24 Biogeochemical Cycling of Trace Elements by Aquatic and Wetland Plants: Relevance to Phytoremediation

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24.1 INTRODUCTION

Aquatic ecosystems (freshwater, marine, and estuarine) act as receptacles for trace elements [1–3]. Several angiospermous families — namely, Cyperaceae, Potamogetonaceae, Ranunculaceae, Haloragaceae, Hydrocharitaceae, Najadaceae, Juncaceae, Pontederiaceae, Zosterophyllaceae, Lemnaceae, Typhaceae, etc. — have aquatic and semiaquatic environments. Aquatic/wetland plants play a crucial role in biogeogenic cycling of trace elements through their active and passive cycling of elements. They act as "pumps for essential and nonessential elements" [3]. Uptake of elements into plant tissue promotes immobilization in plant tissues and thus constructed wetlands are gaining significance for wastewater treatment [4].

Aquatic and wetland plant assemblages occupy specific zones, including the position of aboveground structures and roots in relation to the sediment surface and water table. A typical zonation in tropical aquatic and wetland macrophytes is comprised of:

- Free-floating plants: except for roots, which are situated in the water, most of the plant body is above the water, e.g., *Eichhornia crassipes* (water hyacinth), *Ludwigia* sp. (water primrose), *Pistia stratiotes* (water lettuce), *Lemna* sp., *Wolffia* and *Spirodela* (duckweeds), *Ceratophyllum demersum* (coontail), *Salvinia* sp., and *Azolla* (water ferns).
- Submerged (rooted) plants: these remain submerged in water, e.g., *Egeria densa* (Brazilian elodea), *Elodea canadensis* (elodea), *Hydrilla* and *Vallisneria* (tape grass).
- Emergent (rooted) plants: these plants are rooted to sediments but emergent above the water, e.g., *Alternanthera philoxeroides* (alligator weed), *Typha latifolia* (cattail), and *Phragmites communis* (reed).

Industrialization increased trace element fluxes from terrestrial and atmospheric sources towards the aquatic environment. Industrial effluents, mine discharges, and run-off from agroecosystems often contain metalliferous substrates, which get discharged into nearby aquatic ecosystems. Aquatic systems receive run-offs that contain high levels of contaminants, such as heavy metal effluents from industries, oil and petrol residues, fertilizers, pesticides and animal wastes [5]. Consequently, elevated concentrations of heavy metals, such as lead (Pb), chromium (Cr), cadmium (Cd), copper (Cu), and zinc (Zn), are usually found at high concentrations in the aquatic ecosystem. These metals are progressively added to the aquatic sediments, where they pose threats to the benthic organisms [6].

Sediments formed in the aquatic ecosystems substitute for the role of soil in terrestrial ecosystems. Sediments form biologically important habitats and microenvironments for aquatic life. The metalliferous discharges not only contaminate the interstitial water but also contribute to the metal reservoir pool in sediments.

Many environmental factors are known to modify the availability of metals in water to aquatic plants. Such factors include chemical speciation of the metals, pH, organic chelators, humic substances, particles and complexing agents, and presence of other metals and anions. Rate of influx of these heavy metals into the environment exceeds their removal by natural processes. Therefore, there is enhancement of heavy metals accumulating in the environment.

24.1.1 Aquatic Sediments as Reservoir of Trace Elements

Sediments also act as reservoirs of contaminants, which may enter the water through the desorption process and can be taken up by rooted macrophytes. The availability of metals to the organisms of the upper strata is directly reflected by the sediment characteristics. The major mechanism of accumulation of heavy metals in sediments led to the existence of five categories: exchangeable, bound to carbonates, bound to reducible phases (iron and manganese), bound to organic matter, and residual fraction [6]. These categories have different behaviors with respect to remobilization under changing environmental conditions.

By studying the distribution of metals between the different phases, their availability and toxicity can be ascertained [7,8]. The fraction of metals introduced by human activity pertains to the adsorptive, exchangeable forms bound to carbonates, which are weakly bound and thus equilibrate with the aqueous phase and become more rapidly available [9]. The metal present in the inert fraction, which is of detrital and lattice origin, can be taken as a measure of contribution by natural sources [10]. The fraction of metals bound to organic matter and Fe–Mn oxides is unavailable forms providing a sink for heavy metals; their release from this matrix will be affected only by high redox potential and pH [11]. The criteria of risk assessment code (RAC) indicating sediment that releases in exchangeable and carbonate fractions is shown in Table 24.1 [12].

It is known that metals have shorter retention time in air and water than sediments. However, this depends on the element. For example, Pb has a very short retention time in water and Zn has a longer retention time. Equilibrium is always maintained in the interface between metals in interstitial water and metals in sediment. Therefore, external factors would affect this equilibrium and availability of metals to the aqueous system [13].

Processes responsible for availability of metals from sediments to interstitial waters, biotic and abiotic factors regulating the metal bioavailability in sediments are mentioned below (Figures 24.1 and 24.2):

- Geochemical processes like methylation, metal–metal interactions, and displacement reactions; redox changes; temperature; pH-related adsorption–desorption at sediment particulate surface changes [6,14,15]
- Partitioning of metals between sediment particles and interstitial water, depending on bound forms like sulfides, carbonates, hydroxides, and humic substances [9,11,15–17]
- Speciation of metals in water and "carrier" chelating agents aiding in metal transport. Trace metals in natural waters exist in several different forms (as different oxidation states or forms complexed or bound to inorganic and organic matter). The distribution between these forms is often referred to as the speciation of a metal (Figure 24.3). It has been shown that the toxicity of a metal is related to its speciation; some forms of the

TABLE 24.1
Criteria of Risk Assessment Code

S. no.	Risk assessment code	Criteria (%)
1	No risk	<1
2	Low risk	1–10
3	Medium risk	11–30
4	High risk	31–50
5	Very high risk	>50

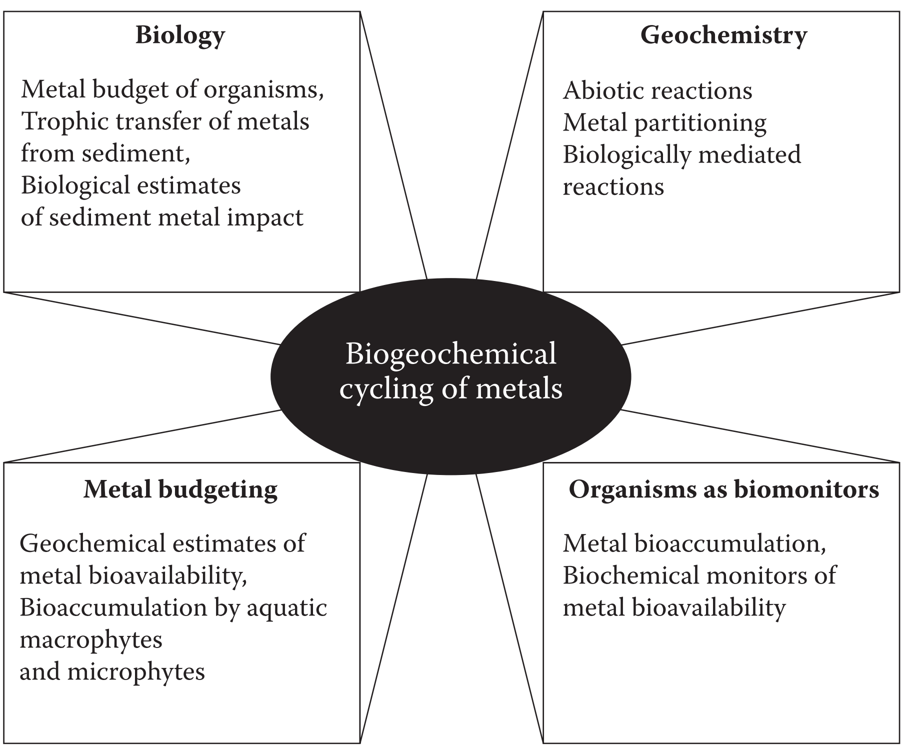

FIGURE 24.1 Processes responsible for biogeochemical cycling of metals from sediments to interstitial waters.

