alternifolius*, *Acorus calamus*, *Iris pseudacorus*, *Lythrum salicaria*, *Arundo donax*, *Juncus effusus, Azolla* sp., *Lemna* sp. and *Eichhornia crassipes*. Submerged aquatic vegetation species, such as *Ceratophyllum demersum*, *Elodea*

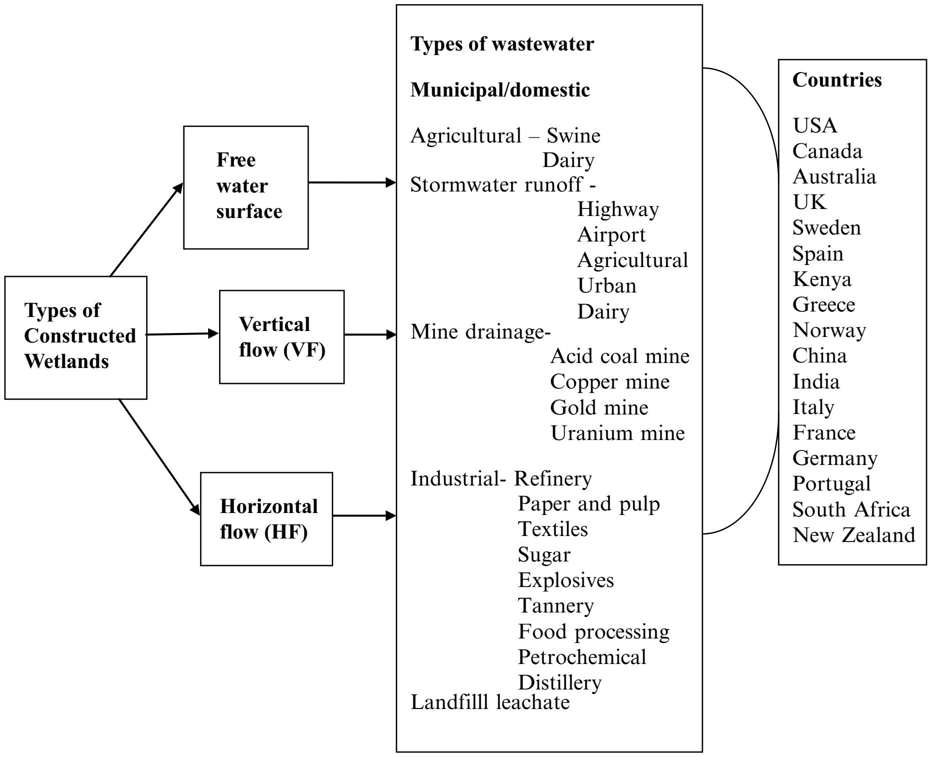

Fig. 4.2 Types of wetlands for removing wastewaters from different sources

nuttallii, *Potamogeton pusillus* and *Najas guadalupensis* are present in many natural and constructed wetlands (Chen 2011).

Free water surface wetlands comprise of macroscopic vegetation such as *Typha* and *Phragmites,* but more often they contain a diversity of other emergent and floating plants such as *Pontederia, Sagittaria, Eleocharis, Utricularia* and *Lemna.* Subsurface flow wetlands usually remain dominated by the species *Phragmites*, *Scirpus* and *Typha*. It is difficult to establish seeds and other propagules on the bed's surface because of high organic loading provided to SSF systems. *Typha latifolia* have been used successfully to treat groundwater contaminated with explosives and heavy metals from coal combustion by-product leachate. The growth and adaptation of plants to the anoxic conditions in wetland sediments drives many of the degradation processes (Horne 2000). For example, the activity of the plant roots alters the chemical conditions of the surrounding sediment, enhancing the rate of transformation and fixation of metals. In subsurface flow systems, aerobic processes only predominate near roots and on the rhizoplane (the surface of the roots). In the zones that are largely free of oxygen, anaerobic processes such as denitrification, sulphate reduction and/or methanogenesis take place.

4.1.4 Factors Affecting Functioning of Wetlands

1. The supply of oxygen plays a crucial role in the activity and type of metabolism performed by microorganisms in the root zone.
2. Selection of plant species to use in CWs is important, since plants are involved in the input of oxygen into the root zone, uptake of nutrients and direct degradation of pollutants.
3. The input of carbon from plants into their rhizosphere is known as rhizodeposition. Rhizodeposition products (exudates, mucigels,

dead cell material, etc.) cause various biological processes to take place in the rhizosphere. The chemical composition of the exudates is very diverse. Root exudates are sugars and vitamins such as thiamine, riboflavin and pyridoxine; organic acids such as malate, citrate, amino acids, benzoic acids and phenol; and other organic compounds. The range of substances varies from one species to other. Sugars and amino acids can be used by microorganisms as substrates, and excreted vitamins stimulate microbial growth. Furthermore, it has been shown that organic compounds released by plants and plant residues influence the microbial degradation of xenobiotics (Horswell et al. 1997; Moormann et al. 2002).

4.2 Mechanism of Contaminant Removal by Wetlands

Wetlands encompass many processes and mechanisms in the removal of contaminants. The basic three are physical, biological and chemical removal processes.

1. *Physical processes*—They are often used in primary treatment of wastewater. Surface water typically moves very slowly through wetlands due to the characteristic broad sheet flow and the resistance provided by rooted and floating plants. Water that flows through wetlands moves rather slowly due to resistance from plant matter and a uniform sheet flow of water. The plants in the wetland help trap sediment (DeBusk 1999a). By using gravity and the differences in relative densities of suspended material, particles are allowed to settle in the wetland. Mats of floating plants in wetlands may serve as sediment traps, but their primary role in suspended solids removal is to limit resuspension of settled particulate matter. Sedimentation of suspended solids is promoted by the low flow velocity and by the fact that the flow is often laminar (not turbulent) in wetlands.
2. *Biological processes*—It represents a prominent pathway of contaminant removal in wetlands (DeBusk 1999a). This involves phytodegradation, rhizodegradation and phytovolatilization processes. Wetland plants readily take up essential nutrients, such as nitrate, ammonium and phosphate and metals (Cheng et al. 2009a, b). The rate of contaminant removal by plants varies widely, depending on the plant growth rate and the concentration of the contaminant in the plant tissue. Woody plants, trees and shrubs provide relatively long-term storage of contaminants compared with herbaceous plants. Contaminant uptake rate per unit area of land is often much higher for herbaceous macrophytes such as *Typha*. Algae also provide a significant amount of nutrient uptake but are relatively susceptible to the toxic effects of heavy metals. Bacteria and other microorganisms also provide uptake and short-term storage of nutrients and some other contaminants in the soil (Stottmeister et al. 2003). Plants directly take up contaminants into their root structure and secrete substances that add to biological degradation, and contaminants that entered the plant biomass are transpired through the plant leaves. Microorganisms in wetland soils take up and store nutrients but the metabolic functions assist in organic pollutant removal. The bacteria, mostly present in soil, use the carbon found in organic matter as an energy source and convert to carbon dioxide in aerobic conditions and methane in anaerobic conditions. The microbial metabolism is also very important in the removal of inorganic nitrogen (DeBusk 1999a).
3. *Chemical processes*—This process includes sorption, photo-oxidation, and volatilization. Sorption is the most important chemical process which results in short-term retention or long-term immobilization of several classes of contaminants. It involves the moving of charges or transfer of ions (or molecules with positive or negative charges) from the aqueous phase (water) to the solid phase (soil). Sorption includes the processes adsorption and precipitation. Adsorption refers to the attachment of ions to soil particles, either by cation exchange or chemisorption. Cation exchange involves the physical attachment of

cations, or positively charged ions, to the surfaces of clay and organic matter particles in the soil. Cations are bonded to the soil by electrostatic attraction. Many contaminants in wastewater and runoff exist as cations. Cation exchange capacity (CEC), i.e. capacity of soils for retention of cations, generally increases with increasing clay and organic matter content. Photo-oxidation utilizes the power of sunlight to break down and oxidize compounds. Volatilization breaks down the compound and expels it into the air as a gaseous state (DeBusk 1999a; DeBusk and DeBusk 2001).

4.3 Contaminants Removed by Wetlands

In CWs, domestic wastewaters and emerging contaminants are eliminated by photodegradation, biodegradation, sedimentation, plant uptake and/or adsorption (Matamoros and Bayona 2008). Wastewater is detoxified by immobilizing and/or transforming pollutants to less toxic forms (Fig. 4.3).

4.3.1 Inorganic Contaminants

Wetlands have shown capacity to treat inorganic contaminants such as metals, nutrients and radionuclides.

4.3.1.1 Metals

Metal (Al, As, Cd, Co, Cu, CN-, Fe, Pb, Mn, Ni, U and Zn) removal in natural wetlands has been widely reported (Hadad et al. 2010; Knox et al. 2010; Marchand et al. 2010; Lesage et al. 2007a, b; Groza et al. 2010; Dotro et al. 2012). Metal removal in wetlands depends on the type of element, their ionic forms, substrate conditions, season and plant species. Metal removal in wetlands occurs by plant uptake, soil adsorption, precipitation and cation exchange through plant-induced chemical changes in rhizosphere.

The major mechanisms of metal removal in wetlands have been summarized as follows:

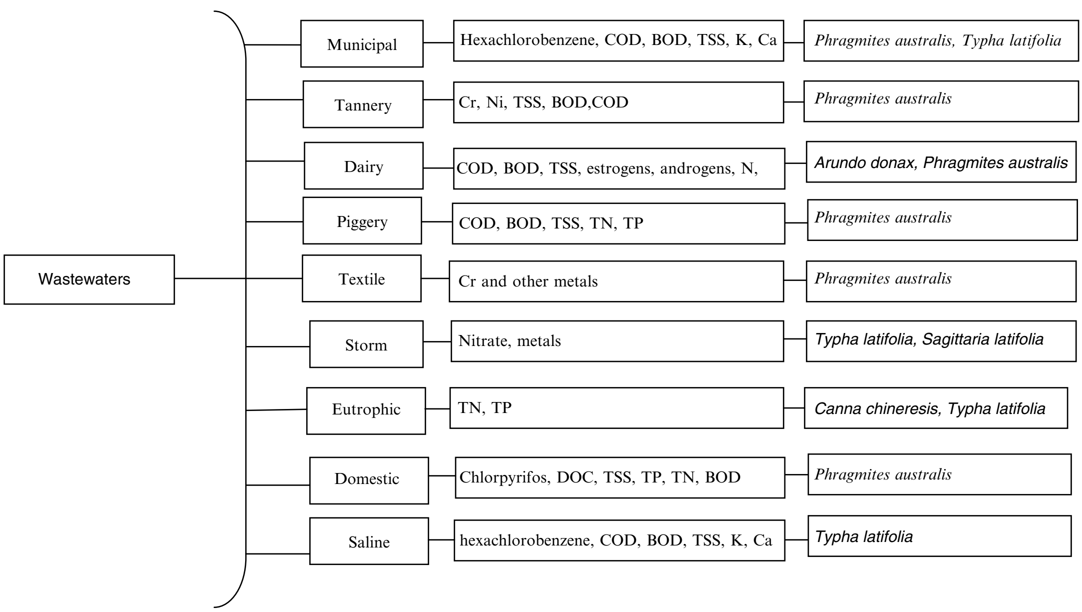

Fig. 4.3 Types of wastewaters treated by wetlands. (*COD* Chemical oxygen demand, *BOD* Biochemical oxygen demand, *TN* total nitrogen, *TP* total phosphorus, *TSS* total suspended solids, *DOC* Dissolved organic carbon)

- Sorption and/or exchange onto organic matter (detritus)
- Filtration of solids and colloids
- Formation of carbonates
- Association with iron and manganese oxides
- Metal hydrolysis (catalyzed by bacteria under acidic conditions)
- Reduction to nonmobile forms (also catalyzed by bacteria)
- Formation of insoluble metal sulphide precipitates resulting from microbial reduction
- Biological methylation followed by volatilization
- Ion-exchange capacity of the mineral and humic fractions of soil
- Accumulation into plant matter
- Coprecipitation of some elements such as arsenic with iron

Lesage et al. (2007b) reported adsorption and precipitation as insoluble salts (mainly sulphides and oxyhydroxides), deposition and rhizosphere activity as the main mechanisms for metal removal. Adsorption is an important mechanism for removal of metals in wetlands. It involves transfer of ions from a soluble phase to a solid phase and results in short-term retention or long-term stabilization. Metals are adsorbed to particles of fine-textured sediments and organic matter by either ion exchange depending upon factors such as the type of element or the presence of other elements competing for adsorption sites (Seo et al. 2008). Metals such as Fe, Al and Mn form insoluble compounds through hydrolysis and/or oxidation. This leads to formation of a range of oxides, oxyhydroxides and hydroxides (Sheoran and Sheoran 2006). Fe(II) can be oxidized to Fe(III) which can deposit onto root surfaces of aquatic macrophytes (Weiss et al. 2003), forming plaques with a large capacity to adsorb metals (Cambrolle et al. 2008), aided by the action of Fe(II)-oxidizing bacteria. Fe(III) can precipitate to produce oxides, hydroxides and oxyhydroxides. Fe(II) can also precipitate as oxides (Jonsson et al. 2006) or coprecipitate with other metals such as Zn, Cd, Cu or Ni (Matagi et al. 1998). Arsenic may also be removed from the water column by adsorbing onto amorphous iron hydroxides or by coprecipitating with iron oxyhydroxides. Absorption and deposition of suspended solids in sediments is followed by accumulation of some amount by plants and bacteria (Kadlec and Knight 1996). The efficiency of systems depends strongly on (1) inlet metal concentrations and (2) hydraulic loading (Kadlec and Knight 1996).

Metals can also form insoluble compounds through reduction. Under chemically reducing conditions ($Eh < 50$ mV), sulphates can be reduced to sulphides. Reductive conditions into the substrate (Dorman et al. 2009) promote massive ion release, particularly of Fe and Mn, into the water by reduction of the oxides and oxyhydroxides trapped in the substrate. Precipitation of metal as oxides or adsorption onto organic matter is dependent upon redox potential. At redox potential above 100 mV, metal oxides are reduced, resulting in a release of dissolved metals, while below 100 mV, metals may be mainly associated with sulphides. Most macrophytes play a role in maintaining oxidizing conditions by shoot-to-root oxygen transport. Such conditions promote formation of iron oxides, hydroxides and oxyhydroxides, such as the iron plaques, and consequently result in metal removal by adsorption and coprecipitation. Since As(III) is more mobile and toxic than As(V), active As remediation may require conversion of As(III) to As(V) in the rhizosphere and subsequent immobilization of As(V) by adsorption or coprecipitation (Guan et al. 2009). Fe oxides in the rhizosphere have a strong adsorptive capacity for arsenate. Arsenic is not the only inorganic ion present in natural waters, and adsorption of As(V) and As(III) oxyanions by ferric hydroxide may be adversely affected by anions such as carbonate, sulphate, phosphate and silicate and also by organic matter.

Metals may also form metal carbonates. Although carbonates are less stable than sulphides, they can contribute to initial trapping of metals (Sheoran and Sheoran 2006). The pH strongly affects the efficiency of metal removal in wetlands. Ammonium conversion into nitrites during nitrification leads to proton production.

These hydrogen ions are then neutralized by bicarbonate ions. Macrophytes, in releasing oxygen, promote the nitrification process. Protons produced due to nitrification may not all be neutralized by HCO_3^- ions, resulting in a pH decrease. Alkaline conditions are necessary to promote coprecipitation of cationic metals, such as Cu, Zn, Ni and Cd. A high rate of nitrification can therefore reduce the efficiency of a constructed wetland in terms of cationic metal removal. In the special case of acid mine drainage, the water and substrates are characterized by high metal concentrations and a low pH.

Macrophytes, such as *Phragmites australis*, promote sedimentation of suspended solids and prevent erosion by decreasing water flow rates by increasing the length per surface area of the hydraulic pathways through the system (Lee and Scholz 2007). Under static conditions, the wetland behaves like a stagnant pond in which displacement effects caused by submerged plant mass decrease retention times. Retention times increase with increasing vegetation density, thus enabling better sedimentation. Flocs may adsorb other types of suspended materials, including metals.

Rhizosphere bacteria possess an ability to utilize efficiently growth substrates available in the rhizosphere and to cope with toxic environments due to the presence of detoxifying enzymes (Chaudhry et al. 2005). The genera commonly found in rhizospheres include *Rhizobium, Azotobacter and Pseudomonas*. Besides forming a habitat for microorganisms, plant roots also provide substrates such as sugars in exchange for phosphate or nitrogen (N_2 fixation). Organic compounds exuded by the roots, fungi and bacteria, e.g. saponins, proteins and enzymes, may mobilize soil-born pollutants, including metals. Sulphate-reducing bacteria such as *Desulfovibrio* spp. take part in the reduction of sulphates to sulphites and subsequently to sulphides (Garcia et al. 2001). Then these sulphides react with metals such as Cu, Zn and Fe to form insoluble precipitates (Murray-Gulde et al. 2005b). Optimal conditions for sulphate-reducing bacteria are redox potentials lower than 100 mV and pH greater than 5.5 (Garcia et al. 2001). Precipitation of metal sulphides in an organic substrate improves water quality by decreasing the mineral acidity without causing an increase in proton acidity (Sheoran and Sheoran 2006). Macrophytes transport oxygen to their rhizosphere. This, coupled with the action of nitrifying bacteria such as *Nitrosomonas* spp. and *Nitrobacter* spp., enables ammoniacal N removal of the soil environment (Lee and Scholz 2007). Furthermore, oxidizing soil conditions promote formation of iron oxides, hydroxides and oxyhydroxides and consequently result in metal removal by coprecipitation.