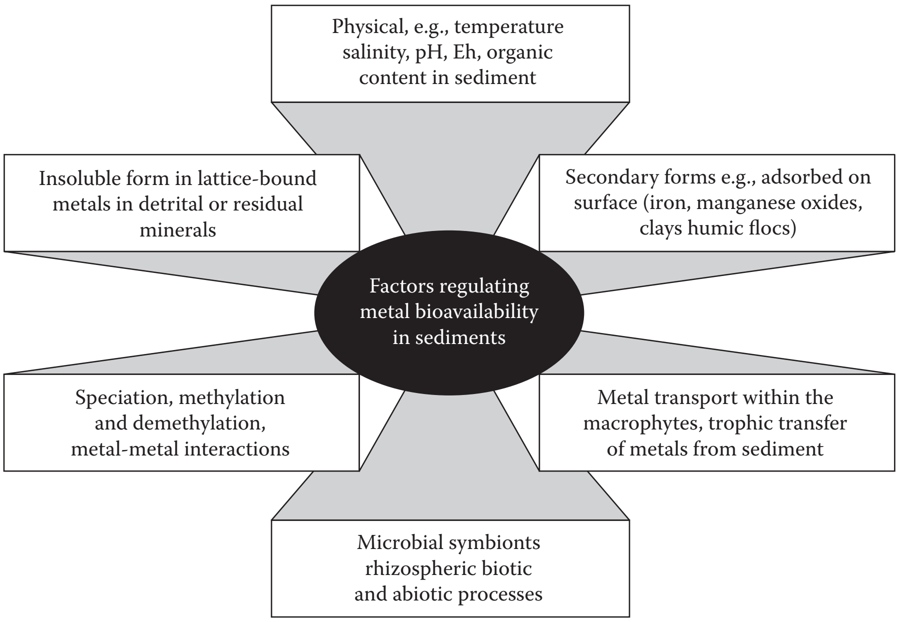

FIGURE 24.2 Biotic and abiotic factors regulating the metal bioavailability in sediments.

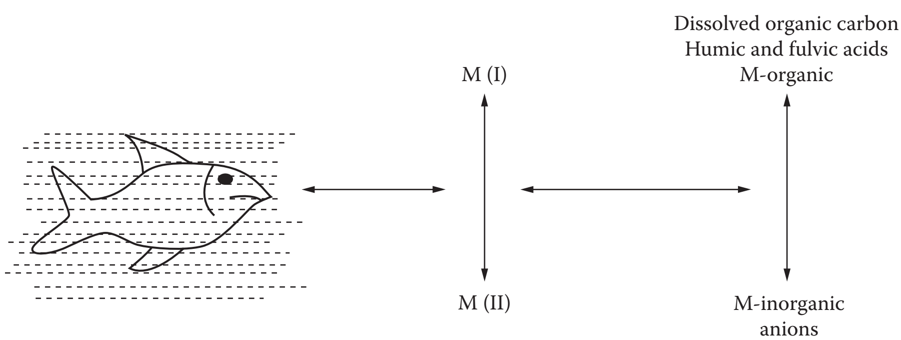

FIGURE 24.3 Trace metals in natural waters exist in different oxidation states or forms complexed or bound to inorganic and organic matter and the distribution of these forms is often referred to as the speciation.

metal are more available and toxic than others. This fact has been recognized in recent environmental legislation relating to surface water quality, e.g., for copper, aluminum, and silver [16]. As a consequence, industry and environmental regulators require an increasing amount of information on metal speciation.

- Microbial activity and animal activity (bioturbation) releasing bound metals [18]; exchange of ions between rhizosphere and metals partitioned in interstitial waters [18] (Figure 24.3 and Figure 24.4)

Once released into the interstitial water, metals become available in the waters of upper surface and thus facilitate the process of bioconcentration. In wetland ecosystems, physicochemical and biological processes operate that provide a suitable situation for removal of metals [19]. It is clear that development of a rational, effective, and economic strategy to remediate contaminated sedi-

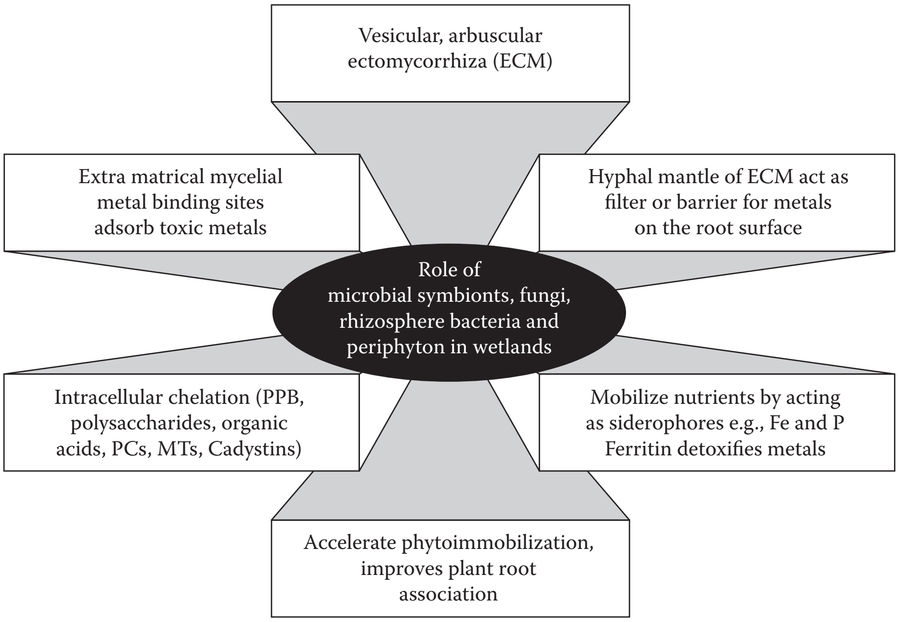

FIGURE 24.4 Role of microbial symbionts, fungi, rhizosphere bacteria, and periphyton in wetlands.

ments concerns understanding of the biogeochemical processes governing metal accumulation in aquatic plants.

24.2 FUNCTIONS OF AQUATIC PLANTS

Aquatic macrophytes are extremely important components of an aquatic ecosystem vital for primary productivity and nutrient cycling [19]. They provide habitat, food, and refuge for a variety of organisms [20]. Therefore, direct effects on macrophytes may lead to indirect effects on the organisms and nutrient cycles dependent on or associated with the plants. Given the ubiquity of submerged plants, their annual growth cycle, and their known capacity to concentrate certain elements in their tissues, it is clear that macrophytes could influence the seasonal storage and cycling of these elements in the aquatic environment. In principle, the submerged plant beds influence the cycling of metal elements by bioconcentration or indirectly by reducing current velocity, thereby favoring sedimentation of suspended particles and thus trace metals.

Depending on the species, a seasonal cycle of submerged plants is characterized by more or less rapid growth in spring, a peak at the end of summer, and more or less rapid decline in autumn in temperate situations, and a decline of growth observed only in summer in tropics [8]. The trend for greater dependence upon roots for heavy metal uptake was in rooted floating leaved taxa with lesser dependence in submerged taxa [21]. The tendency to use shoots as sites of heavy metal uptake instead of roots increases with progression towards submergence and simplicity of root structure.

Submerged rooted plants had some potential for the extraction of metals from water as well as sediments; rootless plants extracted metals rapidly only from water [22]. In submerged plants, leaves are the site of mineral uptake [23]. The foliar absorption of heavy metals is by passive movement through the cuticle, where the negative charges of the pectin and cutin polymers of the thin cuticle and the polygalacturonic acids of the cell walls create a suck inwards. Due to the increase in the charge density inwards, transport of positive metal ions takes place [23,24]. No ions enter stomata and, in submerged plant leaves, no stomata are present.