Metal removal have been reported by *Phragmites australis, Phragmites karka, Phalaris arundinacea, Typha domingensis* and *Typha latifolia* (Lesage et al. 2007a; Vymazal et al. 2007; Maine et al. 2009; Scholz and Hedmark 2010). Metals are efficiently removed by plants, and this mainly occurs by immobilizing them in the rhizosphere and storage in the below-ground biomass (Baldantoni et al. 2009; Zhang et al. 2010). Macrophytes remove only a small amount of metals most of which is taken up by root and only a small amount is transported to shoot (Lee and Scholz 2007). Poor translocation may be due to sequestration of most of the metals in the vacuoles of root cells to escape toxic effects. Plants trap metals into the substrate via rhizodeposition (Kidd et al. 2009). Root-exuded organic acids such as citrate, oxalate, malate, malonate, fumarate and acetate chelate metallic ions to varying degrees and thus decrease their phytotoxicity (Chaudhry et al. 2005). Floating aquatic plants provide good metal absorption (Vymazal et al. 1998). The species include *Eichhornia crassipes, Pistia stratiotes* and *Salvinia herzogii* (Maine et al. 2001, 2004; Suné et al. 2007; Dhote and Dixit 2009). Floating plants do not actively promote metal adsorption to the substrate, but store them into their biomass. Submerged aquatic plants such as *Potamogeton* spp., *Ceratophyllum demersum, Myriophyllum spicatum* and *Hydrilla verticillata* possess high potential to decontaminate water (Bunluesin et al. 2007). Nyquist and Greger (2009) proposed to use submerged plants to stabilize acid mine drainage because these plants take up more metals, using their whole biomass. Submerged macrophytes are probably not suitable for the conditions prevailing in acid mine drainage because of excessive Fe precipitation onto their surfaces, which inhibits light penetration and photosynthesis (Nyquist and Greger 2009). Removal of metals (Al, As, Cd, Co, Cu, Fe, Pb, Mn, Ni, Se, U and Zn) present in mine drainage have been documented. Aquatic macrophytes play an essential role in creating the environment for metal uptake, but their removal of metals usually accounts for a minor proportion of the total mass removed. Metals such as Al, Fe and Mn are often removed by hydrolysis. The resulting acidification of water buffered by alkalinity produced in wetland sediments by anaerobic bacteria. Bacterial sulphate reduction accounts for much of this alkalinity. It can also contribute significantly to metal removal by formation of insoluble sulphides. Other important processes include the formation of insoluble carbonates, reduction to nonmobile forms and adsorption onto iron oxides and hydroxides.

Wetland plants can accumulate heavy metals in their tissues. Previous studies indicated that some wetland plants have the ability to take up > 0.5 % dry weight (DW) of a given element and bioconcentrate the element in its tissues to 1,000-fold the initial element supply concentration. For instance, duckweed (*Lemna minor*) and water hyacinth (*Eichhornia crassipes*) are excellent accumulators of Cd (6,000–130,000 mg kg^{-1} DW) and Cu (6,000–7,000 mg kg^{-1} DW) (Zayed et al. 1998; Zhu et al. 1999). The plants are capable of storing large amounts of metals in plant biomass and in its roots (DeBusk 1999b). Many wetland plants accumulated higher concentrations of metals in roots than in shoots (Ye et al. 1997a, b, c; Deng et al. 2004, 2006). Hyperaccumulators have been part of many wetlands. Constructed wetlands have been used for removing significant levels of trace elements such as Se, As and B from the effluent (Terry et al. 2000; Ye et al. 2003). Plants are used in conjunction with microbial activity associated with the plants to extract, accumulate and volatilize Se. Once absorbed by plant roots, Se is translocated to the shoot where it may be harvested and removed from the site. A successful implementation of constructed wetlands for removing significant levels of trace elements such as selenium (Se) from the effluents was seen at oil refineries at San Francisco Bay Delta and Tulare Lake Drainage District of San Joaquin Valley, California. Some proportion of the soluble Se entering the wetland became chemically reduced and bound to sediments, but a major portion of it was absorbed by plants, accumulated in roots and volatilized. The plants and microbes (present in the roots) took up Se mainly in the form of selenate or selenite and metabolized it to volatile forms like dimethyl selenide (DMSe), which escaped to the atmosphere, minimizing the effects to other components of food chain. The process was referred as biological volatilization. Volatilization of Se involves the assimilation of inorganic Se into the organic selenoamino acids selenocysteine (SeCys) and selenomethionine (SeMet) (Hafeznezami et al. 2012). Accumulation in plant tissues accounted for only 2–4 %, while 3 % of the Se was removed by biological volatilization to the atmosphere. Cattail, Thalia and rabbitfoot grass are highly tolerant species and exhibit no growth retardation. In the aqueous phase of surface flow wetlands to treat mine drainage, Fe(II) is oxidized to Fe(III) by abiotic and microbial oxidation. Other heavy metals are immobilized in the mainly anoxic soil by microbial dissimilatory sulphate reduction and the H_2S formed. Constructed wetlands using emergent plant species such as *Scirpus cyperinus*, *Myriophyllum spicatum* and *Typha latifolia* have been used successfully to treat groundwater contaminated with heavy metals from coal combustion by-product leachate.

Carex pendula, a common *wetland* plant found in Europe, accumulated considerable amounts of Pb, particularly in root biomass, and contributed to cleanup of Pb contaminated wastewaters. The *wetland* system efficiently removed U (95 %) from contaminated water from the tailing pond located near U processing plant. *Typha domingensis* used in constructed *wetland* receiving metallurgical effluent showed higher affinity for metal (Cr, Ni and Zn) and total phosphorus removal. The chlorophyll concentration showed maximum sensitivity to effluent toxicity in comparison to other parameters such as biomass and plant height. The highest root and stele cross-sectional areas, number of vessels and biomass registered in inlet plants promoted the uptake, transport and accumulation of contaminants in tissues. The adaptability of *T. domingensis* to the prevailing conditions in the constructed wetland allowed it to become the dominant species and enabled the wetland to maintain a high contaminant retention capacity. The pattern of metal distribution in wetland plants is suitable to restrict metals being transported from roots to shoots. However, the degree of upward translocation is dependent on plant species, particular metal and a number of environmental conditions, such as pH, redox potential (Eh), temperature and salinity (Fitzgerald et al. 2003; Fritioff et al. 2005). In addition, other factors, such as soil particle size, organic matter content, nutrients and the presence of other ions may also influence metal uptake by wetland plants (Greger 1999). The soils present in the wetland immobilize heavy metals in a highly reduced sulphite or metallic form. The roots act as filters, removing suspended particles from the water through mechanical and biological activity. Phytostabilization is the major approach for immobilization of metals in plants and storage in below-ground parts such as root and soil, while phytoextraction involves the use of hyperaccumulators to remove metals. Ion uptake results from the contact of the plant with the medium and occurs directly through leaf cells. The site of metal accumulation and form in which they are absorbed varies from species to species. The submerged aquatic plant species such as *Elatine triandra* accumulate heavy metals such as As mainly in organic forms (e.g. methylarsonic acid and methylarsinic acid), while semiaquatic plant species such as *Spartina alterniflora* and *Spartina patens* accumulate inorganic arsenic in roots, and organic form dimethylarsenic acid is translocated to shoots.

The tolerance mechanism in plants includes the sequestration of metals in tissues or cellular compartments (vacuoles), restricting the movement to shoots (avoidance). The plant species also tend to alter speciation of metals in the process of uptake/removal. For example, the uptake of Cr^{6+} by *Eichhornia crassipes* subsequently results in the reduction of toxic Cr^{6+} to less toxic Cr^{3+}. The root surface of wetland plants possesses some specialized structures called metal-rich rhizoconcretions or plaques, which are mainly composed of iron hydroxides and/or Mn, which are immobilized and precipitated on the root surface. The plaques restrict metal uptake at low pH conditions but enhance that at higher pH (Dhir et al. 2009; Dhir 2010). The rhizosphere associated with the plants also plays an important role in the degradation and breakdown of contaminants.

Plants resist excessive exposure through several routes. One mechanism is biomineralization onto roots leading to metal precipitation. Another is formation of complexes with glutathione (GSH) and transport into the vacuole (e.g. unidentified ATP-binding cassette transporter of As(III)-GS3 or Cd(II)-GS2 (Verbruggen et al. 2009)) where high molecular weight complexes (HMWC) may be formed that contain sulphides (S2_). The third is production of organic ligands rich in cysteine and non-protein thiols (NP-SH), such as phytochelatins (PC) and metallothioneins (MT). Phytochelatins chelate metals and complexes to be transported into the vacuoles (Pal and Rai 2010). Metallothioneins and metallochaperones contribute to maintain the homeostasis, bind metals and protect against oxidative stress. The fourth mechanism is hyperactivity of antioxidant systems to minimize reactive oxygen species (ROS) (Sharma and Dietz 2009). *Potamogeton pusillus* responds positively to short Cu exposure by inducing activity of antioxidant enzymes like glutathione peroxidase (GPX), glutathione reductase (GR) and peroxidase (POD) (Monferran et al. 2009). In *Najas indica* exposed to Pb, the activities of antioxidant enzymes such as superoxide dismutase (SOD), ascorbate peroxidase (APX), guaiacol peroxidase (GPX), catalase (CAT) and glutathione reductase (GR) were elevated along with the induction of the antioxidants GSH, cysteine, ascorbic acid and proline (Singh et al. 2010). *Iris pseudacorus* also responds to Pb and Cd exposure by enhancing POD activities and proline concentrations in roots and shoots. Exposure of *Egeria densa* to Cd resulted in both a formation of thiol-enriched Cd complexing peptides and a synthesis of low molecular weight, unidentified metal chelators in shoots. Cd and Cu exposure also lead to coordinated responses of PC synthase (PCS) and MT genes in black mangrove *Avicennia germinans*. Both MT and PCS gene expression increased in *A. germinans* leaves in response to metal exposure, which supports the hypothesis that MTs and PCS are part of the metal tolerance mechanism in this species (Gonzalez-Mendoza et al. 2007).

Wetland plants tolerate heavy metals by various means such as (Yang and Ye 2009) the following:

(a) Restricting upward movement into shoots and translocation of excessive metals into old leaves before shedding or secreting excessive metals by special organs such as salt glands. Some studies show that *Avicennia marina* and *Spartina alterniflora* can excrete metals in salt crystals released through hydathodes (salt glands) (Kraus 1988; MacFarlane and Burchett 2000).

(b) Sequestering heavy metals in organs or subcellular compartments with little or no sensitive metabolic activity. Vesk et al. (1999) found that Cu and Zn mainly localized inside cells of roots of free-floating water hyacinth (*E. crassipes*), with a less but significant amount in the stele cell wall, whereas Zn and Cu increased centripetally in the stele cell walls. In the roots of grey mangrove (*Avicennia marina*), metals (Cu, Pb and Zn) were concentrated predominantly in cell walls (MacFarlane and Burchett 2000).

(c) Synthesizing phytochelatins (PCs), peptides and exudates to chelate-free metal ions or increasing antioxidant enzyme activities. Fediuc and Erdei (2002) studied the physiological and biochemical aspects of Cd-protective mechanisms induced in *P. australis and T. latifolia*. Different defence strategies were operated by the two species under Cd stress. In *Typha*, the increasing accumulation of Cd was in positive correlation with the increases in free thiol content, while in *Phragmites,* glutathione reductase, catalase and peroxidase activities were increased. The authors concluded that *Typha* relies more on thiol induction and metal binding for metal avoidance, while *Phragmites* is based on increased antioxidant enzyme activities and thus scavenging of active oxygen species.

(d) Presence of microbial symbionts in rhizosphere soils. The presence of periphyton associated with the root of *P. australis* in freshwater wetlands enhanced the ability of the reed to accumulate and retain metals. However, Khan et al. (2000) suggested that mycorrhizae play a protective role, restricting the uptake of metals by plants through immobilizing metals in the fungal tissues.

(e) Iron plaque as a barrier to heavy metals. Fe plaque may act as a barrier to toxic metals. Otte et al. (1989) found that a heavy coating of Fe plaque may act as a barrier to Zn uptake. Iron plaques have also been shown to act as a filter for the movement of Fe, Cu, Zn, Ni and Cd into rhizomes and shoots. This may be achieved by adsorption onto Fe compounds or coprecipitation (Bostick et al. 2001; Hansel et al. 2002). However, other studies have shown that Fe plaque does not impede the uptake of toxic metals although it can immobilize metals.

Usefulness in large-scale constructed wetlands is uncertain, particularly due to their low winter performance and the necessity for harvesting biomass in order to maintain an efficient system (Kivaisi 2001). On the other hand, the role of plants as suppliers of organic matter is far more important, and so differences in metal accumulation between the two types are minor.

Microorganism-mediated alteration of metals occurs via oxidation and reduction. Furthermore, oxidizing soil conditions promote formation of iron oxides, hydroxides and oxyhydroxides and consequently result in metal removal by coprecipitation. Bacteria participate in oxidation of sulphides to sulphites and then to sulphates. Because sulphides take part in metal coprecipitation in the substrate, oxidation may lead to metal mobilization. Under reducing conditions, sulphate-reducing bacteria such as *Desulfovibrio* spp. take part in the reduction of sulphates to sulphites and subsequently to sulphides. Then these sulphides react with metals such as Cu, Zn and Fe to form insoluble precipitates. Optimal conditions for sulphate-reducing bacteria are redox potentials lower than 100 mV and pH greater than 5.5. Precipitation of metal sulphides in an organic substrate improves water quality by decreasing the mineral acidity without causing an increase in proton acidity.

Role of Plants

Macrophytes are key players in wetlands, both natural and constructed. Plant-derived organic matter in wetlands over time continuously provides sites for metal sorption, as well as carbon sources for bacterial metabolism, thus promoting long-term functioning.

Emergent Plants

Several emergent plants have been tested in constructed wetlands, achieving variable metal removal rates. *Phragmites australis* is the species used most. *Phalaris arundinacea* displays capacities similar to *Phragmites australis*, as do *Typha domingensis, Typha latifolia* and *Phragmites karka*. Suspended organic matter and metals are efficiently removed in the presence of plants mainly by immobilization in the rhizosphere and storage in the below-ground biomass (Baldantoni et al. 2009; Zhang et al. 2010; Abou-Elela and Hellal 2012). The highest plant metal concentrations occur in the winter in rhizomes (Baldantoni et al. 2009), but overall, less than 2 % of the trapped metals are stored in the plant biomass (Lee and Scholz 2007). Therefore, macrophytes are not important sinks for metal removal. Generally, only a small amount of metals taken up by roots is transported to the shoots. Long-distance translocation of metal ions between roots and shoots is summarized elsewhere (Lu et al. 2009). Poor translocation may be due to sequestration of most of the metals in the vacuoles of root cells, which may be a natural response to alleviate potentially toxic effects (Shanker et al. 2005). However, other studies have shown that metals such as Cr are efficiently stored into the whole plant (Zhang et al. 2010). Plants certainly contribute to metal trapping into the substrate via rhizodeposition.

4.3.1.2 Nitrogen

Nitrate removal in wetlands is usually very high (DeBusk 1999b; Correa-Galeote et al. 2013; Lee et al. 2012). The removal of nitrogen using wetlands involves a number of processes. These processes include ammonia volatilization, ammonification, nitrification, denitrification, plant and microbial uptake, ammonia adsorption, organic nitrogen buria l and ANAMMOX (anaerobic ammonia oxidation). All processes reduce the amount of nitrogen in the system. Nitrogen removal in *wetlands* occurs from direct assimilation by plants and through microbial nitrification and denitrification. The spatial distribution of the N-cycling microbial communities of sediments was heterogeneous and complex. Nitrogen exists in many forms such as inorganic and organic forms. Inorganic nitrogen includes nitrates, nitrites and ammonium. In natural environments where oxygen is in surplus, nitrogen usually exists as nitrates and nitrites. In environments that lack oxygen, nitrogen is available as ammonium in wetland soils. Nitrogen present in wetlands is either taken up by plants or broken down by microorganisms. Plants use nitrates and ammonium as nutrients which can be stored as organic nitrogen. Microorganisms break down inorganic nitrogen mostly by denitrification which convert nitrate to nitrogen gas. Ammonia taken up by plants is converted to nitrate by nitrification.

Steps involved in nitrogen removal in wetlands include the following:

1. Ammonification—It is the process where organic nitrogen is converted to ammonia. The process converts amino acids into ammonia. The majority of ammonification is done by anaerobic and obligate anaerobic mineralization. The rates of ammonification depend on temperature, pH, C/N ratio, available nutrients and soil conditions. This step is crucial before ammonium is then absorbed by plants, solubilized and returned to the water column, converted to gaseous ammonia or aerobically nitrified by aerobic organisms (EPA 1999).

2. Nitrification—Ammonia is biologically oxidized to nitrite and then finally to nitrate. Nitrifying bacteria utilize carbon dioxide as a carbon source and oxidize ammonia or nitrite to derive energy. Nitrification is carried out by two types of nitrifying organisms. The first step converts ammonium to nitrite (aerobic conditions), and the second converts nitrite to nitrate. Soil organisms include *Nitrosospira, Nitrosovibrio, Nitrosolobus, Nitrosococcus* and *Nitrosomonas*. The second step converts nitrite to nitrate and is accomplished by facultative chemolithotrophic bacteria which can utilize organics for cell growth an energy. The only organism found in soil of freshwater which oxidizes nitrites is *Nitrobacter*. Nitrification also is influenced by temperature, pH, alkalinity present and dissolved oxygen. The ideal temperature is from 30 to 40 °C. The pH values range from 6.6 to 8.8 and proper amounts of alkalinity and dissolved oxygen must be present.

In wetlands, the nitrogen removal process starts with the nitrification. It is a two-step process, where the nitrogen fixing bacteria takes energy from the process of ammonification and carbon source to convert nitrogen to different forms (He et al. 2012). Ammonia ion is oxidized in the presence of oxygen by *Nitrosomonas* bacteria.

$$NH_4^+ + O_2 \rightarrow NO_{2^-} + 2H^+ + H_2$$

The nitrite is then oxidized to nitrate in the absence of oxygen by the nitrobacter bacteria.

$$2NO_{2^-} + O_2 \rightarrow 2NO_{3^-}$$

The next step is denitrification, where nitrates are reduced to organic N. Denitrification occurs under anaerobic conditions and in the presence of organic matter—which is the carbon source. This reaction is catalyzed by *Pseudomonas* sp. bacteria. The N formed from denitrification is released in to the atmosphere in the form of nitrous oxide, thereby removing nitrogen from the wetland system.

$$NO_{3^-} + C(\text{organic}) \rightarrow N_2 + CO_2 + H_2O$$

Nitrification is effected by factors like availability of dissolved oxygen, temperature and pH of the wastewater. Denitrification is effected by factors like absence of oxygen, temperature, pH, availability of carbon source, nitrate availability, hydraulic load and HRT. Nitrogen in wetlands can also be removed by nutrient uptake of plants. The plants uptake nitrogen in the form of ammonium or nitrate, which is then stored in the plant in the organic form. The uptake capacity of emergent plant species in constructed wetlands can vary from 200 to 2,500 $kg.ha^{-1}$ $year^{-1}$. Factors effecting nutrient uptake of plants is growth rate of plants, concentration of nutrients in the plant tissues and climatic conditions. The major portion of the nitrogen removal is through bacterial conversion as compared to nutrient uptake by plants.