24.3 TRACE ELEMENT UPTAKE

Different plant species take up different amounts of metals [13,25–33]. In addition, the concentration found in various plant materials varies from site to site due to environmental pollution situations at that site. The variation within the same species can therefore be large. There are also differences in uptake between various metals. Not only the uptake but also the toxicity among different metals varies. Toxicity of different metals to *Elodea canadensis* and *Myriophyllum spicatum* is highest with Cu > Hg > As > Cd > Zn > Pb [34]. Submerged plant leaves have a very thin cuticle. The leaves of submerged plants are therefore very good at taking up metals directly from the water. The foliar uptake of Cd by *Potamogeton pectinatus* was nearly ten times higher than that of *Pisum sativum* [13]. It was shown that lead was accumulated in the shoots via absorption from water [25].

Macrophytes take up heavy metals via roots from the sediment and via shoots directly from the water. Therefore, the integrated amounts of available metals in water and sediment can be indicated by using macrophytes. Plants can also evolve ecotypes fairly soon and thereby be used in unfavorable conditions. Plants are also stationary and long lived and accumulate metals; therefore, they are suitable in monitoring of polluted sites. Metal concentration in plants must be related to the time of the year because the metal concentrations vary by season [35]. Aquatic plants also release metals through their leaves. Plants used as bioindicators must retain the metals in their plant body. *Ceratophyllum demersum, Myriophyllum spicatum, Potamogeton pectinarus, P. perfoliatus,* and *Zannichellia palustris* are proposed as bioindicators [36–42].

The uptake of metals by roots and by leaves increases with increasing metal concentration in the external medium. However, the uptake is not linear in correlation to the concentration increase because the metals are bound in the tissue, causing saturation that is governed by the rate at which the metal is conducted away. The effective uptake (or accumulation factor) is therefore highest at low external concentrations. This is shown for Cd in solution culture and also demonstrated as increased uptake from one and the same metal concentration with increasing root absorption area (root mass) [13]. External factors, such as temperature and light, influence growth and also affect metal uptake [43].

In aquatic macrophytes, the metal removal is accomplished through uptake by roots, chemical precipitation, and ion exchange with or absorption of settled clay and organic compounds [44–46]. Metal uptake is enhanced due to the presence of metal-binding ligands, such as thiols, or synthesis of metal-chelating peptides/proteins (namely, phytochelatins [47–54]) or surfactants such as linear alkyl benzene sulphonate [55]; combinations of metals in wastewaters may exert synergistic or antagonistic influence on metal uptake [56]. Aquatic macrophytes typically have much higher metal contents than nearby terrestrial plants, even when the total metal content of the soils is equivalent. Fritioff and Greger also found that this was the case [57].

However, this is due to the fact that the plant shoot takes up metals from the water, a high shoot biomass and less problematic uptake due to thin cuticle, and that shoots do not need to release metals from colloids or complexes before uptake. The shoot biomass is also much bigger in relation to the root mass in the case for terrestrial plants and, in terrestrial plants, the metals must be translocated a longer distance than in the case of submerged plants. Risk assessment of toxic trace metals in aquatic biota and use of in-built water-renovating strategies on ecologically acceptable principles has gained considerable significance in the field of environmental biotechnology and biotechnological methods of pollution control [58–61].

Aquatic macrophytes such as water hyacinth [*Eichhornia crassipes*] and several duckweeds have attracted the attention of scientists for their ability to accumulate trace metals. Using *E. crassipes*, heavy metal uptake from metal-polluted water, metal speciation, synthesis and characterization of heavy metal-binding complexes in root, and sorption of heavy metals from metal-containing solutions has been extensively investigated [62]. Metals found in nature in more than one valence state are more readily taken up by plants in the reduced form. Often, the metal is reoxidized within the plant tissues [23].

In aquatic ecosystems, the sediments and water interface serve as the habitat for a diverse community in which aquatic macrophytes are prominent. Metals present in surficial sediments in particulate form may exist as constituent elements present in the essentially insoluble products of physical weathering form, i.e., lattice bound (metal in detrital or residual minerals), or in a variety of secondary forms adsorbed on surfaces (iron/manganese oxides, clays, humic flocs) associated with organic matter, with sulphides, etc. The secondary forms are more reactive and more likely to be available.

Many environmental factors are known to modify the availability of metals in water to aquatic plants. As earlier mentioned, such factors include chemical speciation of the metal, pH, organic chelators, humic substances, particles and complexing agents, presence of other metals and anions, ionic strength, temperature, salinity, light intensity, and oxygen level and thus the redox potential [63]. In lakes, pH is important for speciation and thus also for the availability of metals to macrophytes. Most metal concentrations in water increase with decreasing pH, with the highest pH value of about 4. Especially in aquatic systems, the redox potential is important. At low redox potential, metals become bound to sulfides in sediments and are thus immobilized. In water, salinity affects the availability of metals because high salinity causes formation of metal–chloride complexes, which are difficult for plants and other organisms to take up.

External factors can decrease or enhance the efficiency to remove the pollutants from the water. High particle concentration binds elements and organic substances and sediments to the bottom. High cation exchange capacity [CEC] of the particles increases the binding of the positive ions. Outlets at treatment of stormwater, sewage water, and leakage water commonly contain high levels of particles. Plants increase the sedimentation of them, which is one of the mechanisms behind removal of metals from water by plants.

In temperate aquatic ecosystems, the temperature varies with the season. Uptake of metals is influenced by temperature and the uptake increases with increased temperature [64]. The removal efficiency of metals can therefore be season dependent in temperate climate. Another external factor that varies with season is salinity in stormwater. This is due to deicing of roads during winter, using sodium chloride. Salinity decreases the uptake of metals in plants [64]; due to complex formation with chloride, complexes prevent metal uptake. However, in the presence of sediment, sodium can be exchanged with sediment-bound metals and thereby increase the total metal concentration in the water phase, which increases the shoot metal uptake [65] (Figure 24.5). In stormwater treatments, various plants have been tested and it has been found that submerged plants do take up more metals than emergent plant species [57]. *Potamogeton natans* and *Elodea canadensis* were the two species mostly found in the stormwater treatment basins and they took up most metals by their shoots.

24.3.1 Aquatic Macrophytes for Trace Element Biomonitoring and Toxicity Bioassays

Aquatic plants are represented by a variety of macrophytic species that occur in various types of habitats. Extensive experimentation on various macrophytes such as *Eichhornia* [66–69], *Elodea* [25,33,70–72], *Lemna* [19,73–82], *Myriophyllum* [25,33,83–85], *Potamogeton* [25,33,77,83,86–91], and various other aquatic macrophytes has been conducted and indicates the potential utilization of macrophytes as biomonitor systems for toxic metals (Table 24.2).

Aquatic macrophytes have paramount significance in the monitoring of metals in aquatic ecosystems [129–132]. The use of aquatic plants in water-quality assessment has been common for years as *in situ* biomonitors [133,134]. According to Sawidis et al. [135], the occurrence of aquatic macrophytes is unambiguously related to water chemistry and using these plant species or communities as indicators or biomonitors has been an objective for surveying water quality [136].

In addition, considerable research has been focused on determining the usefulness of macrophytes as biomonitors of polluted environments [60,61,137]. The response of an organism to

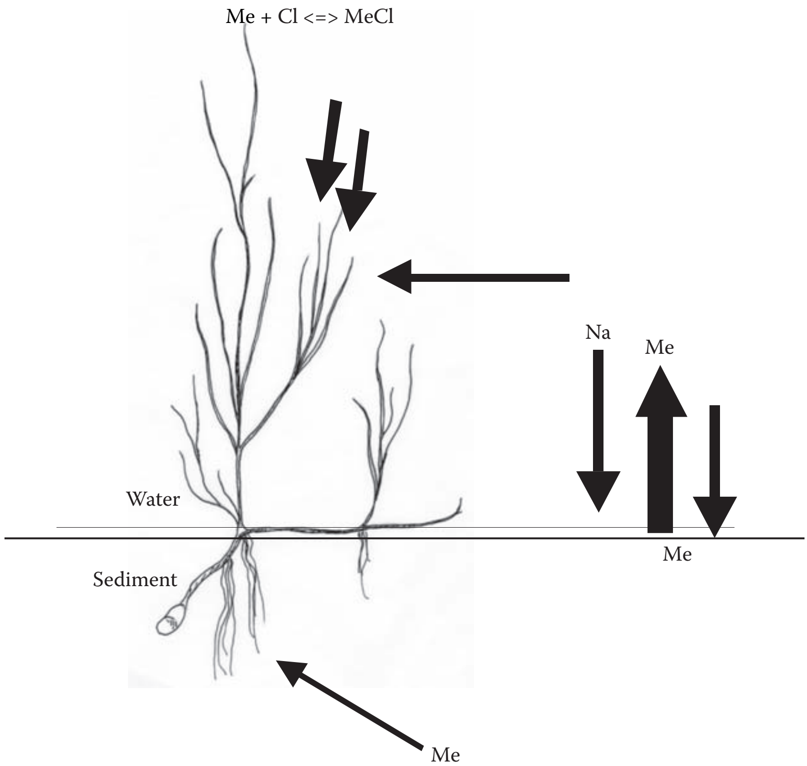

FIGURE 24.5 Influence of sodium chloride on the metal circulation in plant–water–sediment system.