Major nitrogen transformations occur in a FWS wetland. *Bacillus, Micrococcus* and *Pseudomonas* are important denitrifying organisms in soils, and *Pseudomonas, Aeromonas* and *Vibrio* are important in aquatic environments. In the presence of oxygen, the organisms break down organics into carbon dioxide and water. The electron transport system enables the organisms to denitrify in anaerobic conditions. Under low oxygen levels, the production of nitrite from ammonia is favoured over nitrate formation from ammonia. There are a variety of wetland plants that can fix nitrogen but the process requires a large amount of cellular energy (Vymazal 2006). Biological removal involves uptake and assimilation of nitrogen by wetlands plants that convert inorganic nitrogen to organic nitrogen. The assimilated nitrogen is further converted to ammonia and nitrate. Burial of organic nitrogen leads to its incorporation into wetland soil.

FWS wetlands have different ways of removing nitrogen than VSB wetlands. Plant uptake is the primary mechanism for reducing nitrogen in FWS wetlands. Volatilization also offers large reducer of nitrogen in FWS wetlands. Ammonification gets organic nitrogen in the state of ammonia so that it can be removed by other processes. Denitrification is the primary mechanism of removing nitrogen in wastewater wetlands (Vymazal 2006).

Above-ground biomass and total biomass were significantly correlated with ammonia nitrogen removal and below-ground biomass with soluble reactive phosphorus removal. In subsurface horizontal flow systems, the oxidized nitrogen is immediately reduced, preventing the enrichment of nitrite and nitrate. Horizontal subsurface flow constructed wetlands in the Mediterranean and continental Mediterranean region of Spain planted with *Phragmites australis* showed higher ammonium mass removal efficiency in the summer than in the winter. Fibrous-root plants showed significantly greater root biomass and a larger root surface area per plant than the rhizomatic-root plants and exhibited accelerated growth in both shoots and roots compared to the rhizomatic-root plants (Obarska-Pempkowiak and Gajewska 2003, 2004; González-Alcaraz et al. 2012). The wetland microcosms planted with fibrous-root plants showed significantly higher ammonium–nitrogen (NH_4–N) and nitrate–nitrogen (NO_3–N) removal rates than those planted with the rhizomatic-root plants. Studies suggested that root characteristics of wetland plants related to root distribution and decontamination ability are critical for selection of wetland plants with a higher contaminant removal capacity and in the construction of a multi-species wetland plant community (Fig. 4.4).

The hybrid constructed wetlands ensure more stable removal rates of nitrogen in comparison to one-stage systems. The removal of nitrogen takes place in VF beds and HF beds (denitrification), but efficiency of nitrogen removal by nitrification was limited in VF beds in wetland systems. Studies indicate that pilot-scale and full-scale surface constructed wetlands remove COD, total suspended solids, nitrate and ammonium and hence improve water quality of waters (Díaz et al. 2012). Simulated vertical flow constructed wetlands (VFCWs) planted with *Canna indica* showed significant removal of nitrogen (N), ammonium N (NH_4^+–N) and phosphorus (P). Lower hydraulic loading rate or longer hydraulic retention time (HRT) result in a higher removal of TP, NH_4^+–N and TN because of more contacts and interactions among nutrients, substrates and roots under the longer HRT (Cui et al. 2010).

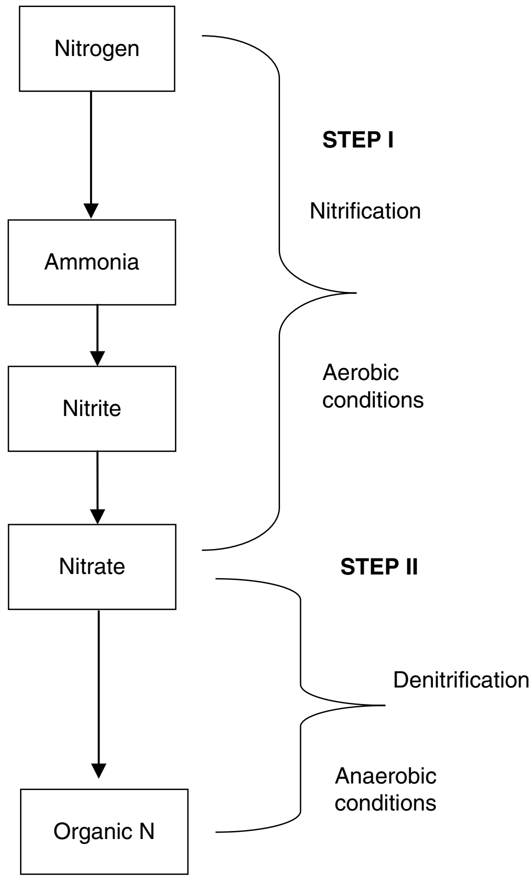

Fig. 4.4 Steps involved in nitrogen removal from wetlands

4.3.1.3 Phosphorus

Wetlands do not provide the direct metabolic pathway to remove phosphorus. The major phosphorus transformation in wetlands is done by physical/chemical/biological means (DeBusk et al. 1996b). Inorganic form, i.e. orthophosphate, is removed by algae and macrophytes. The major uptake is by plant roots (Vymazal 2006). The absorption through leaves and plant parts is usually very low. The storage of phosphorus in plants varies depending upon plant type and storage occurs preferably in below-ground parts. Some amount of chemical transformation through soil adsorption and precipitation is also reported. The extent at which phosphorus can be removed or stored is dependent on the type of wetland. Removal mechanism includes sorption, storage in biomass and formation of new soil media

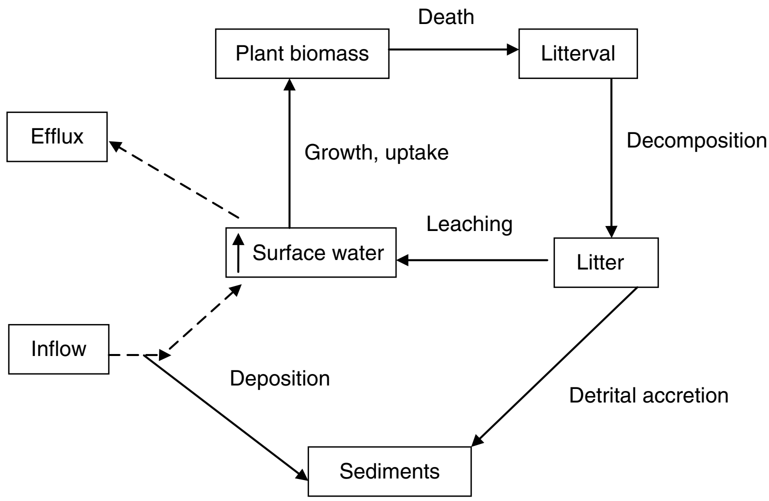

Fig. 4.5 Phosphorus cycle in wetlands (Sundaravadivel and Vigneswaran 2001)

(Kang 2012). Phosphorus is also released after a plant dies and begins to decay. The decaying plant matter above ground releases phosphorus into the water while decaying roots secrete phosphorus into the soil. Another important chemical transformation is soil adsorption and precipitation. This process involves soluble inorganic phosphorus moving from the pores in the soil media to the soil surface.

Phosphorus is present in the water in the form of orthophosphate and organic phosphorus. It is found in the wetlands as part of sediments. Phosphorus cycle in wetlands is shown in Fig. 4.5. Adsorption is the most important phosphorus removal process in the wetlands. Adsorption of phosphorus occurs due to reactions with iron, calcium and magnesium present in sediments. Adsorption of phosphorus to iron ions takes places under aerobic and neutral to acidic conditions to form stable complexes. If the conditions are anaerobic, adsorption to iron ions is less strong. Adsorption to calcium ions takes place under basic to neutral pH conditions. Thus adsorption of phosphorus to the ions removes it from the wastewater. Adsorption is reversible process and each substrate has a particular capacity until it cannot absorb any more phosphorus. Phosphorus can also get precipitated with iron or aluminium ions. Under this process, phosphate from the water is fixed in the matrix of phosphates and metals. Decomposition of litter (dead plants) and organic matter in the wetland also takes up phosphorus. This process results in storage of phosphorus in the organic matter which will be released eventually. Growing plants take up nutrients like phosphorus, thereby reducing levels in the wetland. The plant uptake of phosphates varies from 30 to 150 kg ha^{-1}year^{-1} (Sundaravadivel and Vigneswaran 2001).

4.3.1.4 Suspended Solids

Suspended solids are removed by two different approaches. Free water surface wetland removes suspended solids primarily by flocculation/sedimentation and filtration/interception. Both of these processes are influenced by particle size, shape, specific gravity, and properties of the fluid medium. Flocculant settling involves the interacting of particles changing size and characteristics. If larger flocculants are formed, then the settling of the new particle will occur faster. FWS wetlands can typically see hydraulic loads about 0.01 m day^{-1} to 0.5 m day^{-1}. Smaller particles would take about 200 days to settle out. Filtration does not typically play a large part in suspended soils removal of FWS wetlands since the plant stems of plants are too far apart. Interception and adhesion to plant surfaces play an important part in solid removal. The surfaces of plants in wetlands are coated with active layer of biofilm called periphyton which can absorb colloidal and soluble matter. These solids may then be metabolized and then converted to gases or biomass. Removal of suspended solids in VSB wetlands depends upon hydraulic design and microbial characteristics of the substrate. VSB wetlands are effective in removing suspended solids due to low velocity and large surface area of the media. VSB wetlands offer gravity settling, straining and adsorption onto gravel and plant media (EPA 1999). It has been found that 60–75 % percent of solids removal in VSB wetland occur in the first one third of the wetland. One of the major concerns with VSB wetlands is the clogging of the filter media. As suspended solids pass through the soil media, it can clog pores and reduce the hydraulic conductivity of the media producing head losses at the entrance of the wetland (Manios et al. 2003; Wei et al. 2012). In order to stop clogging larger particle media (10–15 cm) that offer larger void space and less shear resistance to flow were chosen. The larger void space also decreased the surface area for which bacteria to grow, thus helping in proper removal of suspended solids.

4.3.1.5 PCPPs

The main PPCP removal processes suggested for the systems studied are based on biodegradation, plant exudates and uptake and photodegradation. Studies indicate that the removal of many PPCPs from wastewater is favoured by oxic conditions, since the most feasible biodegradation process of these substances is an aerobic microbiological pathway. Ibuprofen removal efficiency is favoured in aerobic environments. Naproxen, salicylic acid, caffeine and methyl dihydrojasmonate were more efficiently removed by the wetland with higher redox potential. Nevertheless, some PPCPs like diclofenac are degraded anaerobically (Zwiener and Frimmel 2003; Quintana et al. 2005). The coexistence of aerobic and anaerobic conditions in the natural systems studied would allow for the degradation of different kinds of PPCPs. Andreozzi et al. (2003) and Matamoros et al. (2009) have suggested that some PPCPs can also be removed by photodegradation. It has been demonstrated that ketoprofen can be removed from surface and sea waters through photodegradation processes.

CWs offer as good efficiencies as conventional WWTPs for the removal of caffeine, naproxen, methyl dihydrojasmonate, salicylic acid and ibuprofen. This good efficiency of CWs could be related to the coexistence of various microenvironments with different physicochemical conditions in CWs and ponds, which would allow for the degradation of PPCPs following several metabolic pathways. Physicochemical conditions in WWTPs are more homogeneous and would induce fewer degradation pathways. Furthermore, photodegradation processes are easier in ponds and surface flow CWs, since they are shallower than WWTPs (Hijosa-Valsero et al. 2010a).

4.3.2 Organic Contaminants

Small-scale constructed wetlands remove organic load efficiently (Imfeld et al. 2009; De Biase et al. 2011; Agudelo et al. 2012; Zhou et al. 2013). Physical, chemical and biological processes interact and work in concert during attenuation of organic chemicals in wetland systems. Degradation pathways work for different groups of contaminants. In constructed wetlands, transformation and mineralization of nutrients and organic pollutants is facilitated by microorganisms. The contaminants in the wastewater are metabolized in various ways depending on the oxygen input and the availability of other electron acceptors. Uptake of xenobiotics (organic pollutants) by the plants is influenced by several physicochemical factors such as the octanol–water partition coefficient (log K_{OW}), acidity constant (pKa) and concentration (Wenzel et al. 1999). Compounds with a log K_{OW} between 0.5 and 3 are taken up best. The metabolism of xenobiotics is divided in plants into three phases: transformation, conjugation and compartmentalization (Sandermann 1992). The enzymes involved are cytochrome P450, glutathione transferase, carboxylesterase, *O*- and *N*-glucosyl transferases and *O*- and *N*-malonyl transferases. After

Fig. 4.6 Examples of different categories of organic contaminants

Organic contaminants

Pharmaceuticals

carbamazepine,

naproxen,

diclofenac,

ibuprofen,

caffeine,

salicylic acid,

ketoprofen

clofibric acid

Pesticides

dichlorodiphenyltrichloroethane (DDT),

others-

polycyclic aromatic hydrocarbons (PAH),

bisphenol A,

BTEX,

glycol,

polychlorinated biphenyls (PCB),

cyanide,

benzene,

chlorophenols

transformation, detoxification occurs via export into the cell vacuole, extracellular space and integration into lignin or other components of the cell membrane. In subsurface flow systems, aerobic processes only predominate near roots and on the rhizoplane (the surface of the roots).

In case of chlorinated organic compounds, corresponding carbon atoms are attacked by nucleophile rather than oxidative reactions. Highly chlorinated hydrocarbons are dehalogenated. The only realistic possibility of biologically degrading hexachlorobenzene perchloroethylene or highly chlorinated biphenyls is reductive dehalogenation. The low-chlorinated products can then undergo further biological degradation under aerobic conditions. The degradation of 4-chlorophenol by a mixed bacterial culture obtained from *Phalaris arundinacea* roots was enhanced by the rhizodeposition products. Phenol degradation chiefly takes place via catechol and further meta-ring cleavage. In *Lemna gibba*, phenyl-beta-D-glucopyranoside was identified as a metabolite of phenol degradation (Barber et al. 1995; Fig. 4.6).

Organic removal is different for FWS and VSB wetlands. FWS wetlands remove organic matter by physical means and biological means (Sobolewski 1999). The biofilms located on plant surfaces offer pathways for plants to break down organics. The biological separation processes of organics include sorption and volatilization. The main types of reactions involved in organic matter breakdown and transformation include aerobic, anoxic and anaerobic via respiration, denitrification, acid fermentation, sulphate reduction and methanogenesis. In an aerobic environment, oxygen is present and serves as the terminal electron acceptor. In an anoxic environment, nitrates, sulphates and carbonates serve as the terminal electron acceptors which are reduced to form oxides. Amount of volatile organic compounds entering wastewater wetlands is fairly low; hence, 80–96 % removal is achieved. The aerobic microorganisms consume oxygen to break down organics which provides energy, while anaerobic bacteria break down organic matter to produce methane. In an aerobic environment, oxygen serves as the terminal electron acceptor. In an anoxic environment, nitrates, sulphates and carbonates serve as the terminal electron acceptors which are reduced to form oxides. Aquatic macrophytes located on top of the surface of the water play an important role in producing oxygen to the water. Anaerobic bacteria break down organic matter to produce methane. Organisms break organics into energy including oxidation and reduction reactions, hydrolysis and photolysis. Bacteria, actinomycetes and fungi play maybe the most important role in breaking down organic matter. Macrophytes are aquatic plants located on top of the surface of the water which play an important role in producing oxygen to the water (EPA 1999).

The mechanism for organic removal in VSB wetlands is a little different than in FWS wetlands since VSB wetlands function as fixed film bioreactors. The particulate organic material entering a VSB wetland undergoes a similar mechanism as suspended solids. The particulate organic material entering a VSB wetland undergoes hydrolysis and produce soluble organic matter which enter the media and attach to biofilm media and then further decomposed. The amount of decomposition of organic matter is low since average dissolved oxygen concentrations in a VSB wetland are less than 1 mg L^{-1}. The predominant biological mechanism for organic removal is done by aerobic/facultative means. VSB wetlands have strong reducing capabilities which make the predominant metabolic mechanism an aerobic manner. Anaerobic functions include methanogenesis, sulphate reduction and gentrification which all produce gaseous products. These functions vary with temperature and it is possible that as temperatures increase, greater amounts of gas can be released (EPA 1999).

Mesocosm-scale constructed wetlands showed pharmaceutical removal capacity (carbamazepine, naproxen, diclofenac, ibuprofen, caffeine, salicylic acid, ketoprofen and clofibric acid) from synthetic wastewater. Pharmaceutical removal efficiency was significantly and inversely correlated with log D_{ow} value, but not with log K_{ow} value. The horizontal subsurface flow CWs (i) efficiently removed compounds ketoprofen and salicylic acid; naproxen, ibuprofen and caffeine; and carbamazepine, diclofenac and clofibric acid. Removal of compounds followed first-order decay kinetics with decay constants higher in the planted beds than the unplanted beds.

Constructed wetland removed emerging contaminants (i.e. pharmaceuticals, sunscreen compounds, fragrances, antiseptics, fire retardants, pesticides and plasticizers) efficiently, presumably due to the presence of plants (*Phragmites and Typha*) as well as the higher hydraulic retention time (HRT) in the CW (Matamoros et al. 2007, 2010, 2012a, b; Zhang et al. 2012a, b). Studies demonstrated that aquatic plants contribute directly and indirectly to the aqueous depletion of emerging organic pollutants in wetland systems through both active and passive processes that involved microbial degradation and sorption. Removal of atrazine, meta-*N*,*N*-diethyl toluamide (DEET), picloram and clofibric acid and depletion of fluoxetine, ibuprofen, 2,4-dichlorophenoxyacetic acid and triclosan by aquatic plants have been reported. Wetlands reduce concentrations of personal care products (PPCPs). Oxygen status may affect the attenuation of PPCPs in wetland sediments by influencing microbial activity. Redox conditions, aerobic/anaerobic conditions and other factors effect sorption and degradation of PPCPs. Sorption of PPCPs like *N*,*N*-diethyl-meta-toluamide (DEET), carbamazepine and gemfibrozil has been reported. Degradation of the selected PPCPs was enhanced under aerobic conditions. Studies indicated that PPCP removal associated with the dissolved phase exhibited a seasonal pattern. In the dissolved phase, the overall removal efficiency in summer ranged from 70 to 85 % for salicylic acid (SAL), methyl dihydrojasmonate, caffeine (CAF), ketoprofen and triclosan, whereas in winter it declined for most of the PPCPs to between 30 and 50 %. SF CW generally exhibited the highest removal efficiency for most of the contaminants (Matamoros and Salvadó 2012).