deficient or excess levels of metal (i.e., bioassays) can be used to estimate metal impact. Such studies done under defined experimental conditions can provide results that can be extrapolated to natural environments. Heavy metals or even lighter metals in excess are often toxic to plants. Even at sublethal concentrations, physiological tests such as changes in pigment composition, photosynthesis, and respiration can reflect stress and predict future plant damage [106,138,139].

Using an aquatic macrophyte as a study material has multifold advantages. Rooted macrophytes, especially, play an important role in metal availability through rhizosphere secretions and exchange processes. This naturally facilitates metal uptake by other floating and emergent forms of macrophytes. The immobile nature of macrophytes makes them a particularly effective bioindicator of metal pollution because they represent real levels present at that site. Data on phytotoxicity studies are considered in the development of water-quality criteria to protect aquatic life and the toxicity evaluation of municipal and industrial effluents [80,140,141]. In addition, aquatic plants have been used to assess the toxicity of contaminated sediment and hazardous waste leachates [142].

Several of the aquatic macrophytes — namely, *Hydrilla verticillata, Certophyllum demersum*, *Vallisneria Americana*, etc. — detoxify toxic trace elements by inducing phytochelatins [47–55]. In North America, manganese and lead (from methylcyclopentadienyl manganese tricarbonyl [MMT]) uptake by plants growing near highways was much greater in aquatic plants than in terrestrial plants [77]. Plants growing close to the roadway and heavy motor vehicle traffic significantly contributed to these toxic elements [87,143].

Industrial discharge pollutes the bottom sediments with toxic trace elements. Increased density causes turbidity, thereby causing reduced light intensity; thus, the ability for plants to grow on these bottoms will be low. In the sediment, the redox potential is low and most of the trace elements are therefore firmly bound to sulfides. When industrial outlet has been shut down, new, unpolluted

TABLE 24.2
Toxicity Parameters Tested in Various Aquatic Macrophytes

Plant species studied	Concentrations tested	Parameters tested	Contaminants tested	Environment tested	Ref.
Ceratophyllum demersum	Cd: 0.01 to 2 ppm (maximum period of testing: up to 2 weeks) Cu: 0.01 to 64 ppm, Cr: 0.01 to 4.86 μM Fe: 0.01 to 75 μM Pb: 0.01 to 64 ppm Mn: 0.01 to 6.6 μM Zn: 2–64 ppm	Growth; fresh weight; dry weight ratios; metal uptake; mechanism of metal uptake; concentration factors; levels of antioxidant enzymes reflecting metal toxicity; carbonic anhydrase activity; levels of photosynthetic pigments and rate of photosynthesis; electron transport processes; metal–metal interactions between Cd–Zn and Cd–Ca	Cd, Cu, Cr, Pb, Hg, Fe, Mn, Zn, P, Ni, Co	Erlenmayer flasks, aquaria and samples from natural pond system	37, 54, 84, 92–97, 99–106
Myriophyllum *M. spicatum* *M. alterniflorum* *M. aquaticum* *M. exalbescens*	Natural metal concentrations existing in field conditions	Metal content, root/shoot metal ratio	Cd, Cu, Zn, Pb, Ni, Cr, Fe, Hg	Natural wetland systems	25, 83, 85
Elodea *E. canadensis* *E. nuttallia* *E. densa*	Cu: 1, 5, 10 ppm	Toxicity symptoms; shoot length variations; dry mass index	Cu, Pb, Cd, Zn, Cr, Ni, Hg, methyl-Hg	Laboratory aquaria	25, 33, 34, 70–72, 108
Potamogeton *P. crispus* *P. perfoliatus* *P. pectinatus* *P. filiformis* *P. orientalis* *P. lapathifoilum* *P. attenuatum* *P. subsessils* *P. richardsonii*	Radiotracers used: 76As, 109Cd, 115Cd, 64Cu, 65Zn, and 69mZn	Biomass and metal content; multispectral remote sensing data; seasonal storage of metals; mass balance calculations; organic selenium, free seleno-amino acids; glutathione-S-transferase activity; bioconcentration factors; metal mobility; single-tracer experiments and double-labeling experiments for estimating metal transport activity	Cu, Pb, Mn, Fe, Cd, Zn, Ni, Cr, Mn, As, Se	Natural lake system; agricultural drainage water medium and laboratory culture media; hydroculture two-compartment system; samples form natural aquatic systems	7, 8, 25, 33, 77, 83, 88, 90, 91, 109, 110
Littorella uniflora			Cu, Pb		25

TABLE 24.2
Toxicity Parameters Tested in Various Aquatic Macrophytes (continued)

Plant species studied	Concentrations tested	Parameters tested	Contaminants tested	Environment tested	Ref.
Isoetes lacustris			Cu. Pb		25
Ruppia maritima	Natural metal concentrations existing in field conditions	Metal content, organic selenium, free seleno-amino acids	Mn, Pb, Cd, Pb, Fe, Se	Agricultural drainage water medium and laboratory culture media	89, 109, 110
Ranunculus *R. baudotii* *R. aquatilis*	Natural metal concentrations existing in field conditions		Cd, Cu, Cr, Zn, Ni, Pb	Samples collected from natural ecosystems	33, 109
Scirpus *S. lacustris* *S. acutes* *S. maritimus*			Cr, Cd, Fe, Pb, Mn		109, 110
Chara spp.			Mn, Pb, Cd, Fe		109–111
Lemna *L. minor* *L. gibba* *L. trisulca* *L. paucicostata* *L. valdivinia* *L. polyrrhiza* *L. perpusilla*	Fe: 1, 2, 4, and 8 ppm Cu: 1, 2, 4, and 8 ppm Pb: 0–7 ppm Ni: 0–5 ppm Cu, Zn, Cr: 5, 10, 15, 20 ppm Cd: 0.25–10 m*M* Ca: 1.1 to 17.6 ppm As: up to 1 ppm	Growth; fresh weight; fronds number; metal content; metal uptake kinetics; photosynthetic rate; total protein content; vegetative propagation; cadmium content; growth rates; operational PS II quantum yield; nonphotochemical quenching; hydrophobic components bioassay; determination of EC_{50} values	Mn, Pb, Ba, B, Cd, Cu, Cr, Ni, Se, Zn, Fe	Laboratory cultures; aquaria; natural effluents; sterile cultures; semicontinuous; flow through culture system; sewage stabilization systems	74, 75, 19, 56, 73, 76, 78, 79, 81, 82, 110–116
Najas marina			Cd, Fe, Pb, Mn		109
Distichlis spicata			Cd, Fe, Pb, Mn		109
Nuphar *N. lutea* *N. variegatum*		Metal content; uptake potential; glutathione-S-transferase activities	Cu, Ni, Cr, Co, Zn, Mn, Pb, Cd, Hg, Fe	Samples from natural wetlands	96, 117
Phragmites *P. karka* *P. communis*	Natural metal concentrations of the wetland ecosystem	Metal uptake	Ni, Cr, Co, Zn, Mn, Pb, Cd, Cu, Hg, Fe	Natural wetland ecosystem	119, 96, 18
Bacopa monnieri			Cr		119