Constructed wetlands mainly VFSSCWs with gravel matrix and a plant-root mat showed potential for groundwater and surface water remediation as removal of benzene, aniline, nitrobenzene, BTEX, MTBE, ammonia-N and gasoline-range organics was achieved. Constructed wetlands exhibited capacity for treatment of domestic wastewater where BOD and COD (biochemical and chemical oxygen demand, respectively) are used as a sum parameter for organic matter (Seeger et al. 2011; Yada et al. 2011). Wetlands may be considered as a feasible alternative for mitigating emerging contaminants from river water. Case studies highlight the treatment of wastewaters contaminated with aromatic organic compounds and sulphonated anthraquinones, olive mill wastewater, landfill leachate and groundwater contaminated with hydrocarbons, cyanides and chlorinated volatile. Wetlands planted with *Phragmites australis* showed removal of monochlorobenzene (MCB), 1,4-dichlorobenzene (1,4-DCB) and 1,2-dichlorobenzene (1,2-DCB). Removal efficiency in the CW generally decreased with depth and seasonal variations. Increased contaminant loss was found during summer. Removal potential was attributable to microbial degradation, volatilization and plant uptake. MCB removal was caused by improved oxygen supply and direct plant uptake.

Engineered treatment system (EETS) showed natural attenuation of estrogenic endocrine disrupting compounds (EDCs) such as estriol (E3, natural) and 17α-ethinylestradiol (EE2, synthetic) (Kumar et al. 2011). These two estrogens are the major contaminants of sewage and found to cause adverse effects on the endocrine system of humans and animals when exposed even in nanogram concentrations. The EETS consisted of diverse biota, namely, aquatic macrophytes, submerged plants, emergent plants, algae and bacteria present in the system mimic the natural cleansing functions of wetlands and help in the treatment of pollutants present in wastewater. The floating macrophytes system was more effective in removing estrogens compared to the submerged–emergent macrophyte-based integrated system and submerged–rooted macrophytes system. On the whole, EETS can effectively treat EDCs and remove COD, nitrates and turbidity (Cai et al. 2012).

Constructed wetlands (CWs), along with other vegetative systems, help in mitigating pesticides. Operational CWs located in the Central Valley of California explored the mechanisms of removal of pyrethroids and chlorpyrifos from agricultural runoff water. Chlorinated ethenes (CEs) are groundwater contaminants. CEs polluting the groundwater can be remediated both naturally and cost-effectively by biodegradation in wetland environments. Highly chlorinated CEs, such as tetrachloroethene (PCE), have the potential to undergo reductive biodegradation in the reducing environments, and less-chlorinated CEs, such as trichlorethene (TCE), dichloroethene (DCE) isomers, vinyl chloride (VC), can undergo oxidative biodegradation both in the near-surface environment and root zone, also called rhizosphere, of wetland plants. Wetland roots provide several potential oxidative pathways for the biodegradation of CEs. The greatest potential is for oxidation with oxygen as the electron acceptor, either co-metabolically or metabolically, which is leaked from the roots into the soil. Co-metabolic oxidation of CEs with CH_4 as a growth substrate is highly likely because wetland soil is rich in organic matter produce an abundance of CH_4 to be used by methanotrophic bacteria inhabiting the root zone. Constructed wetland (at the Wright-Patterson Air Force Base (WPAFB)) in Dayton exhibited potential for removal of PCE in the groundwater. PCE degrades in the deeper, anaerobic portions of treatment wetland, as measured by its disappearance along with formation of its daughter products (e.g. TCE, DCEs and VC). The daughter CEs appear to readily degrade at the shallower depths, possibly due to the activities associated with the wetland vegetation. The biogeochemical factors affect the oxidative degradation of daughter CEs. There is a redox gradient in the wetlands with reducing conditions near the bottom and more oxygenated conditions near the surface and in the root zone. Oxygenated conditions and methanotrophic activity in the plant rhizosphere support co-metabolic and metabolic aerobic degradation of CEs in the shallow vegetated wetland.

Wetland species *Myriophyllum spicatum* and *Ceratophyllum demersum* planted in the aquaria showed capability of removing textile dye – Basic Blue 41(BB41). Removal of ~90 % is achieved at hydraulic retention times (HRTs) ranging between 3 and 18 days. The studies provided the evidence that wetland system is also able to remove the dye from influent wastewater (Keskinkan and Göksu 2007).

4.3.2.1 Explosives

Phytoremediation of explosives or ammunition-contaminated water in groundwater using constructed wetlands is a potentially economical remediation alternative. Use of aquatic and wetland plants in constructed wetlands aimed at removing explosives from water need to be checked for considerations such as (1) plant persistence to the exposed levels of explosives, (2) plant weight specific removal rates, (3) plant productivity and (4) fate of parent compounds and transformation products in water, plants and sediments. Field demonstration studies at Milan Army Ammunition Plant, Tennessee (1996), demonstrated the feasibility of constructed wetlands for treating contaminated groundwater. Two different systems, (a) lagoon system planted with sago pondweed, water stargrass, elodea and parrot feather and (b) gravel-bed system planted with canary grass, wool grass, sweet flag and parrot feather, were designed and installed. The gravel-bed wetland reduced 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrobenzene (TNB) concentrations, while gravel-bed wetland removed hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) in the groundwater. Mass balance studies demonstrated that TNT disappeared completely from groundwater with plants. Highest specific removal rates were found in submersed plants and emergent plants. Growth of submersed plants was normal, but that of emergent plants reduced in groundwater amended with RDX. Highest specific RDX removal rates were found in submersed plants in elodea, in emergent plants and in reed canary grass (Best et al. 2012). Parent compounds and transformation products were analyzed using ^{14}C analyses. Groundwater and plant tissue analyses indicated that TNT is degraded to reduced by-products and to other metabolites in the presence of the plants. The kinetics predicts that TNT removal was best modelled using first-order kinetics (25 °C). Hydraulic retention times (HRTs) ranging from 4.9 to 19.8 days for TNT degradation and RDX removal were standardized. Submersed plants are identified as having the highest explosives-removing activity. *Myriophyllum aquaticum* showed potential to transform RDX.

4.3.2.2 Wastewater

Constructed wetlands are an effective and low-cost way to treat water polluted with inorganic and organic compounds. Industrial wastewater, urban storm water, swine wastewater, domestic wastewater, olive mill wastewater, groundwater and landfill leachate contain several different pollutants, including natural organic matter (NOM), effluent organic matter (EfOM), toxic anions, nitrate, bromate, perchlorate, pharmaceutical chemicals, endocrine disrupters aromatic organic compounds, sulphonated anthraquinones, hydrocarbons, cyanides, chlorinated volatile organics and explosives and other micro-pollutants (Vymazal and Sveha 2012a, b; Wu et al. 2012). Constructed wetlands depicted efficacy in treating wastewaters from different sources by removing metals, total suspended solids, BOD, total Kjeldahl nitrogen (TKN), dissolved oxygen (DO) and conductivity. High sequestration of K, Na, Mg and Ca from municipal wastewater by vegetation in subsurface horizontal flow planted with *Phragmites australis* and *Phalaris arundinacea* has been noted. *Arundo* had higher growth rates and biomass and is a preferred species use in CWs treating tannery wastewater and hence decreased the toxicity of the wastewater.

4.4 Limitations

Constructed treatment wetlands have some limitations as follows:

- Relatively large area requirements
- A long starting time period required for growth of vegetation
- Season and climatic conditions

Studies have shown that CWs are more suitable for wastewater treatment in tropical than in temperate areas, because in a warm climate, there is year-round plant growth and microbiological activity, which in general have a positive effect on treatment efficiency (Kadlec and Wallace

2009; Garfí et al. 2012). In cold conditions, CW design can be adapted in order to improve wetland performance, mainly using lower contaminant mass loading rates and longer hydraulic retention times (HRTs) (Akratos et al. 2008; Hijosa-Valsero et al. 2010a, b). Other parameters that affect wetland performance are influent quality and wetland design, such as HRT, plant species, primary treatment and feeding pattern (Hijosa-Valsero et al. 2010a, b; Kotti et al. 2010; Pedescoll et al. 2011; Stefanakis and Tsihrintzis 2012). Biomass disposal problem and seasonal growth of aquatic macrophytes are some limitations in the transfer of phytoremediation technology from the laboratory to the field. Determining the longevity of treatment wetlands is complicated by various factors including inflow hydraulic and pollutant loading rates, natural factors such as extreme weather conditions, and the type of pollutants for which the wetlands are designed.

Studies related to sustainability of FWS wetlands for wastewater treatment is still ongoing, particularly for P removal, and long-term records provide evidence of the longevity of treatment wetlands (Kadlec and Wallace 2009).

4.5 Future

A number of fundamental aspects of exactly how constructed wetlands function are not yet adequately understood. One reason for this is that, compared to other technologies such as activated sludge, constructed wetlands depend on the interaction of many more different components (Rai 2008).

The basic aspects upon which more work is essential include the following:

- Microbial process of anoxic ammonium oxidation and possibilities of stimulating it in constructed wetlands.
- Behaviour of toxicologically highly active trace substances such as persistent drug residues in the complex system of the constructed wetland.
- Removal and detoxification of persistent compounds from wastewater in this complex system.
- Mechanisms of wastewater disinfection.
- The effect of root growth on hydraulic conductivity should be studied in detail.
- Genetic engineering provides a growing number of methods to breed plants, which can, for instance, better accumulate heavy metals or break down persistent contaminants more effectively in constructed wetlands. However, attention must always be paid to how these 'new' plant species can stand up in the long term to the many competing influences such as wild species in these complex technical ecosystems—just as crops in the field permanently have to compete with weeds.
- Interactions of various substance cycles (e.g. carbon, nitrogen, and sulphur), taking into account above all the variability of redox states in the rhizosphere.

Though, constructed wastewater wetlands have shown capability of treating different kinds of wastewater with capacity for removing suspended solids, organic matter, nitrogen, phosphorus, pathogens and metals. Proper understanding of mechanisms for removal of contaminants is required for large-scale implementation of wastewater treatment in constructed wetlands. Though the utility of wetlands for mass-scale removal of contaminants is well established, a few questions regarding their functioning still need to be addressed. It is observed that metals taken up by roots are transported upwards to above-ground tissues, but the route for their excretion is not clearly defined. The decomposing litter of plant species will get enriched with metals over time, which may leach or may become available to detritus feeders. A comprehensive understanding of the uptake, tolerance and transport of heavy metals in the wetland system through aquatic plants will be essential for the development of phytoremediation technologies.

Achieving a better understanding of the complex interactions involved will enable the basic scientific aspects to be optimally combined with the technical possibilities available, thus enabling wetland technologies to be used on a broader scale. Advances in wetland modelling are presented as a powerful tool for understanding multiple interactions occurring in subsurface flow constructed wetlands during the removal of contaminants.

Wetlands can be expected to sustain their performance as long as appropriate hydrology and vegetation are maintained and detritus removal occurs regularly. Two FWS wetlands, the Brillion Marsh in Wisconsin and Great Meadows Marsh in Massachusetts, operated for over 70 years and retained their treatment efficiency (Kadlec and Wallace 2009). In contrast, a tertiary treatment wetland, the Easterly Wetland in Orlando, Florida, has reduced 70–80 % of the nutrient load, but has showed a slight decline in nutrient removal efficiency over time. Proper management is crucial to the sustainability of an effective FWS system (Carty et al. 2008; Rousseau et al. 2008). Self-sustaining system may not be possible for FWSCWs where nutrient loading and/or sedimentation rates are high and system hydrology is altered seasonally or for operational and maintenance purposes. Maintaining healthy vegetation is also imperative to sustaining both effective water quality treatment and habitat value. Minimum maintenance, including adjustment of flows and water levels, is required to achieve successful performance in FWS systems (Carty et al. 2008; Rousseau et al. 2008; Kadlec and Wallace 2009). Wetland design criteria often are not reflective of extreme environmental conditions such as weather and hydrologic fluctuations (Thullen et al. 2005; Mitsch and Gosselink 2007) that can negatively impact wetland functioning and decrease wetland sustainability.

Design features of the San Joaquin Wildlife Sanctuary that provide for the dual purposes of N removal and the creation of avian habitat do not inhibit removal of total N. A number of other benefits of FWS-CTWs such as the creation of wetland habitat and biodiversity conservation are important for sustainable resource management (Rousseau et al. 2008; Carty et al. 2008). Conserving biodiversity is essential to many ecosystem services (e.g. biotic regulation and aesthetic values) in both the wetland and the surrounding landscape (Siracusa and La Rosa 2006). Nutrients accumulating in plants may also be used for composting or energy generation as additional benefits (Cicek et al. 2006). Harvested plants can be used for biogas production through fermentation, a practice widely used in developing countries and Europe. A floating mat-based system (also called floating treatment wetlands) has been developed and used in the UK, Belgium, China and other countries. The floating mat-based system is a variant of the conventional FWS design that employs EAV species growing as a floating mat or raft on the water surface instead of rooted plants in the sediments. Because of this feature, floating treatment wetlands offer a promise for rainfall-driven storm water treatment systems because they are less affected by water level fluctuations. The engineered floating mat-based systems, therefore, incorporate EAV species growing in a hydroponic manner on floating rafts and enable the incorporation of treatment wetland elements into deep pond-like systems. The multiple linear floating wetlands with synthetic textile curtains hanging beneath are used to provide additional substrate for biofilm attachment and to create a lengthy flow path (Todd et al. 2003). Introducing this floating mat-based system into a pond-marsh system or a degraded shallow lake has a number of advantages that may enhance pollutant removal processes or lake restoration. Like any constructed wetland, FWS-CTWs have limitations. In many cases, overloading or uncontrolled discharging of wastewater may result in an irreversible degradation or failure of the system. The buildup of sediment from wastewater and the accretion of peat from decomposed vegetation affect the operation of the CTWs. Over the past several decades, FWS-CTWs have been used extensively throughout North America and many are in operation in Australia, Asian, and European countries (Ghermandi et al. 2007; Kadlec and Wallace 2009). Using FWS-CTWs for water quality improvement is cost effective and environmentally sound. The capabilities of the FWSCTWs in water pollutant removal, together with other ecological services, provide a nature-based technology that supports sustainable resource management.

Literature Cited

Abou-Elela SI, Hellal MS (2012) Municipal wastewater treatment using vertical flow constructed wetlands planted with *Canna*, *Phragmites* and *Cyprus*. Ecol Eng 47:209–213

Agudelo CRM, Jaramillo ML, Peñuela G (2012) Comparison of the removal of chlorpyrifos and dissolved organic carbon in horizontal sub-surface and surface flow wetlands. Sci Total Environ 431:271–277

Akratos CS, Papaspyros JNE, Tsihintzis VA (2008) An artificial neural network model and design equations for BOD and COD removal prediction in horizontal subsurface flow constructed wetlands. Chem Eng 143:96–110

Andreozzi R, Marotta R, Paxéus N (2003) Pharmaceuticals in STP effuents and their solar photodegradation in aquatic environment. Chemosphere 50:1319–1330

Anning AK, Korsah PE, Addo-Fordjour P (2013) Phytoremediation of wastewater with *Limnocharis flava*, *Thalia geniculata* and *Typha latifolia* in constructed Wetlands International. J Phytoremediation 15(5):452–464

Baldantoni D, Ligrone R, Alfani A (2009) Macro- and trace-element concentrations in leaves and roots of *Phragmites australis* in a volcanic lake in Southern Italy. J Geochem Explor 101:e166–e174

Barber JT, Sharma HA, Ensley HE, Polito MA, Thomas DA (1995) Detoxification of phenol by the aquatic angiosperm *Lemna gibba*. Chemosphere 31:3567–3574

Best EPH, Zappi ME, Fredrickson HL, Sprecher SL, Larson SL, Ochman M (1997) Screening of aquatic and wetland plant species for phytoremediation of explosives-contaminated groundwater from the Iowa army ammunition plant. Annu NY Acad Sci 829:179–194

Best EPH, Sprecher SL, Larson SL, Fredrickson HL, Darlene BF (1999) Environmental behavior of explosives in groundwater in groundwater from the Milan army ammunition plant in aquatic and wetland plant treatments. Removal, mass balances and fate in groundwater of TNT and RDX. Chemosphere 38:3383–3396

Best EP, Miller JL, Larson SL (2012) Tolerance towards explosives, and explosives removal from groundwater in treatment wetland mesocosms. Water Sci Technol 44:515–521

Birch GF, Matthai C, Fazeli MS, Suh JY (2004) Efficiency of a constructed wetland in removing contaminants from stormwater. Wetlands 24:459–466

Boreen AL, Arnold WA, McNeill K (2003) Photodegradation of pharmaceuticals in the aquatic environment: a review. Aquat Sci 65:320–341

Bostick BC, Hansel CM, La Force MJ, Fendorf S (2001) Seasonal fluctuations in zinc speciation within a contaminated wetland. Environ Sci Technol 35: 3823–3829

Braeckevelt M, Reiche N, Trapp S, Wiessner A, Paschke H, Kuschk P, Kaestner M (2011) Chlorobenzene removal efficiencies and removal processes in a pilot-scale constructed wetland treating contaminated groundwater. Ecol Eng 37:903–913

Brix H (1994) Functions of macrophytes in constructed wetlands. Water Sci Technol 29:71

Brix H (1997) Do macrophytes play a role in treatment wetlands? Water Sci Technol 35:11

Budd R, O'geen A, Goh KS, Bondarenko S, Gan J (2011) Removal mechanisms and fate of insecticides in constructed wetlands. Chemosphere 83:1581–1587

Bunluesin S, Kruatrachue M, Pokethitiyook P, Upatham S, Lanza GR (2007) Batch and continuous packed column studies of cadmium biosorption by *Hydrilla verticillata* biomass. J Biosci Bioeng 103:e509–e513

Bustamante MA, Mier MV, Estrada JA, Domíguez CD (2011) Nitrogen and potassium variation on contaminant removal for a vertical subsurface flow lab scale constructed wetland. Bioresour Technol 102:7745–7754

Cai K, Elliott CT, Phillips DH, Scippo M-L, Muller M, Connolly L (2012) Treatment of estrogens and androgens in dairy wastewater by a constructed wetland system. Water Res 46(7):2333–2343

Cambrolle J, Redondo-Gomez S, Mateos-Naranjo E, Figueroa ME (2008) Comparison of the role of two *Spartina* species in terms of phytostabilization and bioaccumulation of metals in the estuarine sediment. Mar Pollut Bull 56:e2037–e2042

Carty A, Scholz M, Heal K, Gouriveau F, Mustafa A (2008) The universal design, operation and maintenance guidelines for farm constructed wetlands (FCW) in temperate climates. Bioresour Technol 99:6780–6792

Chaudhry Q, Blom-Zandstra M, Gupta S, Joner EJ (2005) Utilising the synergy between plants and rhizosphere microorganisms to enhance breakdown of organic pollutants in the environment. Environ Sci Pollut Res 12:e34–e48

Chen H (2011) Surface-flow constructed treatment wetlands for pollutant removal: applications and perspectives. Wetlands 31:805–814

Cheng X, Liang M, Chen W, Liu X, Chen Z (2009a) Growth and contaminant removal effect of several plants in constructed wetlands. J Integr Plant Biol 51(3):325–335