Ludwigia		Growth; metal content	Hg, Zn, Cu, Fe,	Laboratory aquatic medium; synthetic river water; dechlorinated tap water	71, 85
L. palustris					
L. natans					
Mentha aquatica			Cd, Zn, Cu, Fe, Hg		85, 119
Azolla	Fe: 1, 2, 4, and 8 ppm	Metal contents; metal uptake kinetics	Cr, Ni, Zn, Fe, Cu, Pb	Laboratory aquaria	78, 76
A. pinnata	Cu: 1, 2, 4, and 8 ppm				
Typha			Ni, Cr, Co, Zn, Mn, Pb, Cd, Cu, Hg, Fe	Plants from natural streams	96, 121
T. domingensis					
T. latifolia					
Eichhornia crassipes	1, 3, 5, 7, 10, 50, and 100 ppm of the mentioned metals	Visual symptoms; metal uptake; variation of pH; conductivity and growth media on metal uptake; nitrogen and phosphorus concentrations; metal uptake	Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn	Laboratory stocks; plants collected from natural ponds	66–69, 122
	Choloro complexes of the mentioned metals		As, Al, Hg, P, Pt, Pd, Os, Ru, Ir, rheffluents		
Pistia stratoites	Hg: 1 to 1000 ppb	Metal content; nitrogen and phosphorus concentrations; foliar injury; chlorophyll content; phytomass; leaf injury index; metal content	Cu, Al, Cr, P, Hg	Plants collected from natural ponds	67, 122, 123
Lysimachia nummularia		Growth; metal content	Hg, methyl-Hg	Laboratory aquatic medium; synthetic river water; dechlorinated tap water	71
Hygrophila onogaria		Growth; metal content	Hg, methyl-Hg	Laboratory aquatic medium; synthetic river water; dechlorinated tap water	71
Carex			Cu, Pb, Zn, Co, Ni, Cr, Mo, U		110, 124
C. juncella					
C. rostrata					
Hydrilla verticillata	Hg: 1–1000 ppb Fe: 0.025–0.150 ppm	Foliar injury; chlorophyll content; phytomass; leaf injury index; metal content	Hg, Fe, Ni, Hg, Pb		51, 123, 124, 125

TABLE 24.2
Toxicity Parameters Tested in Various Aquatic Macrophytes (continued)

Plant species studied	Concentrations tested	Parameters tested	Contaminants tested	Environment tested	Ref.
Eriocaulon septangulare	Sediment concentrations Hg: 0.007–0.247 μg/g Cd: 0.06–2.53 μg/g Fe: 2.55–34.77 μg/g Pb: 2.8–167.6 μg/g	Metal content	Hg, Pb, Cd, Fe	Naturally growing pond vegetation	32
Salvinia *S. molesta* *S. herzogii* *S. natans*	Hg: 1–1000 ppb Cr: 1, 2, 4, and 6 ppm	Metal uptake; translocation efficiency in different parts; growth rate; chlorophyll content foliar injury; chlorophyll content; phytomass; leaf injury index; metal content	Hg, Cr, Pb	Laboratory aquaria	79, 110
Vallisneria *V. spiralis* *V. americana*	Hg: 0.5–20 μ*M*	Metal content; chlorophyll levels; protein content; nitrogen; phosphorus and potassium contents; levels of amino acid-cysteine; nitrate reductase activity; biomass and metal content; multispectral remote sensing data; seasonal storage of metals; mass balance calculations	Cd, Cr, Cu, Ni, Pb, Zn, Hg	Plants from natural river habitat	7, 8, 125
Nymphaea alba			Ni, Cr, Co, Zn, Mn, Pb, Cd, Cu, Hg, Fe		96
Schoenoplectus lacustris			Ni, Cr, Co, Zn, Mn, Pb, Cd, Cu, Hg, Fe		96
Wolffia globosa			Cd, Cr		126
Hydrangea macrophylla	Al: 100 μ*M*	Al content; purification of Al–citrate complex	Al	Hydroponic culture	127

sediment has been deposited on top of the contaminated one and plants are able to colonize the bottom area. Colonization of macrophytes on shallow bottoms brings about increased redox potential in the rhizosphere caused by the photosynthetic oxygen, which has been translocated down to the roots by the lacunar system [144–146] (Figure 24.6). The increased redox potential will increase the availability of heavy metals to the plant roots, thus facilitate the uptake of heavy metals by the roots. Part of the metals taken up will then be translocated to the leaves and thereafter transferred to grazing animals.

Macrophytes can increase metal circulation in the aquatic environment. Thus, several of the macrophytes serve as indicators of metal pollution and also redistribute the metals in the aquatic ecosystem [32,71,136,147–150]. Metals concentrated within macrophytes are available for grazing by fish. These may also be available for epiphytic phytoplankton, herbivorous and detrivorous invertebrates. This may be a major route for incorporating metals in the aquatic food chain [83]. It is therefore of interest to assess the levels of heavy metals in macrophytes due to their importance in ecological processes. The inorganic metal species are, however, not biomagnified and thus do not increase in quantity in higher trophic levels.

In the past, research with macrophytes has been centered mainly on determining effective eradication techniques for nuisance growth of several species, such as *Elodea canadensis, Eichhornia crassipes, Ceratophyllum demersum*, etc. Scientific literature exists for the use of a wide diversity of macrophytes in toxicity tests designed to evaluate the hazard of potential pollutants, but the test species used is quite scattered. Similarly, literature concerning the phytotoxicity tests to be used, test methods, and the value of the result data is scattered. Estuarine and marine plant species are used considerably less than freshwater species in toxicity tests conducted for regulatory reasons [80]. The suitability of a test species is usually based on the specimen availability, sensitivity to toxicant, and reported data.

The sensitivity of various plants to metals was found to be species and chemical specific, differing in the uptake as well as toxicity of metals [151]. Many submerged plants have been used as test species, but no single species is widely used. In a literature survey, only 7% of 528 reported phytotoxicity tests used macrophytic species [152]. Their use in microcosm and mesocosm studies is even rarer and has been highly recommended [153]. Several plant species, such as *Lemna, Myriophyllum,* and *Potamogeton*, have been exhaustively used in phytotoxicity assessment, but

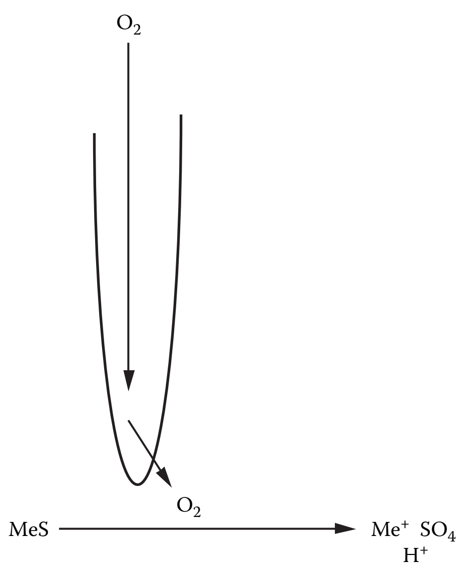

FIGURE 24.6 Changing the redox potential of sediment by roots.

several others have been given less importance as a bioassay tool. Duckweeds have received the greatest attention for toxicity tests because they are relevant to many aquatic environments, including lakes, streams, and effluents. Duckweeds comprise *Spirodela, Wolfiella, Lemna*, and *Wolffia*, of which *Lemna* has been almost exhaustively studied [154].

24.4 REMEDIATION POTENTIAL OF AQUATIC PLANTS

Phytoremediation is the use of green plants to remove or contain environmental contaminants or to render them harmless. Phytoremediation of metals can be divided into the following groups:

- Phytoextraction: metal accumulates in plants that are then harvested and thereby remove the metals from the site
- Phytostabilization: plants reduce the mobility of the metals
- Phyto- and rhizofiltration: the water is cleaned from metals by metal uptake by plant shoot and/or roots and by reducing the water velocity and thereby increasing the sedimentation of metals to the bottom

Aquatic plants have been used frequently to remove suspended solids, nutrients, heavy metals, toxic organics, and bacteria from acid mine drainage, agricultural landfill, and urban stormwater run-off and as bioremediative agents in wastewater treatments [155]

In wetland ecosystems, a wide variety of processes, ranging from physicochemical to biological, operates and can provide a suitable situation for removal of metals. For example, in the case of acidic metal-rich mine drainage, the principal processes include oxidation of dissolved metal ions and subsequent precipitation of metal hydroxides; bacterial reduction of sulphate and precipitation of metal sulphides; the coprecipitation of metals with iron hydroxides; the adsorption of metals onto precipitated hydroxides; the adsorption of metals onto organic or clay substrates; and, finally, metal uptake by growing macrophytes.

The conventional method of removing heavy metals from wastewater has been to mix it with sewage; conventional primary, secondary, and tertiary treatment would then remove them in the site of production of heavy metals. In addition, they provide green space, wildlife habitats, recreational and educational areas. However, secondary and tertiary processes require high input of technology, energy, and chemicals [156]. Such technologies used in the prevention of heavy metal pollution are inadequate or too expensive for some countries. In the past decades, therefore, research efforts have been directed towards wetland plants that comprise rooted, emergent, and surface floating plants as an alternative, low-cost means of removing heavy metals from domestic, commercial, mining, and industrial discharge of wastewater. Macrophytes are cost effective, universally available aquatic plants; with their ability to survive adverse conditions and high colonization rates, they are excellent tools for studies of phytoremediation [157].

24.4.1 Free-Floating Aquatic Plants

Free-floating plants can be used in removal of pollutants from the water phase because they are not in contact with the sediment for e.g., *Lemna* spp., *Eichhornia* spp., and *Azolla* spp. *Eichhornia crassipes* is a species often used in water cleaning. In experiments on metal removal, 0.67 (Cd), 0.57 (Co), 0.18 (Pb), 0.15 (Hg), 0.50 (Ni), and 0.44 (Ag) mg/g DM was accumulated. This gave a removal of 400 (Cd), 340 (Co), 90 (Pb), 110 (Hg), 300 (Ni), and 260 (Ag) g/ha day [158–160].

24.4.2 Emergent Species

Aquatic plants are able to take up elements by roots and by shoots or thallus from the water and sediment. Unlike a terrestrial system, inorganics are in equilibrium between the sediment and the

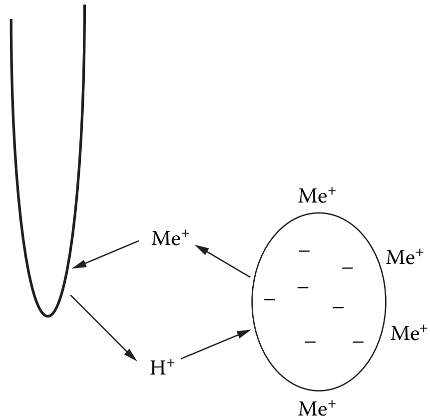

FIGURE 24.7 Release of metals from sediment particles by decreasing the pH.

water phase. Depending on the element, the retention time of the inorganic molecules in water is more or less short. The equilibrium between sediment and water is therefore towards the sediment for inorganic pollutants. Thus, the sediment will be a sink for pollutants. Because plants help to retard the velocity of the bulk flow, they also help in increasing the sedimentation and thus the immobilization of pollutants in wetlands. By influencing the equilibrium, the plants become more or less suitable for phytoextraction or phytostabilization.

Sediment-bound cations may be released from the sediment by roots decreasing the pH in the rhizosphere (Figure 24.7). Also, other mechanisms may occur, such as release of organic acids [161,162] or phytosiderophores [163]; this is the case for some terrestrial plants to be able to make the elements available. Organic substances are also released into the rhizosphere to supply microorganisms with substrate [164] that increases the phytostimulation capacity of bacterial activity in bioremediation. Furthermore, increase in pH of the water by photosynthetic activity and CO_2 uptake [165] of macrophyte shoots will probably change the chemistry of metals in the water. This may increase the precipitation and decrease the retention time of these elements in the water and, thus, phytostabilization.

The redox potential is fairly low in sediment, and most metals are bound to sulphides; thus, hard metal–sulphide complexes are formed. Plants need oxygen for their energy production in the roots. Plants living in such environments have evolved mechanisms to translocate oxygen (photosynthetic or taken up from the air) from shoot to root. Some of this oxygen is then released in the anoxic rhizosphere to protect young root tissue from toxic rhizospheric compounds [166–168]. In addition, this oxygen will change the redox potential of the rhizosphere sediment and thereby release metals from the sulphide complex. Oxygen release rates are highest in the range of -250 mV $<$ Eh $<$ -150 mV [169]. The release of oxygen is species specific under reduced conditions and high rates have been shown for *Typha latifolia* (1.41 mg/h plant), *Phragmites australis* (1 mg/h plant), *Juncus effusus* (0.69 mg/h plant), and *Iris pseudacorus* (0.34 mg/h plant) [169].

24.4.3 Submergent Species

Macroalgae, plants that mostly need some level of salinity to survive, are also submerged. They take up pollutants only from water due to the absence of root system and a primitive anatomy of the plant body. They are able to accumulate some elements to a high extent (Table 24.3).

TABLE 24.3
Trace Element Contents (μg gDW^{-1}) in Macroalgae and Freshwater Vascular Plants[a] Compared to Reference Terrestrial Plants, as well as Hyperaccumulation Levels[b]

Element	Macroalgae mean	Maximum values for contaminated fresh-water vascular plants	Hyperaccumulating level	Reference plant
Ag	<0.8	67	20	0.2
As	8.2	1200	10	0.1
Au	<4	—	0.1	0.001
Ba	<40	—	4000	40
Br	643	—	400	4
Ce	0.94	—	50	0.5
Cd	—	90		
Co	2.5	350	20	0.2
Cr	2.2	65	150	1.5
Cs	0.11	—	20	0.2
Cu	12	190	1000	10
Hf	0.2	—	5	0.05
Hg	—	1000	—	
I	238	—	300	3
La	0.57	—	20	0.2
Mn	—	8370		
Mo	<0.8	—	50	0.5
Ni	<20	290	150	1.5
Pb	—	1200	100	1
Rb	23	—	5000	50
Sb	0.11	—	10	0.1
Sc	0.49	—	2	0.02
Se	—	21		
Sr	696	—	5000	50
Th	0.06	—	0.5	0.005
U	0.44	1.1	1	0.01
V	5.9	—	50	0.5
Zn	37	7030	5000	50

[a] Markert, B., in Adriano, D.C. et al., Eds., *Biogeochemistry of Trace Elements, Science and Technology Letters*, Northwood, New York, 601, 1994.
[b] According to Dunn, C.E., in Brooks, R.R., Ed. *Plants that Hyperaccumulate Heavy Metals. Their Role in Phytoremediation, Microbiology, Archaeology, Mineral Exploration and Phytomining*, CAB International, Washington, D.C., 119, 1998; Brooks, R.R. and Robinson, B.H., in Brooks, R.R., Ed. *Plants that Hyperaccumulate Heavy Metals. Their Role in Phytoremediation, Microbiology, Archaeology, Mineral Exploration and Phytomining*, CAB International, Washington, D.C., 203–226; and Jones, D.L., *Plant Soi*l, 205, 25, 1998.

24.5 WETLANDS

Wetlands are natural or constructed; both types can be used for removal of metals, particles, etc. In constructed wetlands, the flow is constructed as surface flow, subsurface flow or vertical flow, or a mixture [4]. The most important role of plants in wetlands is that they increase theresidence time of water, which means that they reduce the velocity and thereby increase the sedimentation of particles and associated pollutants. Thus, they are indirectly involved in water cleaning. Plants also add oxygen, thus providing a physical site of microbial attachment to the roots and generating

TABLE 24.4
Examples of Plants Used in Treatment of Wetlands [99]

Species	Ref.	Species	Ref.
Emergent plants		**Submerged**	
Scirpus spp.	174	*Ceratophyllum demersum*	174
Typha spp.	174	*Potamogeton* spp.	174
Iris spp.	174	*Elodea canadensis*	174
Phragmites australis	175	*Vallisneria americana*	175
Juncus spp.	174		
Floating		**Rooted floating leaved**	
Spirodela spp.	176	*Nelumbo lutea*	174
Lemna spp.	176	*Nymphoides* spp.	174
Salvinia spp.	177	*Nymphaea* spp.	174

Source: Hammer, D.A., in Constructed Wetland for Wastewater Treatment Conference. Middleton, County Cork, Ireland, 1993.

positive conditions for microbes and bioremediation. For efficient removal of pollutants, a high biomass per volume of water of the submerged plants is necessary. Thus, common and abundant growing plants are probably the best remediators (Table 24.4).