Cheng X, Chen W, Gu B, Liu X, Chen F, Chen Z, Zhou X, Li Y, Huang H, Chen Y (2009b) Morphology, ecology, and contaminant removal efficiency of eight wetland plants with differing root systems. Hydrobiologia 623:77–85

Choudhary AK, Kumar S, Sharma C (2011) Constructed wetlands: an option for pulp and paper mill wastewater treatment. Electron J Environ Agric Food Chem 10(10):3023–3037

Cicek N, Lambert S, Venema HD, Snelgrove KR, Bibeau EL, Grosshans R (2006) Nutrient removal and bio-energy production from Netley-Libau Marsh at Lake Winnipeg through annual biomass harvesting. Biomass Bioenergy 30:529–536

Comino E, Riggio V, Rosso M (2011) Mountain cheese factory wastewater treatment with the use of a hybrid constructed wetland. Ecol Eng 37(11):1673–1680

Conkle JL, White JR, Metcalfe CD (2008) Reduction of pharmaceutically active compounds by a lagoon wetland wastewater treatment system in Southeast Louisiana. Chemosphere 73:1741–1748

Conkle JL, Gan J, Anderson MA (2012) Degradation and sorption of commonly detected PPCPs in wetland sediments under aerobic and anaerobic conditions. J Soils Sediments 12(7):1164–1173

Correa-Galeote D, Marco DE, Tortosa G, Bru D, Philippot L, Bedmar EJ (2013) Spatial distribution of N-cycling microbial communities showed complex patterns in constructed wetland sediments. FEMS Microbiol Ecol 83(2):340–351

Cui L, Ouyang Y, Lou Q, Yang F, Chen Y, Zhu W, Luo S (2010) Removal of nutrients from wastewater with *Canna indica* L. under different vertical-flow constructed wetland conditions. Ecol Eng 36:1083–1088

De Biase C, Reger D, Schmidt A, Jechalke S, Reiche N, Martínez-Lavanchy PM, Rosell M, Van Afferden M, Maier U, Oswald SE, Thullner M (2011) Treatment of volatile organic contaminants in a vertical flow filter: relevance of different removal processes. Ecol Eng 37:1292–1303

DeBusk WF (1998) Evaluation of a constructed wetland for treatment of leachate at a municipal landfill in northwest Florida. In: Mulamoottil G, McBean E, Rovers FA (eds) Constructed wetlands for the treatment of landfill leachates. Lewis Publishers, Boca Raton

DeBusk WF (1999a) Wastewater treatment wetlands: contaminant removal processes. Soil and Water Science Department, University of Florida, SL155

DeBusk WF (1999b) Wastewater treatment wetlands: applications and treatment efficiency. Soil and Water Science Department, University of Florida, SL15

DeBusk TA, DeBusk WF (2001) Wetlands for water treatment. In: Kent DM (ed) Applied wetlands science and technology. CRC Press LLC, Boca Raton

DeBusk TA, Laughlin RB, Schwartz LN (1996a) Retention and compartmentalization for wastewater treatment: municipal, industrial and agricultural. Water Research 30:2707

DeBusk TA, Peterson JE, Reddy KR (1996b) Use of aquatic and terrestrial plants for removing phosphorus from dairy wastewaters. Ecol Eng 5:371

Deng H, Ye Z, Wong M (2004) Accumulation of lead, copper and cadmium by 12 wetland plant species thriving in metal-contaminated sites in China. Environ Pollut 132:e29–e40

Deng H, Ye Z, Wong M (2006) Lead and zinc accumulation and tolerance in populations of six wetland plants. Environ Pollut 141:e69–e80

Dhir B (2010) Use of aquatic plants in removing heavy metals from wastewater. Int J Environ Eng 2(1/2/3):185–201

Dhir B, Sharmila P, Pardha SP (2009) Potential of aquatic macrophytes for removing contaminants from the environment. Crit Rev Environ Sci Technol 39:754–781

Dhote S, Dixit S (2009) Water quality improvement through macrophytes a review. Environ Monit Assess 152:e149–e153

Díaz FJ, Ogeen AT, Dahlgren RA (2012) Agricultural pollutant removal by constructed wetlands: Implications for water management and design. Agric Water Manage 104:171–183

Dorman L, Castle JW, Rodgers JH (2009) Performance of a pilot-scale constructed wetland system for treating simulated ash basin water. Chemosphere 75:e939–e947

Dotro G, Castro S, Tujchneider O, Piovano N, Paris M, Faggi A, Palazolo P, Fitch M (2012) Performance of pilot-scale constructed wetlands for secondary treatment of chromium-bearing tannery wastewaters. J Hazard Mater 239–240:142–151

Fediuc E, Erdei L (2002) Physiological and biochemical aspects of cadmium toxicity and protective mechanisms induced in *Phragmites australis* and *Typha latifolia*. J Plant Physiol 159:265–271

Fitzgerald EJ, Caffrey JM, Nesaratnam ST, McLoughlin P (2003) Copper and lead concentrations in salt marsh plants on the Suir Estuary, Ireland. Environ Pollut 123:67–74

Fleming-Singer MS, Horne AJ (2006) Balancing wildlife needs and nitrate removal in constructed wetlands: the case of the Irvine Ranch Water District's San Joaquin Wildlife Sanctuary. Ecol Eng 26:147–166

Fritioff A, Kautsky L, Greger M (2005) Influence of temperature and salinity on heavy metal uptake by submersed plants. Environ Pollut 133:265–274

Gao S, Tanji K, Peters D, Lin Z, Terry N (2003) Selenium removal from irrigation drainage water flowing through constructed wetland cells with special attention to accumulation in sediments. Water Air Soil Pollut 144:263

Garcia C, Moreno DA, Ballester A, Blazquez ML, Gonzalez F (2001) Bioremediation of an industrial acid mine water by metal-tolerant sulphate-reducing bacteria. Minerals Eng 14:e997–e1008

García J, Rousseau DPL, Morató J, Lesage E, Matamoros V, Bayona JM (2010) Contaminant removal processes in subsurface-flow constructed wetlands: a review. Crit Rev Environ Sci Technol 40:561–661

Garfí M, Pedescoll A, Bécares E, Hijosa-Valsero M, Sidrach-Cardona R, García J (2012) Effect of climatic conditions, season and wastewater quality on contaminant removal efficiency of two experimental constructed wetlands in different regions of Spain. Sci Total Environ 437:61–67

Ghermandi A, Bixio D, Thoeye C (2007) The role of free water surface constructed wetlands as polishing step in municipal wastewater reclamation and reuse. Sci Total Environ 380:247–258

González-Alcaraz MN, Egea C, Jiménez-Cárceles FJ, Párraga I, María-Cervantes A, Delgado MJ, Álvarez-Rogel J (2012) Storage of organic carbon, nitrogen and phosphorus in the soil-plant system of *Phragmites australis* stands from a eutrophicated Mediterranean salt marsh. Geoderma 185–186:61–72

Gonzalez-Mendoza D, Quiroz-Moreno A, Zapata-Perez O (2007) Coordinated responses of phytochelatin synthase and metallothionein genes in black mangrove, *Avicennia germinans*, exposed to cadmium and copper. Aquat Toxicol 83:e306–e314

Greger M (1999) Metal availability and bioconcentration in plants. In: Pradad MNV, Hagemeyer J (eds) Heavy metal stress in plants: from molecules to ecosystems. Springer, Berlin, pp 1–27

Gross B, Montgomery-Brown J, Naumann A, Reinhard M (2004) Occurrence and fate of pharmaceuticals and alkylphenol ethoxylate metabolites in an effluent-dominated river and wetland. Environ Toxicol Chem 23:2074–2083

Groza N, Manescu A, Panturu E, Filcenco-Olteanu A, Panturu RI, Jinescu C (2010) Uranium wastewater treatment using wetland system. Revista de Chimie 61:680–684

Guan X, Dong H, Ma J, Jiang L (2009) Removal of arsenic from water: effects of competing anions on As(III) removal in KMnO4-Fe(II) process. Water Res (Oxf) 43:e3891–e3899

Gunes K, Tuncsiper B, Ayaz S, Drizo A (2012) The ability of free water surface constructed wetland system to treat high strength domestic wastewater: a case study for the Mediterranean. Ecol Eng 44:278–284

Gustavsson L, Engwall M (2012) Treatment of sludge containing nitro-aromatic compounds in reed-bed mesocosms – water, BOD, carbon and nutrient removal. Waste Manag 32:104–109

Haarstad K, Bavor HJ, Mæhlum T (2012) Organic and metallic pollutants in water treatment and natural wetlands: a review. Water Sci Technol 65(1):76–99

Haber R, Grego S, Langergraber G, Kadlec RH, Cicalini A, Dias SM, Novais JM, Aubert S, Gerth A, Thomas H (2003) Constructed wetlands for the treatment of organic pollutants. JSS J Soils Sediments 3(2):109–124

Hadad HR, Mufarrege MM, Pinciroli M, Di Luca GA, Maine MA (2010) Morphological response of *Typha domingensis* to an industrial effluent containing heavy metals in a constructed wetland. Arch Environ Contam Toxicol 58:666–675

Hafeznezami S, Kim J, Redman J (2012) Evaluating removal efficiency of heavy metals in constructed wetlands. J Environ Eng 138(4):475–482

Hansel CM, Force MJ, Fendorf S, Fendorf S, Sutton S (2002) Spatial and temporal association of As and Fe species on aquatic plant roots. Environ Sci Technol 36:1988–1994

Hansen D, Duda P, Zayed AM, Terry N (1998) Selenium removal by constructed wetlands: role of biological volatilization. Environ Sci Technol 32:591

He Y, Tao W, Wang Z, Shayya W (2012) Effects of pH and seasonal temperature variation on simultaneous partial nitrification and anammox in free-water surface wetlands. J Environ Manage 110:103–109

Hencha KR, Bissonnettea GK, Sexstonea AJ, Coleman JG, Garbutt K, Skousen JG (2003) Fate of physical, chemical, and microbial contaminants in domestic wastewater following treatment by small constructed wetlands. Water Res 37:921–927

Hijosa-Valsero M, Matamoros V, Sidrach-Cardona R, Martín-Villacorta J, Bécares E, Bayona JM (2010a) Comprehensive assessment of the design configuration of constructed wetlands for the removal of pharmaceuticals and personal care products from urban wastewaters. Water Res 44:3669–3678

Hijosa-Valsero M'a, Matamoros V'c, Martı'n-Villacorta J, Be'cares E, Bayona JM (2010b) Assessment of full-scale natural systems for the removal of PPCPs from wastewater in small communities. Water Res 44:1429–1439

Horne AJ (2000) Phytoremediation by constructed wetlands. In: Terry N, Banuelos G (eds) Phytoremediation of contaminated soil and water. Lewis, Boca Raton, pp 13–40

Horswell J, Hodge A, Killham K (1997) Influence of plant carbon on the mineralisation of atrazine residues in soils. Chemosphere 34:1739–1751

Idris SM, Jones PL, Salzman SA, Croatto G, Allinson G (2012) Evaluation of the giant reed (*Arundo donax*) in horizontal subsurface flow wetlands for the treatment of dairy processing factory wastewater. Environ Sci Pollut Res 19(8):3525–3537

Imfeld G, Braeckevelt M, Kuschk P, Richnow HH (2009) Monitoring and assessing processes of organic chemicals removal in constructed wetlands. Chemosphere 74(3):349–362

Jackson J (1989) Man-made wetlands for wastewater treatment: two case studies. In: Hammer DA (ed) Constructed wetlands for wastewater treatment: municipal, industrial and agricultural. Lewis Publishers, Boca Raton

Jonsson J, Jonsson J, Lovgren L (2006) Precipitation of secondary Fe(III) minerals from acid mine drainage. Appl Geochem 21:437–445

Kadlec RH (1998) Constructed wetlands for treating landfill leachate. In: Mulamoottil E, McBean G, Rovers FA (eds) Constructed wetlands for the treatment of landfill leachates. Lewis Publishers, Boca Raton

Kadlec RH, Knight RL (1996) Treatment wetlands. Lewis Publishers, Boca Raton

Kadlec RH, Wallace S (2008) Treatment wetlands, 2nd edn. CRC Press, Boca Raton, p 1048

Kadlec RH, Wallace SD (2009) Treatment wetlands, 2nd edn. Taylor and Francis Group, Boca Raton

Kang J (2012) Purification effect of constructed wetland on TN and TP removal from eutrophic wastewater. Adv Mat Res 356–360:2638–2642

Keskinkan O, Göksu MZL (2007) Assessment of the dye removal capability of submersed aquatic plants in a laboratory-scale wetland system using anova. Braz J Chem Eng 24:193–202

Khan AG, Kuek C, Chaudhry TM, Koo CS, Hayes W (2000) Role of plants, mycorrhizae and phytochelators in heavy metal contaminated land remediation. Chemosphere 41:197–207

Kidd P, Barcelo J, Pilar Bernal M, Navari-Izzo F, Poschenrieder C, Shilev S, Clemente R, Monterroso C (2009) Trace element behaviour at the root-soil interface: implications in phytoremediation. Environ Exp Bot 67:243–259

Kivaisi AK (2001) The potential for constructed wetlands for wastewater treatment and reuse in developing countries: a review. Ecol Eng 16:545–560

Knight RL, Ruble RW, Kadlec RH, Reed S (1993a) Wetlands for wastewater treatment. J Environ Eng 138:475–482

Knight RL, Ruble RW, Kadlec RH, Reed S (1993b) Wetlands for wastewater treatment: performance database. In: Moshiri GA (ed) Constructed wetlands for water quality improvement. Lewis Publishers, Boca Raton

Knox AS, Dunn D, Paller M, Nelson EA, Specht WL, Seaman JC (2006) Assessment of contaminant retention in constructed wetland sediments. Eng Life Sci 6:31

Knox AS, Nelson EA, Halverson NV, Gladden JB (2010) Long-term performance of a constructed wetland for metal removal. Soil Sediment Contam 19:667–685

Kotti P, Georgios DG, Tsihrintzis A (2010) Effect of operational and design parameters on removal efficiency of pilot-scale FWS constructed wetlands and comparison with HSF systems. Ecol Eng 36(7):862–875

Kraus ML (1988) Accumulation and excretion of five heavy metals by the salt marsh grass *Spartina alterniflora*. Bull Nor Acad Sci 33:39–43

Kumar AK, Chiranjeevi P, Mohanakrishna G, Mohan SV (2011) Natural attenuation of endocrine-disrupting estrogens in an ecologically engineered treatment system (eets) designed with floating, submerged and emergent macrophytes. Ecol Eng 37:1555–1562

Kurzbaum E, Kirzhner F, Armon R (2012) Improvement of water quality using constructed wetland systems. Rev Environ Health 27(1):59–64

Lee BH, Scholz M (2007) What is the role of *Phragmites australis* in experimental constructed wetland filters treating urban runoff? Ecol Eng 29:87–95

Lee S, Maniquiz MC, Choi J, Kang J-H, Jeong S, Kim LH (2012) Seasonal treatment efficiency of surface flow constructed wetland receiving high nitrogen content wastewater. Desalination Water Treat 48(1–3):9–16

Lesage E, Rousseau DPL, Meers E, Van de Moortel AMK, Du Laing G, Tack FMG, De Pauw N, Verloo MG (2007a) Accumulation of metals in the sediment and reed biomass of a combined constructed wetland treating domestic wastewater. Water Air Soil Pollut 183:253

Lesage E, Rousseau DPL, Meers E, Tack FMG, De Pauw N (2007b) Accumulation of metals in a horizontal subsurface flow constructed wetland treating domestic wastewater in Flanders, Belgium. Sci Total Environ 380:102–115

Lin M, Han Y (2012) Treatment of the domestic sewage by the lab-scale sub-surface horizontal-flow wetland. Adv Mater Res 374–377:1036–1039

Livingston EH (1989) Use of wetlands for urban stormwater management. In: Hammer DA (ed) Constructed wetlands for wastewater treatment: municipal, industrial and agricultural. Lewis Publishers, Boca Raton

Lu LL, Tian SK, Yang XE, Li TQ, He ZL (2009) Cadmium uptake and xylem loading are active processes in the hyperaccumulator *Sedum alfredii*. J Plant Physiol 166:579–587

MacFarlane GR, Burchett MD (2000) Cellular distribution of copper, lead and zinc in the grey mangrove, *Avicennia marina* (Frosk.) Vierh. Aquat Bot 68:45–59

Maine MA, Duarte MV, Suné NL (2001) Cadmium uptake by *Pistia stratiotes*. Water Res 35:2629–2634

Maine MA, Suné NL, Lagger SC (2004) Chromium bioaccumulation: comparison of the capacity of two floating aquatic macrophytes. Water Res 38:1494–1501

Maine MA, Suné N, Hadad H, Sanchez G, Bonetto C (2009) Influence of the vegetation on the removal of heavy metals and nutrients in a constructed wetland. J Environ Manage 90:355–363

Manios T, Stentiford EI, Millner P (2003) Removal of total suspended solids from wastewater in constructed horizontal flow subsurface wetlands. J Environ Sci Health A 36:1073–1085

Marchand L, Mench M, Jacob DL, Otte ML (2010) Metal and metalloid removal in constructed wetlands, with emphasis on the importance of plants and standardized measurements: a review. Environ Pollut 158:3447–3461

Matagi SV, Swai D, Mugabe R (1998) A review of heavy metal removal mechanisms in wetlands. Afr J Trop Hydrobiol Fish 8:23–35

Matamoros V, Bayona JM (2008) Behavior of emerging pollutants in constructed wetlands handbook. Environ Chem 5:192–217

Matamoros V, Salvadó V (2012) Evaluation of the seasonal performance of a water reclamation pond-constructed wetland system for removing emerging contaminants. Chemosphere 86(2):111–117

Matamoros V, Arias C, Brix H, Bayona JM (2007) Removal of pharmaceuticals and personal care products (PPCPs) from urban wastewater in a pilot vertical flow constructed wetland and a sand filter. Environ Sci Technol 41:8171–8177

Matamoros V, García J, Bayona JM (2008) Organic micropollutant removal in a full-scale surface flow constructed wetland fed with secondary effluent. Water Res 42:653–660

Matamoros V, Duhec A, Albaigés J, Bayona JM (2009) Photodegradation of carbamazepine, ibuprofen, ketoprofen and 17a-ethinylestradiol in fresh and seawater. Water Air Soil Pollut 196:161–168

Matamoros V, Reyes C, Bayona JM, Valsero MH (2010) Use of constructed wetlands to eliminate organic microcontaminants in domestic effluents. Tecnologia del Agua 30:22–26

Matamoros V, Arias CA, Nguyen LX, Salvadó V, Brix H (2012a) Occurrence and behavior of emerging contaminants in surface water and a restored wetland. Chemosphere 88:1083–1089