Wetlands serve as sinks for pollutants, reducing contamination of surrounding ecosystems. Although sediments, which tend to be anoxic and reduced, act as sinks, the marsh can become a source of metal contaminants through the activities of the plant species. Plants can oxidize the sediments, making the metals more available. Metals can be taken up by roots and transported upward to above-ground tissues, from which they can be excreted. Decaying litter can accumulate more metals, which may leach or may become available to detritus feeders. Using wetlands for water purification may serve only to delay the process of releasing toxicants to the water. As levels of pollutants increase, the ability of a wetland system to incorporate wastes can be impaired and the wetland can become a source of toxicity.

Uptake of metals in emergent plants only accounts for 5% or less of the total removal capacity in wetlands [170]. Not many studies have been performed on submerged plants. However, higher concentrations of metals in submerged than emerged plants have been found and, in microcosm wetlands, the removal by *Elodea canadensis* and *Potamogeton natans* showed up to 69% removal of Zn [171]. Dushenko et al. [172] found differences in accumulation of As between submerged and emerged plants. When comparing free-floating plants (*Lemna minor*) with emergent plants (*Typha domingensis*), a similar removal of Pb and Cd to about 50% [174] was found. Because *Lemna minor* was the easiest plant to remove the metals, this species is preferred in water cleaning — at least for these two metals.

In salt marshes about 50% of the absorbed metals are retained, and the remaining get transported [178]. Despite the ability of plants for bioconcentrating metals, the overall outcome with regard to biogeochemistry and mobility is that the wetlands generally act as sinks rather than sources for metals. Thus, the mangrove communities also act as effective traps for immobilizing heavy metals, with relatively low export to adjacent ecosystems [180]. However, because many wetland plants, unlike mangroves, are relatively short lived, their ability to stabilize metals may be only for the short term.

Different plant species have different allocation patterns of metals and can have different effects on salt marsh ecosystems. Weis and Weis [180] indicated that the replacement of *S. alterniflora* by invading *P. australis* would be predicted to lead to a reduction in mercury, chromium, and lead availability because of the higher allocation of these metals to leaf tissues in *S. alterniflora*. For a given metal burden, *P. australis* allocates more of the metal pool into below-ground biomass, and recalcitrant tissues (stems, rhizomes, and roots) than *S. alterniflora*. Furthermore, the excretion of metals by leaves is also greater for *S. alterniflora* than for *P. australis*, probably because of the presence of salt glands in the former species.

The movement of metals from below-ground to above-ground tissues and their release from leaf tissue may be important steps in metal flux in marsh ecosystems. Although metals remaining in the roots are generally considered "out of trouble" as far as release to the environment is concerned, studies are needed regarding the turnover of nutritive roots and the potential release of metals from decomposing roots. Decomposing litter of both species becomes highly enriched in metals over time, and evidence indicates that these metals are probably available to detritus feeders

24.5.1 Significance of Metal-Rich Rhizoconcretions, or Plaque, on Roots

A striking feature of roots of some wetland plants is the presence of metal-rich rhizoconcretions, or plaque, on the roots [181–183]. The metals are mobilized from the reduced anoxic estuarine sediments and concentrated in the oxidized microenvironment around the roots. Their concentrations can reach five to ten times the concentrations seen in the surrounding sediments [184]. At higher pH conditions, the presence of plaque enhanced Cu uptake into roots. However, in *T. latifolia* (cattail), the presence of iron plaque did not reduce uptake of toxic metals [184]. Iron plaque increased zinc uptake by rice (*O. sativa)* and movement into shoots [185]. In contrast, Al was not adsorbed onto the iron or the manganese plaque, but rather formed a separate phosphate deposit that resembled the iron and manganese plaques [186].

The discrepancies in effects of plaque on metal uptake need to be resolved by further study. Different metals, environmental conditions, or physiologies may account for these differences. By oxidizing the soil in the immediate vicinity of the rhizosphere, plants can alter the distribution of metals in wetland sediments. Plant activity (metal mobilization by oxidation of the root zone and movement into the rhizosphere) was considered responsible for the increase. The salt marsh metallophyte *S. maritima* roots concentrated trace elements from sediments by producing complex organic compounds and oxidizing the rhizosphere [187].

In macrophytes of Bull Island in Dublin, Ireland, the anaerobic conditions caused iron plaque formation on roots of plants because of oxidation of iron in the rhizosphere. Using six different species of grasses and flowering plants, a comparison has been made on the degree of iron plaque formation [188–190]. It can be added that submerged plants will not survive iron plaque because the plaque prevents photosynthesis by the plant leaves (Nyquist and Greger, unpublished). However, emergent plants with plaque only formed in the rhizosphere and on the part of the shoot situated in the water, survive iron plaque formation.

24.5.2 Influence of Wetland Plants on Weathering of Sulphidic Mine Tailings

Oxygen causes weathering of mine tailings, and if they contain pyrite acid mine drainage (AMD) water containing free metal ions and sulfuric are formed. This can be prevented by covering the tailings with moraine (dry cover technique) or with a high water table (wet cover technique). However, a wetland producing oxygen-consuming organic material on the tailings will enable us to decrease the water table from a couple of meters down to some centimeters. This will prevent accidents in which impoundment walls break due to the high pressure from the water (Figure 24.8).

Wetlands are naturally formed on mine tailings, as long as nutrients are added, because the tailings are nutrient-poor substrate. Twenty years' addition of sewage waters has self-established wetland species like *Carex rostrata*, *Eriophorum angustifolium*, and *Phragmites australis* [191]. However, wetland plants have the ability to take up oxygen from the air or use photosynthetic oxygen and translocate the oxygen to the roots and out into the rhizosphere (Figure 24.9). Thus,

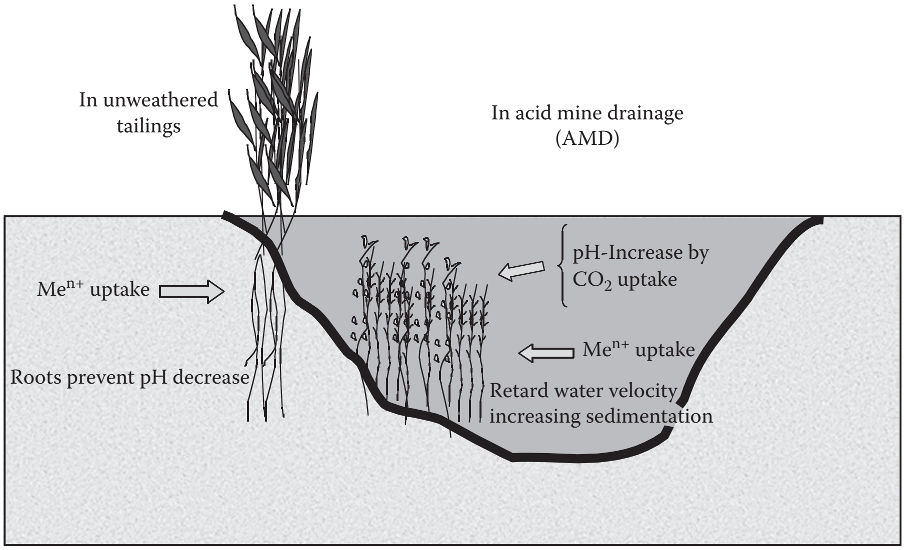

FIGURE 24.8 Remediation of mine tailings by emergent and submerged plants by a) preventing formation of AMD; or b) cleaning AMD from metals and increasing the pH.