Matamoros V, Nguyen LX, Arias CA, Salvadó V, Brix H (2012b) Evaluation of aquatic plants for removing polar microcontaminants: a microcosm experiment. Chemosphere 88:1257–1264

Mitsch WJ, Gosselink JG (2007) Wetlands, 4th edn. Wiley, New York

Mohan BS, Hosetti BB (1999) Aquatic plants for toxicity assessment. Environ Res 81:259–274

Monferran MV, Sanchez Agudo JA, Pignata ML, Wunderlin DA (2009) Copper induced response of physiological parameters and antioxidant enzymes in the aquatic macrophyte *Potamogeton pusillus*. Environ Pollut 157:2570–2576

Moormann H, Kuschk P, Stottmeister U (2002) The effect of rhizodeposition from helophytes on bacterial degradation of phenolic compounds. Acta Biotechnol 22:107–112

Murray-Gulde CL, Bearr J, Rodgers JH (2005b) Evaluation of a constructed wetland treatment system specifically designed to decrease bioavailable copper in a wastestream. Ecotoxicol Environ Saf 61:60–73

Nyquist J, Greger M (2009) A field study of constructed wetlands for preventing and treating acid mine drainage. Ecol Eng 35:630–642

O'Sullivan AD, Moran BM, Otte ML (2004) Accumulation and fate of contaminants (Zn, Pb, Fe and S) in substrates of wetlands constructed for treating mine wastewater. Water Air Soil Pollut 157:345

Obarska-Pempkowiak H, Gajewska M (2003) The removal of nitrogen compounds in constructed wetlands in Poland. Polish J Environ Stud 12:739–746

Obarska-Pempkowiak H, Gajewska M (2004) The removal of nitrogen compounds in constructed wetlands in Poland. Wetlands 24(2):459–466

Otte ML, Rozema J, Koster L, Haarsma MS, Broekman RA (1989) Iron plaque on roots of *Aster tripolium* L. interaction with zinc uptake. New Phytol 111: 309–317

Pal R, Rai JPN (2010) Phytochelatins: peptides involved in heavy metal detoxification. Appl Biochem Biotechnol 160:945–963

Pal A, Gin HKY, Lin AYC, Reinhard M (2010) Impacts of emerging organic contaminants on freshwater resources: review of recent occurrences, sources, fate and effects. Sci Total Environ 408:6062–6069

Pedescoll A, Corzo A, Álvarez E, Puigagut J, García J (2011) Contaminant removal efficiency depending on primary treatment and operational strategy in horizontal subsurface flow treatment wetlands. Ecol Eng 37:372–380

Qian JH, Zayed A, Zhu ML, Yu M, Terry N (1999) Phytoaccumulation of trace elements by wetland plants. III: uptake and accumulation of ten trace elements by twelve plant species. J Environ Qual 28:1448

Quintana JB, Weiss S, Reemtsma T (2005) Pathways and metabolites of microbial degradation of selected acidic pharmaceuticals and their occurrence in municipal wastewater treated by a membrane bioreactor. Water Res 39:2654–2664

Rai PK (2008) Heavy metal pollution in aquatic ecosystems and its phytoremediation using wetland plants: an ecosustainable approach. Int J Phytoremediation 10:131–158

Rousseau DPL, Lesage E, Story A, Vanrolleghem PA, De Pauw N (2008) Constructed wetlands for water reclamation. Desalination 218:181–189

Sandermann H (1992) Plant metabolism of xenobiotics. Trends Biochem Sci 17(2):82–84

Scholz M, Hedmark A (2010) Constructed wetlands treating runoff contaminated with nutrients. Water Air Soil Pollut 205:323–332

Seeger EM, Kuschk P, Fazekas H, Grathwohl P, Kaestner M (2011) Bioremediation of benzene, MTBE and ammonia-contaminated groundwater with pilot-scale constructed wetlands. Environ Pollut 159:3769–3776

Seo DC, Yu K, DeLaune RD (2008) Comparison of monometal and multimetal adsorption in Mississippi River alluvial wetland sediment: batch and column experiments. Chemosphere 73:1757–1764

Shanker AK, Cervantes C, Loza-Tavera H, Avudainayagam S (2005) Chromium toxicity in plants. Environ Int 31:739–753

Sharma SS, Dietz KJ (2009) The relationship between metal toxicity and cellular redox imbalance. Trends Plant Sci 14(1):43–50

Sheoran AS, Sheoran V (2006) Heavy metal removal mechanism of acid mine drainage in wetlands – a critical review. Minerals Eng 19:105–116

Sikora FJ, Behrends LL, Phillips WD, Kelley DA, Coonrod HS, Bailey E (1995) Phytoremediation of explosives-contaminated groundwater in constructed wetlands: I- batch study. U.S. Army Environmental Center report no. SFIM-AEC-ET-CR-96166

Singh R, Tripathi RD, Dwivedi S, Kumar A, Trivedi PK, Chakrabarty D (2010) Lead bioaccumulation potential of an aquatic macrophyte *Najas indica* are related to antioxidant system. Bioresour Technol 101:3025–3032

Siracusa G, La Rosa AD (2006) Design of a constructed wetland for wastewater treatment in a Sicilian town and environmental evaluation using the energy analysis. Ecol Model 197:490–497

Sobolewski A (1999) A review of processes responsible for metal removal in wetlands treating contaminated mine drainage. Int J Phytoremediation 1:19–51

Stefanakis AI, Tsihrintzis VA (2012) Effect of loading, resting period, temperature, porous media, vegetation and aeration on performance of pilot-scale vertical flow constructed wetlands. Chem Eng J 181–182:416–430

Stottmeister U, Wießner A, Kuschk P, Kappelmeyer U, Ka¨stner M, Bederski O, Mu¨ller RA, Moormann H (2003) Effects of plants and microorganisms in constructed wetlands for wastewater treatment. Biotechnol Adv 22:93–117

Sudarsan JS, Thattai D, Das A (2012) Phyto-remediation of dairy-waste water using constructed wetland. Int J Pharma Bio Sci 3(3):B745–B755

Sundaravadivel M, Vigneswaran S (2001) Constructed wetlands for wastewater treatment. Crit Rev Environ Sci Technol 31(4):351–409

Suné N, Sanchez G, Caffaratti S, Maine MA (2007) Cadmium and chromium removal kinetics by two aquatic macrophytes. Environ Pollut 145:467–473

Terry N, Zayed AM, de Souza MP, Tarun AS (2000) Selenium in higher plants. Ann Rev Plant Physiol Plant Mol Biol 51:401

Thullen JS, Sartoris JJ, Nelson SM (2005) Managing vegetation in surface-flow wastewater-treatment wetlands for optimal treatment performance. Ecol Eng 25:583–593

Todd J, Brown EJG, Wells E (2003) Ecological design applied. Ecol Eng 20:421–440

United States Environmental Protection Agency (1999) Constructed wetlands treatment of municipal wastewaters; EPA/625/R-99/010; Cincinnati

Verbruggen N, Hermans C, Schat H (2009) Mechanisms to cope with arsenic or cadmium excess in plants. Curr Opin Plant Biol 12:364–372

Vesk PA, Nockold CE, Allaway WG (1999) Metal localization in water hyacinth roots from an urban wetland. Plant Cell Environ 22:149–152

Vymazal J (2005) Horizontal sub-surface flow and hybrid constructed wetlands systems for wastewater treatment. Ecol Eng 25:478–490

Vymazal J (2006) Removal of nutrients in various types of constructed wetlands. Sci Total Environ 380:48–65

Vymazal J, Sveha J (2012a) The use of integrated constructed wetlands (ICW) for the treatment of separated swine wastewaters. Hydrobiologia 692:111–119

Vymazal J, Sveha J (2012b) Removal of alkali metals and their sequestration in plants in constructed wetlands treating municipal sewage. Hydrobiologia 692:131–143

Vymazal J, Brix H, Cooper PF, Green MB, Haber R (1998) Constructed wetlands for wastewater treatment in Europe. Backhuys Publishers, Leiden

Vymazal J, Svehla J, Kropfelova L, Chrastny V (2007) Trace metals in *Phragmites australis* and *Phalaris arundinacea* growing in constructed and natural wetlands. Sci Total Environ 380:154–162

Wei Z-J, Xie J-P, Huang Y-M (2012) Effect of the subsurface constructed wetland evolution into free surface flow constructed wetland on the removal of organic matter, nitrogen, and phosphor in wastewater. Huanjing Kexue/Environ Sci 33(11):3812–3819

Weiss JV, Emerson D, Backer SM, Megonigal JP (2003) Enumeration of Fe(II)-oxidizing and Fe(III)-reducing bacteria in the root zone of wetland plants: implications for a rhizosphere iron cycle. Biogeochemistry 64:77–96

Wenzel WW, Adriano DC, Salt D, Smith R (1999) Phytoremediation: a plant–microbe-based remediation system. In: Adriano DC, Bollag JM, Frankenberger WT, Jr Sims RC (eds) Bioremediation of Contaminated Soils, American Society of Agronomy, Agronomy monograph, vol 37, Madison, pp 457–508

Wu H, Li W, Zhang J, Li C, Zhang J, Xie H (2012) Application of using surface constructed wetland for removal of chemical oxygen demand and ammonium in polluted river water. Desalination Water Treat 44:142–150

Yada BK, Siebel MA, van Bruggen JJA (2011) Rhizofiltration of a heavy metal (Lead) containing wastewater using the wetland plant *Carex pendula*. Clean Soil Air Water 39:467–474

Yang J, Ye Z (2009) Metal accumulation and tolerance in wetland plants. Front Biol China 4(3):282–288

Yang Q, Chen Z, Zhao J, Gu B (2007) Contaminant removal of domestic wastewater by constructed wetlands: effects of plant species. J Integr Plant Biol 49:437–446

Ye ZH, Baker AJM, Wong MH, Willis AJ (1997a) Zinc, lead and cadmium tolerance, uptake and accumulation by *Typha latifolia*. New Phytol 136:e469–e480

Ye ZH, Baker AJM, Wong MH, Willis AJ (1997b) Copper and nickel uptake, accumulation and tolerance in *Typha latifolia* with and without iron plaque on the root surface. New Phytol 136:481–488

Ye ZH, Baker AJM, Wong MH, Willis AJ (1997c) Zinc, lead and cadmium tolerance, uptake and accumulation by the common reed, *Phragmites australis* (Cav.) Trin, ex Steudel. Ann Bot 80:363–370

Ye ZH, Lin ZQ, Whiting SN, de Souza MP, Terry N (2003) Possible use of constructed wetland to remove selenocyanate, arsenic, and boron from electric utility wastewater. Chemosphere 52:1571–1579

Yu R, Wu Q, Lu X (2012) Constructed wetland in a compact rural domestic wastewater treatment system for nutrient removal. Environ Eng Sci 29(8):751–757

Zayed A, Gowthaman S, Terry N (1998) Phytoaccumulation of trace elements by wetland plants: I. Duckweed. J Environ Qual 27:715–721

Zhang CB, Wang J, Liu WL, Zhu SX, Liu D, Chang SX, Chang J, Ge Y (2010) Effects of plant diversity on nutrient retention and enzyme activities in a fullscale constructed wetland. Bioresour Technol 101:1686–1692

Zhang DQ, Gersberg RM, Hua T, Zhu J, Tuan NA, Tan SK (2012a) Pharmaceutical removal in tropical subsurface flow constructed wetlands at varying hydraulic loading rates. Chemosphere 87:273–277

Zhang DQ, Gersberg RM, Zhu J, Hua T, Jinadasa KBSN, Tan SK (2012b) Batch versus continuous feeding strategies for pharmaceutical removal by subsurface flow constructed wetland. Environ Pollut 167:124–131

Zhou Y, Tigane T, Li X, Truu M, Truu J, Mander U (2013) Hexachlorobenzene dechlorination in constructed wetland mesocosms. Water Res 47(1): 102–110

Zhu YL, Zayed AM, Qian JH, Souza M, Terry N (1999) Phytoaccumulation of trace elements by wetland plants. II water hyacinth (*Eichhornia crassipes*). J Environ Qual 28:339

Zwiener C, Frimmel FH (2003) Short-term tests with a pilot sewage plant and biofilm reactors for the biological degradation of the pharmaceutical compounds clofibric acid, ibuprofen and diclofenac. Sci Total Environ 309:201–211

5 Future Prospects

The success of the phytoremediation technology depends upon its implementation at different sites and a potential to treat/remove various contaminants. Many field scale, site-specific and pilot scale studies have been conducted, though remediation conditions are different for each contaminant (Pilon-Smits 2005; Salt et al. 1998). Selection of the most efficient plant species to degrade a particular compound is the most important determining step in this technology.

The rate of remediation of any contaminant depends on selection of plant species which is climatically adapted with desired growth characteristics. A plant with good root system is effective as increased root mass increase the surface area available for microbial colonization and root exudation, hence facilitating higher contaminant removal from the soil. Increased microbial numbers in rhizosphere zone enhance microbial degradation of contaminant.

Technique has been successfully implemented at many sites, but till date most of the success stories have been related terrestrial plants. Trees of the *Salicaceae* family (willow and poplar) have been used at several locations in phytoremediation technology because of their flood tolerance and fast growth. Ecolotree™ reported application of phytoremediation of organic contaminants such as trichloroethylene using poplars. Poplar trees possess extensive root systems that act as pump to draw water from deepwater tables and transpire the water back to the atmosphere. A proprietary technique, called TreeMediation™, also has been developed that uses hybrid poplar trees with a deep root system (up to 30 ft below land surface) to facilitate the uptake of contaminated groundwater. US Air Force also remediated TCE from groundwater using poplar trees. Numerous defence sites across the USA including Milan Army Ammunition Plant had groundwater contaminated with explosives like TNT, RDX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocine (HMX) and DNT. These contaminants have been successfully treated using constructed wetlands. Plant nitroreductase enzyme is able to degrade TNT, RDX and HMX. Remediation of soils contaminated with PAHs have been achieved using plant species *Medicago sativa* (alfalfa), *Panicum virgatum* (switch grass) and *Schizachyrium scoparium* grass (little bluestem). *Myriophyllum aquaticum* has been successfully used in the remediation of soils contaminated with TNT as well as other organic contaminants such as TCE. The plant has also shown potential for phytotransformation of perchlorate (Susarla et al. 2002).

5.1 Limitations of Phytoremediation Technology

Like any other technology, phytoremediation, besides possessing a number of positive points that makes it widely acceptable, have certain limitations. Some of them are listed below:

1. It is generally considered as a time-consuming process and may take at least several growing seasons to clean up a site. For example, in

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one estimate considering the slow growth rate and biomass production, remediation of metals could not be achieved even within 10–20 years (Ernst 1996). Another estimate suggests that treatment of heavy-metal-contaminated site using *Thlaspi caerulescens* would require 13–14 years to be remediated (Salt et al. 1998). Therefore, selection of faster growing plants and hyperaccumulators becomes a prerequisite.

2. Intermediates formed from organic and inorganic contaminants may be cytotoxic to plants.
3. Excavation and disposal or incineration of contaminated plant matter takes weeks to months to accomplish. Harvesting and proper disposal are regulatory requirements for plant biomass that accumulates heavy metals or radionuclides (Adler 1996).
4. Risk analysis for human and other ecological receptors given the potential pathways for contaminant transformation and transfer is also required. Potential risk of horizontal gene transfer to related wild or cultivated plants is an important barrier associated with development of transgenic plants for bioremediation.
5. Depth of plant root is also a main factor that affects the plant's potential for uptake. Selection of deep-rooted plants and the use of techniques to induce deep rooting could help alleviate this disadvantage.
6. Performance of remedial technology is affected by climatic conditions and other biotic factors. Technology can lose its effectiveness during winter (when plant growth slows or stops) or when damage occurs to the vegetation from weather, disease or pests.
7. Transfer of toxic contaminants to various components of food chain or bioconcentration of toxic contaminants by components of food chain and environment is an issue of major concern, especially if there is transformation of the contaminant results into a more toxic, mobile or bioavailable form. Sampling and analysis of the aboveground plant matter and degradation products may be necessary to ensure that the contaminants are not transferred to the food chain.
8. Efficacy for phytoremediation varies for species or varieties. There can be a wide range in their response to a contaminant and concentration of that contaminant, in their uptake or metabolism of the contaminant or in their ability to grow under specific soil and climatic conditions.
9. Site-specific studies may always be necessary prior to implementation.
10. Growth of vegetation requires great care due to abiotic and biotic stresses such as climate and pests. Additions to or modifications of normal agronomic practices might be required and may have to be determined through greenhouse or pilot scale tests.
11. It might require use of a greater land area than other remedial methods.
12. Amendments and cultivation practices might have unintended consequences on contaminant mobility. For example, application of many common ammonium-containing fertilizers can lower the soil pH, which might result in increased metal mobility and leaching of metals to ground water. Potential effects of soil amendments should be understood before their use.
13. Nature and extent of contamination, hydrological and geological characteristics and site characteristics must be assessed.

5.2 Enhancement of Phytoremediation Efficiency

Due to limitations of phytoremediation such as low biomass of hyperaccumulator species, plant sensitivity to high concentrations of environmental pollutants as well as other abiotic stresses and less efficiency of ions and compounds which have low bioavailability to uptake by plants, several approaches have been explored to enhance the efficiency of this technology (Reeves and Baker 1999). Although chemicals (e.g. surfactants and ligands) can increase phytoextraction, phytodegradation or phytostimulation efficiency of pollutants through enhancement of bioavailability of organic and inorganic compounds in media, nature-based methods like using plant–microorganisms symbiosis seem to be more acceptable because of less side effects, hence protecting food chain. Plant symbiosis with fungi and bacteria have been tried to get increase in phytoremediation efficiency of various environmental pollutants.

The various approaches used for enhancing phytoremediation potential have been discussed below:

5.2.1 Plant–Bacteria Symbiosis

Rhizospheric bacteria have shown beneficial effects on various plants and were named as plant growth-promoting rhizobacteria (PGPR). They are categorized into two types: extracellular and intracellular PGPR (Dimkpa et al. 2009). The latter group includes bacteria which are capable of entering the plant as endophytic bacteria and are able to create nodules, whereas extracellular PGPR are found in the rhizosphere and rhizoplane or within the apoplast of the root cortex, but not inside the cells (Dimkpa et al. 2009; Rajkumar et al. 2009). Plant-associated bacteria can promote plant growth as well as reduce and/or control of environmental stresses which together affect phytoremediation efficiency through several approaches directly and indirectly, within the plant and/or in the rhizosphere (Dimkpa et al. 2009; Rajkumar et al. 2009; Yang et al. 2009; Glick 2010; Kang et al. 2010). A number of soil microorganisms are capable of degrading xenobiotic compounds and consequently reduce their related stress to plants in contaminated soils (Glick 2010). Several mechanisms that induce abiotic stress tolerance within the plant or in the rhizosphere include:

1. Production of phytohormones (e.g. auxins, cytokinins, gibberellins) which can change root morphology is an adaptation mechanism of plant species exposed to environmental stresses (Dimkpa et al. 2009; Weyens et al. 2009). Indole acetic acid as a subgroup of auxins together with nitric oxide is produced in plant shoot transported to root tips and consequently enhance cell elongation, root growth, root surface area and development of lateral roots (Dimkpa et al. 2009).

   According to Kang et al. (2010), ACC synthesized in plant tissues by ACC synthase is thought to be exuded from plant roots and be taken up by neighbouring bacteria. Subsequently, the bacteria hydrolyze ACC to ammonia and 2-oxobutanoate. This ACC hydrolysis maintains ACC concentrations low in bacteria and permits continuous ACC transfer from plant roots to bacteria. Otherwise, ethylene can be produced from ACC and then cause stress responses including growth inhibition.
2. Inoculation with nonpathogenic rhizobacteria can induce signalling cascades and plant systemic resistance; alter the selectivity for Na, K and Ca ions resulting in higher K/Na ratios; and change in membrane phospholipid content as well as the saturation pattern of lipids (Dimkpa et al. 2009).
3. Bacteria may produce osmolytes, such as glycine betaine, and act synergistically with plant osmolytes, accelerating osmotic adjustment (Dimkpa et al. 2009).
4. PGPR containing 1-aminocyclopropane-1-carboxylic acid (ACC) deaminase activity reduces ethylene level within the plant and consequently facilitates plant growth under stress conditions (Dimkpa et al. 2009; Kang et al. 2010).

Rhizosphere play a role in abiotic stress tolerance by performing different roles. These include: (1) Nitrogen fixation by rhizobacteria positively influence host plant growth by increasing nitrogen availability (Dimkpa et al. 2009; Kang et al. 2010; Rajkumar et al. 2009). Therefore, they can act as a biofertilizer which affect plant growth. (2) Rhizobacteria reduce the mobility of heavy metals in contaminated soils in root zone bacteria which finally cause precipitation of metals as insoluble compounds in soil and sorption to cell components or intracellular sequestration. (3) Bacterial migration from the rhizoplane to the rhizosphere reduce plant uptake of metals (e.g. Cd). (4) Iron-chelating siderophores complexes can be taken up by the host plant, resulting in higher fitness (Dimkpa et al. 2009). They can also form complexes with other nonsoluble metals (e.g. Pb), enhancing their ability to uptake by hyperaccumulators such as *Brassica napus*. (5) Rhizosphere bacteria influence pH and redox potential in the rhizosphere through the release of organic acids. This increases availability of nutrients (e.g. phosphorous) for the plant. (6) PGPR can act as biocontrol agents which mitigate the effect of pathogenic organisms (Dimkpa et al. 2009; Rajkumar et al. 2009).

5.2.2 Plant–Fungi Symbiosis

Arbuscular mycorrhizal fungi (AMF) that are naturally present in the roots of most plant species form a mutualistic association. Endophytic fungi live systemically within the aerial portion of many grass species and help in improving plant tolerance to biotic and abiotic stresses (Hildebrandt et al. 2007; Lingua et al. 2008; Soleimani et al. 2010a). These fungi reduce abiotic stress by regulating oxidative stress (by reducing the amount of malondialdehyde) (Bressano et al. 2010). AMF are useful for phytoremediation, especially in metal-contaminated soils (Bressano et al. 2010; Jiang et al. 2008; Lingua et al. 2008). Mycorrhizal fungi in association with poplars are suitable for phytoremediation purposes (Lingua et al. 2008). Furthermore, some fungi have the potential to degrade organic pollutants via extracellular or intracellular oxidation using various enzymes, such as laccase, peroxidase, nitroreductase and transferases (Harms et al. 2011), and thereafter reduce stress of organic compounds in soil. AMF reduce metal stress in host plants and improve plant growth and development via production and excretion of organic acids (e.g. citrate and oxalate) which increase dissolution of primary minerals such as phosphate (Harms et al. 2011), release of siderophores can enhance iron uptake by plant and boost the growth. Extra-hyphal immobilization may occur through the complexation of metals by glomalin (i.e. metal-sorbing glycoproteins excreted by AMF) and biosorption to cell wall constituents such as chitin and chitosan (Harms et al. 2011). Metallothionein is another protein excreted by some mycorrhizal fungi which can also be important to reduce heavy metal stress in plants (Schützendübel and Polle 2002).

5.2.2.1 Endophytic Fungi

Endophytes induce mechanisms of drought avoidance (morphological adaptations), drought tolerance (physiological and biochemical adaptations) and drought recovery in infected grasses (Malinowski and Belesky 2000). Aluminium toxicity mainly in acidic soils can be reduced on root surface of endophyte-infected plants through Al sequestration which appears to be related to exudation of phenolic-like compounds with Al-chelating activity (Malinowski and Belesky 2000). Besides, drought and light stress as well as salt stress could be reduced in endophyte-infected plants via release of some proteins (e.g. dehydrins) and phenolic-like compounds in the rhizosphere (Kuldau and Bacon 2008; Malinowski and Belesky 2000). Endophytic fungi positively affect phytoremediation of heavy metals as well as organic pollutants such as petroleum hydrocarbons (Soleimani et al. 2010a, b).

5.2.3 Biotechnological Approach

The use of transgenic plants for phytoremediation applications has been studied extensively. Transgenic plants have been produced for phytoremediation of both heavy metals and organic pollutants (Macek et al. 2000, 2008; van Aken 2009; van Aken et al. 2010). Genetic transformation of plants for enhanced phytoremediation capabilities is achieved by introduction of external genes whose products are involved in various detoxification processes. The genes for metabolic enzymes from microbes and mammals have been introduced to achieve a near-complete mineralization of organic molecules in plants. Genes isolated from various plant, bacterial and animal sources that can enhance metal accumulation or degradation of organics is desired (Newman et al. 1997; Dhanker et al. 2002). These changes will include transformation of plants to add specific proteins or peptides for binding and transporting xenobiotics, increasing the quantity and activity of plant biodegradative enzymes (peroxidases, laccases, oxygenases, dehalogenases, nitroreductases, nitrilases), including those that are exported into the rhizosphere and surrounding soil to improve the performance of soil bacteria. Introduction of foreign genes might be responsible for the synthesis of low-molecular-weight organic molecules to be excreted in exudates, such as some phenolics, flavonoids or coumarins, that induce rhizospheric bacteria to degrade anthropogenic toxins. Transgenic plants with genes for microbial biodegradation can be created. Transgenic approach targets the genes responsible for overexpression or knockdown of membrane transporter proteins to enhance uptake, accumulation and/or degradation of various contaminants. Genetic engineering of plants by insertion of genes allowed metabolism of TCE, chlorinated hydrocarbons, phenolics and herbicides.

Molecular biology techniques will facilitate formation of plants with improvement in phytoremediation technology. This can be done by developing plants specifically for enhanced metal accumulation and degradation of organics by transforming plants by adding specific proteins or peptides for binding and transporting xenobiotics, increasing the quantity and activity of plant biodegradative enzymes (peroxidases, laccases, oxygenases, dehalogenases, nitroreductases, nitrilases). Introduction of foreign genes include those responsible for the synthesis of low-molecular-weight organic molecules (phenolics, flavonoids or coumarins) to be excreted in exudates that induce rhizospheric bacteria to degrade anthropogenic toxins.

5.2.3.1 Metals

Genes for higher tolerance and accumulation of contaminants such as heavy metals have been expressed. The V Framework Research Program of the European Community includes two projects on the production of genetically modified plants for phytoremediation, PHYTAC and metallophytes. PHYTAC aims to transfer genes from the hyperaccumulator *Thlaspi caerulescens* to the high-biomass-producing *Brassica* or tobacco, while the metallophytes project is devoted to engineering *Festuca* for improved metal tolerance and or accumulation. Transformation of plants using modified bacterial *merA* gene (*mer A9*) for detoxifying Hg (II) has been the most successful approach till date. Several plant species including *Arabidopsis*, tobacco, poplar, rice, Eastern cottonwood, peanut, salt marsh grass and *Chlorella* have been transformed with these genes. The merA gene codes for a mercuric ion reductase that removes Hg from stable thiol salts by reducing it to volatile metallic Hg. Mercuric reductase has also been successfully transferred to *Brassica,* tobacco and yellow poplar trees (Pilon-Smits et al. 1999). *merA* or *merB* genes have been expressed in plants via nuclear or chloroplast genome, expressing organomercurial lyase and/or mercuric ion reductase in the cytoplasm, endoplasmic reticulum or within the plastids. Salt marsh cordgrass (*Spartina alterniflora*) modified for Hg phytoremediation showed resistance up to 500 μM $HgCl_2$. Plants tend to accumulate most mercury in roots, and translocation to shoot tends to be a major limitation; therefore, an ability to express membrane proteins, transport proteins and translocators could further enhance mercury phytoremediation capabilities. The recent research focuses on expression of membrane proteins transforming the chloroplast genome with *mer* transporters to enhance Hg accumulation. Alternatively, the *merC* can be coupled to a chelator gene like polyphosphate kinase (*ppk*) or metallothionein (*mt*), to develop transgenic plants that could accumulate Hg (Ruiz and Daniell 2009).

Expression of a yeast metallothionein gene for higher Cd tolerance in tobacco plants, *overexpression of* a Zn transporter protein in *Arabidopsis thaliana* for higher Zn accumulation in roots are few examples of use of biotechnological approach for achieving high phytoremediation potential (Meagher et al. 2000). Genes for heavy metal resistance and uptake such as *AtNramps* (Thomine et al. 2000); *AtPcrs* (Song et al. 2004); *CAD1* from *Arabidopsis thaliana*, library enriched in Cd-induced cDNAs from *Datura innoxia* (Louie et al. 2003); *gshI*, *gshII* (Zhu et al. 1999a); and PCS cDNA clone (Heiss et al. 2003) from *Brassica juncea* (Zhu et al. 1999b) have been isolated and introduced into plants. Other transgenic raised include *A. thaliana* tolerant to Al, Cu and Na with gene *Glutathione S-transferase* from tobacco (Ezaki et al. 2000); tobacco with Ni tolerance and Pb accumulation with gene *Nt CBP4* from tobacco; tobacco and rice (Goto et al. 1998, 1999) with increased iron accumulation with gene *Ferretin* from soybean; *A. thaliana* and tobacco resistant to Hg with gene *merA* from bacteria (Rugh et al. 2000; Bizily et al. 2000; Eapen and D'Souza 2005); Indian mustard tolerant to Se transformed with a bacterial glutathione reductase in the cytoplasm and also in the chloroplast (D'Souza et al. 2000); and transgenic *A. thaliana* plants expressing SRSIp/ArsC and ACT 2p/γ-ECS together showed high tolerance to As.

5.2.3.2 PCBs

Transgenic plants and associated bacteria treat polychlorinated biphenyls (PCBs)-contaminated soil and water in an efficient and environmental-friendly way (Mackova et al. 1997, 2007). Organic contaminants including PCBs are slowly taken up and degraded by plants and associated bacteria because of their hydrophobicity and chemical stability, resulting in incomplete treatment and potential release of toxic metabolites into the environment. In order to overcome these limitations, bacterial genes involved in the metabolism of PCBs, such as biphenyl dioxygenases, have been introduced into higher plants, following a transgenic approach. Bacterial biphenyl dioxygenases produce *cis*-diol intermediates susceptible to ring cleavage and complete mineralization. Francova et al. (2003) genetically modified tobacco plants (*Nicotiana tobacum*) by insertion of the gene responsible for 2,3-dihydroxybiphenyl ring cleavage, *bph*C, from the PCB degrader *Comamonas testosteroni*. Mohammadi et al. (2007) inserted *bph* genes from *B. xenovorans* LB400 into tobacco plants.

5.2.3.3 Herbicides and Explosives

Studies have also been conducted to develop plants with an increased ability to degrade explosives such as GTN and TNT by overexpressing a bacterial NADPH-dependent nitroreductase. Other successful experiments with genetically modified plants have tackled contamination by herbicides (Karavangeli et al. 2005), organomercurials (Bizily et al. 2000), phenolic compounds (Wang et al. 2004), PCBs (Mohammadi et al. 2007) and nitroaromatics (Hannink et al. 2001; Rylott et al. 2006).

Many plant enzymes appear to play important roles in xenobiotic degradation, including mono- and dioxygenases, dehydrogenases, hydrolases, peroxidases, nitroreductases, nitrilases, dehalogenases, phosphatases and carboxylesterases (Dietz and Schnoor 2001; Singer et al. 2003; Pilon-Smits 2005). Biotechnologists are using potential of these enzymes to increase the remediation ability of suitable plant species. Some of these enzymes appear to be naturally released into the soil, where they are capable of degrading organic pollutants ranging from solvents to explosives (Singer et al. 2003). The reactions catalyzed by plant P450s extend from simple hydroxylation or epoxidation steps to more complex phenol coupling, ring formation and modification or decarboxylation of appropriate substrates. *Helianthus tuberosus* CYP76B1 and *soybean* (*Glycine max* (L) Merr.) CYP71A10 were the first plant enzymes shown to actively metabolize a herbicide (Robineau et al. 1998; Siminszky et al. 1999). Since then, several plant P450s have been associated with the degradation of relevant organochemicals, including several POPs. However, most P450s expressed heterologously in plants for remediation purposes are of mammalian origin. Human cytochrome P450 gene CYP2E1has been expressed in *tobacco* to get enhanced metabolism of trichloroethylene (Campos et al. 2008). The expression of mammalian cytochrome P450 genes in transgenic potatoes and rice plants has been used to detoxify herbicides. Rice plants transformed with genes encoding human cytochrome P450 genes CYP1A1, CYP2B6 and/or CYP2C19 showed more tolerance to various herbicides including atrazine, metolachlor and norflurazon. Transgenic rice plants carrying CYP1A1 show herbicide tolerance towards atrazine, chlorotoluron, diuron, quizalofop-ethyl and other herbicides, and they reduce the levels of atrazine and simazine in hydroponic solutions. Transgenic rice carrying CYP2B6 germinate well in medium containing chloroacetanilide herbicides, such as alachlor, metolachlor and thenylchlor. Transgenic plants overexpressing detoxifying enzymes such as laccase 1 (LAC1) showed higher capacity for degrading herbicides in rhizosphere (Kawahigashi et al. 2005a, b, 2007; Kawahigashi 2009). Transgenic plants that produce a root-specific laccase (LAC1) to the rhizosphere have shown enhanced resistance to a variety of phenolic allelochemicals and to 2,4,6-trichlorophenol.

Overexpression of glutathione transferases (GSTs) genes enhances the potential for phytoremediation of herbicides. Introduction of this gene into poplar plants leads to higher concentrations of glutathione, and the plants show tolerance towards two chloroacetanilide herbicides, acetochlor and metolachlor. Indian mustard (*Brassica juncea*) expressing this gene shows increased tolerance to atrazine, 1-chloro-2,4-dinitrobenzene (CDNB), metolachlor and phenanthrene. Maize GSTs are known to detoxify triazine and chloroacetanilide herbicides, and transgenic tobacco plants expressing maize GST I have been shown to remediate alachlor. Transgenic alfalfa, tobacco and Arabidopsis plants expressing a bacterial atrazine chlorohydrolase (atzA) gene show enhanced metabolic activity against atrazine (Flocco et al. 2004; Karavangeli et al. 2005; Kawahigashi 2009).

In context of aquatic plants, genetic engineering of high-biomass-producing, fast-growing aquatic plants with an enhanced capacity to accumulate metals and degrade xenobiotics plants is desirable. Genetic engineering studies for development of transgenic wetland species such as *Spartina* sp., *Typha* sp. and S*cirpus* sp. by insertion of the *Mer* genes are in progress. The wetland species *Scirpus maritimus* and *Typha latifolia* have shown the accumulation of toxic heavy metals such as Se that is facilitated by plant–bacteria interactions at the root interface, as well as further transformation by bacteria to organic form, which can be further excluded by methionine biosynthetic pathway or converted to volatile form that can escape into atmosphere (Dhir et al. 2009). These prospective transgenic wetland plants, namely, *Scirpus maritimus* and *Typha latifolia*, can be planted in contaminated aquatic ecosystems or in constructed wetlands to clean up Hg or Se pollution.

Practical application in case of genetically modified organisms requires a thorough study of ecological, social and legal issues. The potential impact of transgenic plants on the target habitat and the fate of the introduced gene also need to be studied. The potential of transgenic plants needs to be further validated to know the efficiency of this technique for cleanup of contaminated sites and their integration into sustainable cropping and management systems.

5.3 Cost Analysis

Environmental pollution is a global problem with cleanup costs running into billions of dollars using current engineering technologies. The availability of alternative, cheap and effective technologies would significantly improve the prospects of cleaning up contaminated sites. Phytoremediation has been proposed as an economical and ‘green’ method of treating contaminated sites. Economic outlook is an important consideration for any technology to be practically implementable. This mainly includes capital investment required for its operation and maintenance. Phytoremediation is an emerging technology; standard cost information still is being developed on the basis of experiences in implementing phytoremediation projects.

These cost considerations for the implementation of phytoremediation can be divided into four primary categories:

1. Design
2. Installation
3. Operation and maintenance
4. Sampling and analysis

1. Design considerations include feasibility studies, plant selection and the associated engineering costs. Green house studies or pilot scale testing may be needed to determine which plants to use and assess the possibility of phytoremediation as a treatment option for the site. The salaries of manpower performing conceptual work for the site will be the dominant cost in the design phase.

2. Installation costs include site preparation, soil preparation, materials and labour. This includes clearing or levelling land/soil followed by soil preparation that involves pH adjustment, nutrient addition or tilling. Site preparations require labour and materials including equipment, organic matter, irrigation systems, plant stock and vector protection materials for the plants.
3. Operation and maintenance (O&M) costs will include monitoring equipment, power sources, maintenance for the equipment and labour.
4. Sampling and analysis costs will depend upon length of the project as monitoring is required and data analysis is required at frequent intervals. Costs include labour or machinery to collect samples and lab work fees associated with analyzing samples. Data collected during sampling and analysis is crucial for thorough documentation of site progress and the performance of technology. This may dominate the overall cost of the project due to the length of time.

   Phytoremediation costs will vary depending on the treatment strategy. Though phytoremediation is often predicted to be cheaper than comparable technologies, still, costs of phytoremediation are highly site specific. For example, harvesting plants that bioaccumulate metals can drive up the cost of treatment when compared to treatments that do not require harvesting.

Cost comparisons of phytoremediation to other remediation technologies have recently been made. The cost of phytoremediation for 1 acre of sandy loam soil to a depth of 50 cm is estimated to range from $60,000 to $100,000. This is considerably lower than the approximate cost of $400,000 for excavation and disposal of the contaminated soil at the landfill. The cost of plant disposal can be significantly less than the cost of disposal of metal-contaminated soils because contaminants have been concentrated in the much smaller plant biomass. However, the total cost of phytoremediation will depend on the rates of uptake from the soil and the number of crops which are needed to meet cleanup levels. Analysis of the costs of phytoremediation must include the entire remedial process, from growing, maintaining and harvesting plants to disposing or recycling the metals in the plants. The consensus cost of phytoremediation has been estimated at $25–$100 per ton of soil treatment and $0.60–$6.00 per 1,000 gal for treatment of aqueous waste streams. According to 1997 US EPA estimates, the cost of using phytoremediation in the form of an alternative cover (vegetative cap) ranges from $10,000 to $30,000 per acre, which is thought to be two- to fivefold less expensive than traditional methods. The expenses of phytoremediation represent less than half of the price needed for any other effective treatment.

Phytotech, Inc. reports that cleanup costs, including treatment and disposal, can range from $20 to $80 per cubic yard of contaminated soil (Linacre et al. 2005). The cost estimate given includes incineration of plants and ash disposal at a hazardous waste incinerator at a cost of $500 per cubic yard of material. If the plants can be recycled at a smelter, costs near the low end of the range can be expected. The costs of cleanup of various heavy metals at the Twin Cities Army Ammunition Plant Project, Minneapolis, St. Paul, MN, were reported in the Federal Remediation Technologies Roundtable to be $153 per cubic yard of soil over the life of the project. The costs of removing radionuclides from water with sunflowers have been estimated to be $2–$6 per 1,000 gal of water (Dushenkov et al. 1997). Costs of cleanup of explosives at the Milan Army Ammunition Plant, Milan, TN, were reported in the Federal Remediation Technologies Roundtable (see Supporting Resources) to be $1.78 per 1,000 gal of water over the life of the project. Estimated costs for hydraulic control of an unspecified contaminant in a 20-foot-deep aquifer at a 1-acre site were $660,000 for conventional pump and treat and $250,000 for phytoremediation (EPA/600/R-99/107). Studies indicate that phytoremediation is competitive with other treatment alternatives, as costs are approximately 50–80 % of the costs associated with physical, chemical or thermal techniques at applicable sites (Thomas et al. 2003). Some more actuarial studies need to be carried out to give an estimate of the perceived costs of remediation works that

Estimates of phytoremediation costs versus costs of established technologies (USEPA 2000)

Contaminant	Phytoremediation costs	Estimated cost using other technologies
Metals	$80 per cubic yard	$250 per cubic yard
Site contaminated with petroleum hydrocarbons	$70,000	$850,000
10 acres of lead-contaminated land	$500,000	$12 million
Radionuclides in surface water	$2–$6 per 1,000 gal treated	None listed
1 ha to 15 cm depth (various contaminants)	$2,500–$15,000	None listed

Ecolotree Inc.'s cost estimates of a poplar tree phytoremediation system (USEPA 2000)

Activity	Cost
Installation of trees at 1,450 trees/acre	$12,000–$15,000
Predesign	$15,000
Design	$25,000
Site Visit	$5,000
Soil cover and amendments	$5,000
Transportation to site	$2.14/mile
Operation and maintenance	$1,500/acre with irrigation
	$1,000/acre without irrigation
Pruning	$500
Harvest	$2,500

Courtesy: http://clu-in.org/products/intern/phytotce.htm#1

will be useful for project sanctioning authorities or decision-makers.

According to laboratory, pilot scale work and field information costs associated with these four categories are relatively small in phytoremediation in comparison to traditional remediation technologies. The primary factor in cost reduction is the energy source of the operating systems. Traditional systems utilize electric power, at a substantial cost, to pump water, while phytoremediation systems take advantage of free solar energy. Moreover, phytoremediation is in situ and requires no digging or hauling of contaminated soil. Apart from this, little or no mechanical equipment is required to operate the phytoremediation process. Individual sites will vary in cost regardless of the technology being applied. In contrast, monitoring costs could be higher than with conventional treatment technologies because monitoring typically is required for a longer period of time at sites where phytoremediation is used.

5.4 Conclusions and Future Developments

Phytoremediation is fast becoming recognized as a cost-effective method for remediating sites contaminated with toxic metals, radionuclides and hazardous organics at a fraction of the cost of conventional technology. Phytoremediation is predicted to account for approximately 10–15 % of the growing environmental remediation market by the year 2010. Research related to this relatively new technology needs to be promoted and emphasized and expanded in developing countries. In addition, environmental aesthetics should not be ignored. Under phytoextraction, the cost of processing and ultimate disposal of biomass generated is likely to account for a major percentage of overall costs (USEPA 2000). The use of plant roots as 'biocurtains' or 'biofilters' for the passive remediation of shallow groundwater is also an active area of research. The establishment of vegetation on a site also reduces soil erosion by wind and water, which helps to prevent the spread of contaminants and reduces exposure of humans and animals. Yet in many ways, this technology is still in its infancy. Scientifically valid cost estimates of phytoremediation are a critical element in the acceptance of phytoremediation in the market and should be a major goal of the demonstration projects now underway. The public acceptance of technology depends upon the fact that field testing of genetically engineered plants is done. The application of phytoremediation is being driven by its technical and economic advantages over conventional approaches.

Literature Cited

Adler T (1996) Botanical clean up crews. Sci News 150:42–43

Bizily SP, Rugh CL, Meagher RB (2000) Phytodetoxification of hazardous organomercurials by genetically engineered plants. Nat Biotechnol 18:213–217

Bressano M, Curetti M, Giachero L, Gil SV, Cabello M, March G, Ducasse DA, Luna CM (2010) Mycorrhizal fungi symbiosis as a strategy against oxidative and environment stress in soybean plants. J Plant Physiol 167:1622–1626

Campos VM, Merino I, Casado R, Pacios LF, Gómez L (2008) Review. Phytoremediation of organic pollutants. Span J Agric Res 6(Special issue):38–47

D'Souza MP, Pilon-Smits EAH, Terry N (2000) The physiology and biochemistry of selenium volatilization by plants. In: Raskin I, Ensley BD (eds) Phytoremediation of toxic metals: using plants to clean up the environment. Wiley, New York, pp 171–188

Dhanker OP, Li YR, Barry PS, Jin SD, Senecoff JF, Sashti NA, Meagher RB (2002) Engineering tolerance and hyperaccumulation of arsenic in plants by combining arsenate reductase and y-glutamylcysteine synthetase expression. Nat Biotechnol 20: 1140–1145

Dhir B, Sharmila P, Saradhi PP (2009) Potential of aquatic macrophytes for removing contaminants from the environment. Crit Rev Environ Sci Technol 39:754–781

Dietz AC, Schnoor JL (2001) Advances in phytoremediation. Environ Health Perspect 109:163–168

Dimkpa C, Weinand T, Asch F (2009) Plant–rhizobacteria interactions alleviate abiotic stress conditions. Plant Cell Environ 32(12):1682–1694

Dushenkov S, Kaplunik Y, Fleisher DKC, Ensley B (1997) Removal of uranium from water using terrestrial plants. Environ Sci Technol 31:3468–3474

Eapen S, D'Souza SF (2005) Prospects of genetic engineering of plants for phytoremediation of toxic metals. Biotechnol Adv 23:97–114

Ernst WHO (1996) Bioavailability of heavy metals and decontamination of soils by plants. Appl Geochem 11: 163–167

Ezaki B, Gardner RC, Ezaki Y, Matsumoto H (2000) Expression of aluminium induced genes in transgenic *Arabidopsis* plants can ameliorate aluminium stress and/or oxidative stress. Plant Physiol 122:657–665

Flocco CG, Lindblom SD, Smits EA (2004) Overexpression of enzymes involved in glutathione synthesis enhances tolerance to organic pollutants in *Brassica juncea*. Int J Phytoremediation 6:289–304

Francova K, Sura M, Macek T, Szekeres M, Bancos S, Demnerova K, Sylvestre M, Mackova M (2003) Preparation of plants containing bacterial enzyme for degradation of polychlorinated biphenyls. Fresenius Environ Bull 12:309–313

Glick BR (2010) Using soil bacteria to facilitate phytoremediation. Biotechnol Adv 28(3):367–374

Goto F, Yoshihara T, Saiki H (1998) Iron accumulation in tobacco plants expressing soybean ferritin gene. Transgenic Res 7:173–180

Goto F, Yoshihara T, Shigemoto N, Toki S, Takaiwa F (1999) Iron accumulation in rice seed by soybean ferritin gene. Nat Biotechnol 17:282–286

Hannink N, Rosser SJ, French CE, Basran A, Murray JAH, Nicklin S, Bruce NC (2001) Phytodetoxification of TNT by transgenic plants expressing a bacterial nitroreductase. Nat Biotechnol 19:1168–1172

Harms H, Schlosser D, Wick LY (2011) Untapped potential: exploiting fungi in bioremediation of hazardous chemicals. Nat Rev Microbiol 9(3):177–192

Heiss S, Wachter A, Bogs J, Cobbett C, Rausch T (2003) Phytochelatin synthase (PCS) protein is induced in *Brassica juncea* leaves after prolonged Cd exposure. J Exp Bot 54:1833–1839

Hildebrandt U, Regvar M, Both H (2007) Arbuscular mycorrhiza and heavy metal tolerance. Phytochemistry 68:139–146

Jiang M, Cao L, Zhang R (2008) Effects of Acacia (*Acacia auriculaeformis* A. Cunn)- associated fungi on mustard (*Brassica juncea* (L.) Coss. var. Foliosa Bailey) growth in Cd- and Ni-contaminated soils. Lett Appl Microbiol 47(6):561–565

Kang BG, Kim WT, Yun HS, Chang SC (2010) Use of plant growth-promoting rhizobacteria to control stress responses of plant roots. Plant Biotechnol Rep 4(3):179–183

Karavangeli M, Labrou NE, Clonis YD, Tsaftaris A (2005) Development of transgenic tobacco plants overexpressing maize glutathione S-transferase I for chloroacetanilide herbicides phytoremediation. Biomol Eng 22:121–128

Kawahigashi H (2009) Transgenic plants for phytoremediation of herbicides. Curr Opin Biotechnol 20:225–230

Kawahigashi H, Hirose S, Inui H, Ohkawa H, Ohkawa Y (2005a) Enhanced herbicide cross-tolerance in transgenic rice plants coexpressing human CYP1A1, CYP2B6, and CYP2C19. Plant Sci 168:773–781

Kawahigashi H, Hirose S, Ohkawa H, Ohkawa Y (2005b) Phytoremediation of metolachlor by transgenic rice plants expressing human CYP2B6. J Agric Food Chem 53:9155–9160

Kawahigashi H, Hirose S, Ohkawa H, Ohkawa Y (2007) Herbicide resistance of transgenic rice plants expressing human CYP1A1. Biotechnol Adv 25:75–84

Kuldau G, Bacon C (2008) *Clavicipitaceous* endophytes: their ability to enhance resistance of grasses to multiple stresses. Biol Control 46(1):57–71

Linacre NA, Whiting SN, Angle JS (2005) The impact of uncertainty on phytoremediation project costs. Int J Phytoremediation 7(4):259–269

Lingua G, Franchin C, Todeschini V, Castiglione S, Biondi S, Burlando B, Parravicini V, Torrigiani P, Berta G (2008) Arbuscular mycorrhizal fungi differentially affect the response to high zinc concentrations of two registered poplar clones. Environ Pollut 153:137–147

Louie M, Kondor N, Witt JG (2003) Gene expression in cadmium-tolerant *Datura innoxia*: detection and characterization of cDNAs induced in response to Cd^{2+}. Plant Mol Biol 52:81–89

Macek T et al (2000) Exploitation of plants for the removal of organics in environmental remediation. Biotechnol Adv 18:23–35

Macek T, Kotrba P, Svatos A, Novakova M, Demnerova K, Mackova M (2008) Novel roles for genetically modified plants in environmental protection. Trends Biotechnol 26:146–152

Mackova M, Macek T, Ocenaskova J, Burkhard J, Demnerova K, Pazlarova J (1997) Biodegradation of polychlorinated biphenyls by plant cells. Int Biodetermination Biodegradation 39:317–325

Mackova M et al (2007) Biotransformation of PCBs by plants and bacteria – consequences of plant-microbe interactions. Eur J Soil Biol 43:233–241

Malinowski DP, Belesky DP (2000) Adaptations of endophyte infected cool-season grasses to environmental stresses: mechanisms of drought and mineral stress tolerance. Crop Sci 40:923–940

Meagher RB, Rugh CL, Kandasamy MK, Gragson G, Wang NJ (2000) Engineered phytoremediation of mercury pollution in soil and water using bacterial genes. In: Terry N, Bañuelos G (eds) Phytoremediation of contaminated soil and water. Lewis Publishers, Boca Raton, pp 201–219

Mohammadi M, Chalavi V, Novakova-Sura M, Laliberte JF, Sylvestre M (2007) Expression of bacterial biphenyl-chlorobiphenyl dioxygenase genes in tobacco plants. Biotechnol Bioeng 97:496–505

Newman LA, Strand SE, Choe N, Duffy J, Ekuan G, Ruszaj M, Shurtleff BB, Wilmoth J, Heilman P, Gordon MP (1997) Uptake and biotransformation of trichloroethylene by hybrid poplars. Environ Sci Technol 31:1062–1067

Pilon-Smits E (2005) Phytoremediation. Annu Rev Plant Biol 56:15–39

Pilon-Smits EA et al (1999) Overexpression of ATP sulfurylase in indian mustard leads to increased selenium uptake, reduction and tolerance. Plant Physiol 119:123–132

Rajkumar M, Ae N, Freitas H (2009) Endophytic bacteria and their potential to enhance heavy metal phytoextraction. Chemosphere 77(2):153–160

Reeves RD, Baker AJM (1999) Metal-accumulating plants. In: Raskin I, Ensley BD (eds) Phytoremediation of toxic metals using plants to clean up the environment. Wiley, New York, pp 193–229

Robineau T, Batard Y, Nedelkina S, Cabello-Hurtado F, LeRet M, Sorokine O et al (1998) The chemically inducible plant cytochrome P450 CYP76B1 actively metabolizes phenylureas and other xenobiotics. Plant Physiol 118:1049–1056

Rugh CL, Bizily SP, Meagher RB (2000) Phytoremediation of environmental mercury pollution. In: Raskin I, Ensley BD (eds) Phytoremediation of toxic metals using plants to clean up the environment. Wiley, New York, pp 151–171

Ruiz ON, Daniell H (2009) Genetic engineering to enhance mercury phytoremediation. Curr Opin Biotechnol 20:213–219

Rylott EL, Jackson RG, Edwards J, Womack GL, Seth-Smith HMB, Rathbone DA, Strand SE, Bruce NC (2006) An explosive-degrading cytochrome P450 activity and its targeted application for the phytoremediation of RDX. Nat Biotechnol 24:216–219

Salt DE, Smith RD, Raskin I (1998) Phytoremediation. Annu Rev Plant Physiol Plant Mol Biol 49:643–668

Schützendübel A, Polle A (2002) Plant responses to abiotic stresses: heavy metal-induced oxidative stress and protection by mycorrhization. J Exp Bot 53(372): 1351–1365

Siminszky B, Corbin FT, Ward ER, Fleischmann TJ, Dewey RE (1999) Expression of a soybean cytochrome P450 monooxygenase cDNA in yeast and tobacco enhances the metabolism of phenylurea herbicides. Proc Natl Acad Sci USA 96:1750–1755

Singer AC, Crowley DE, Thompson IP (2003) Secondary plant metabolites in phytoremediation and biotransformation. Trends Biotechnol 21:123–130

Soleimani M, Afyuni M, Hajabbasi MA, Nourbakhsh F, Sabzalian MR, Christensen JH (2010a) Phytoremediation of an aged petroleum contaminated soil using endophyte infected and non-infected grasses. Chemosphere 81(9):1084–1090

Soleimani M, Hajabbasi MA, Afyuni M, Mirlohi AF, Borggaard OK, Holm PE (2010b) Effect of endophytic fungi on Cd tolerance and bioaccumulation by *Festuca arundinacea* and *Festuca Peratensis*. Int J Phytoreme diation 12(6):535–549

Song WY, Martinoia E, Lee J, Kim D, Kim DY, Vogt E, Shim D, Choi KS, Hwang I, Lee Y (2004) A novel family of cys-rich membrane proteins mediates cadmium resistance in *Arabidopsis*. Plant Physiol 135:1027–1039

Susarla S, Medina VF, McCutcheon SC (2002) Phytoremediation: an ecological solution to organic chemical contamination. Ecol Eng 18:647–658

Thomas GJ, Lam TB, Wolf DCA (2003) Mathematical model of phytoremediation for petroleum contaminated soil: sensitivity analysis. Int J Phytoremediation 5(2):25–36

Thomine S, Wang R, Ward JM, Crawford NM, Schroeder JI (2000) Cadmium and iron transport by members of a plant metal transporter family in *Arabidopsis* with homology to *Nramp* genes. Proc Nat Acad Sci USA 97:4991–4996

USEPA (2000) Introduction to phytoremediation. United States Environmental Protection Agency, Washington, DC

Van Aken B (2009) Transgenic plants for enhanced phytoremediation of toxic explosives. Curr Opin Biotechnol 20:231–236

Van Aken B, Correa PA, Schnoor JL (2010) Phytoremediation of polychlorinated biphenyls: new trends and promises. Environ Sci Technol 44(8): 2767–2776

Wang GD, Li QJ, Luo B, Chen XY (2004) *Ex planta* phytoremediation of trichlorophenol and phenolic allelochemicals via an engineered secretory laccase. Nat Biotechnol 22:893–897

Weyens N, van der Lelie D, Taghavi S, Newman L, Vangronsveld J (2009) Exploiting plant–microbe partnerships to improve biomass production and remediation. Trends Biotechnol 27:591–598

Yang J, Kloepper JW, Ryu CM (2009) Rhizosphere bacteria help plants tolerate abiotic stress. Trends Plant Sci 14:1–4

Zhu YL, Pilon-Smits EAH, Jouanin L, Terry N (1999a) Overexpression of glutathione synthetase in Indian mustard enhances cadmium accumulation and tolerance. Plant Physiol 119:73–79

Zhu YL, Pilon-Smits EAH, Tarun AS, Weber SU, Jouanin L, Terry N (1999b) Cadmium tolerance and accumulation in Indian mustard is enhanced by overexpressing g-glutamylcysteine synthetase. Plant Physiol 121:1169–1177

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