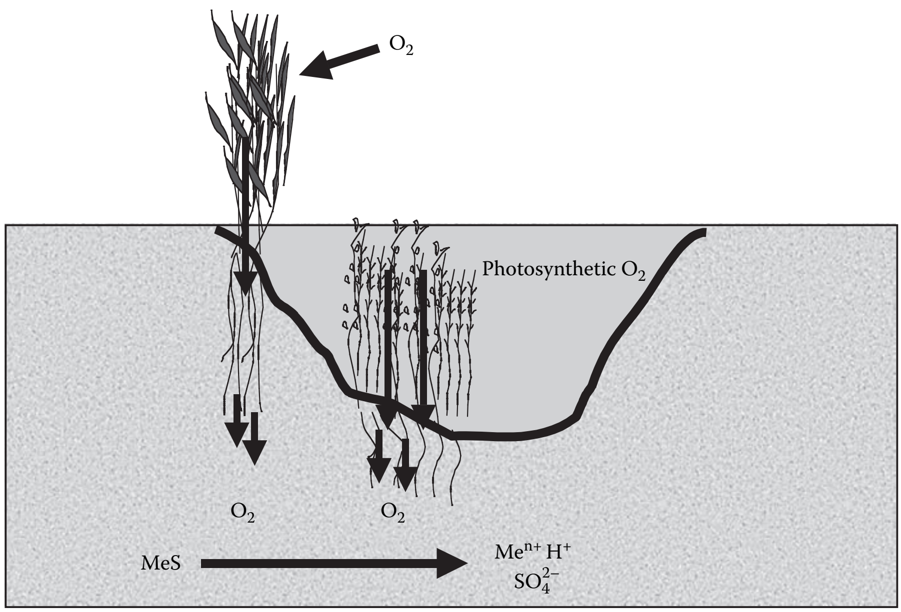

FIGURE 24.9 Weathering of tailings by submerged and emergent plants.

they will increase the redox potential, decrease the pH, and increase the release of metals for uptake. The work by Stoltz and Greger [191], however, showed that established *E. angustifolium* prevented a pH decrease from 6 to 2.6 and decreased the release of As, Cu, Cd, Pb, and Zn up to 99%. In later work [194], it was shown that the signal behind the prevention of pH decrease was to prevent a too high free metal concentration from forming in the tailings. Aquatic plants can tolerate a very low pH, which can be necessary when treating AMD. The mechanisms behind treatment of AMD by aquatic plants are summarized in Figure 24.8.

Eriophorum angustifolium survives in substrates with a wide pH range, from pH 11.0 [192] to about 2.6 [193]. Other wetland plant species that have been found to grow on mine tailings and tolerate a low pH are *Carex rostrata, E. scheuchzeri, Phragmites australis, Typha angustifolia,* and *T. latifolia*; these have been found growing under field conditions in pH as low as 2.1, 4.4, 2.1, 3.0, and 2.5, respectively [193–195].

24.5.3 Constructed Wetlands for Removal of Metals

Constructed wetlands with reed beds and floating-plant systems have been common for the treatment of various types of wastewaters for many years. This strategy is currently gaining importance globally and expanding to address contaminated/polluted soils and water bodies [179, 196–198].

Natural wetland ecosystems are inherently complex. Thus, for the purpose of treatment of metal-contaminated waters, it is advantageous to construct separate tanks within the treatment system, with each tank designated to perform a particular function maximally (occasionally, more than one would be beneficial). The design of wetlands constructed for the treatment of metal-contaminated waters attempts to identify and optimize the key processes that promote the removal of specific targeted metal. Alternatively, this also includes suppression of potentially interfering and competing processes.

Treatment of wastewaters/natural waters containing a single metal such as iron can be achieved using a constructed wetland designated to optimize only one of the possible process. For example, removal of iron involves precipitation of iron hydroxide in an aerobic environment. In contrast, if the water contains a mixture of metals, e.g., iron and zinc in high concentrations, the constructed wetland must adapt different strategies, such as application of aerobic and anaerobic processes. An aerobic environment promotes the precipitation of aluminum and iron hydroxides and coprecipitation of arsenic [1]. An anaerobic situation promotes the reduction of sulphates and the consequent precipitation of sulphides, primarily for copper, cadmium, and zinc [1].

The precipitation of hydroxides is regulated by pH and the availability of oxygen, which can be ensured by

- Construction of shallow wetlands with a maximal depth of about 3 m water
- Organic detritus to be minimized because it demands oxygen for decomposition (it is preferable to use large inorganic substrate)
- Designing the landscaping into ridges and gullies to ensure continual mixing of the water within the system so as to prevent stratification of water into oxygen-rich and oxygen-depleted zones
- Incorporating cascades at the point of influence to promote oxygenation of air
- Utilizing reed beds comprising *Phragmites australis* (common reed), *Typha latifolia* (cattail), etc., which have the ability to transfer oxygen to the root zone [1,4,197]

Glyceria fluitans (floating sweetgrass) is an amphibious plant found growing in the tailings pond of an abandoned lead/zinc mine in Glendalough County, Wicklow, Ireland [190]. Greenhouse experiments demonstrated that *G. fluitans* could grow in sand culture treated with high zinc sulphate solution. Further research confirmed that two populations of *G. fluitans* — one from a metal contaminated and the other from a noncontaminated site — could be grown successfully on mine tailings with a high zinc content. *G. fluitans* and two other wetland plants, *Phragmites australis* and *Typha latifolia*, have since been grown on alkaline and acidic zinc mine tailings in field conditions under fertilized and nonfertilized conditions. Research findings obtained thus far indicate that *G. fluitans* can be easily established on zinc mine tailings. It appears also to have a very low nutrient requirement, thus keeping fertilizer costs to a minimum during rehabilitation of mine tailings.

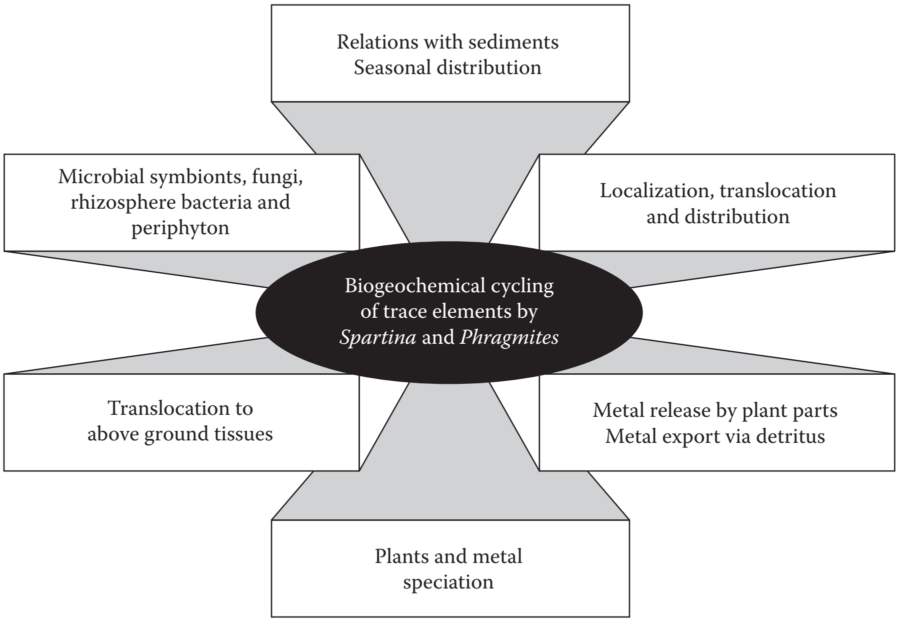

FIGURE 24.10 Role of prominent wetland species in biogeochemical cycling of trace elements.

Wetlands have been constructed in Ireland for the passive treatment of tailing water originating from a lead/zinc mine. Water originating from mine tailings is often characterized by high metal and sulphate concentrations compared to background levels. Conventional methodology of tailing water treatment involves chemical treatment, which is a costly procedure requiring intensive chemical and labor inputs.

Therefore, more recently constructed and natural wetlands have been utilized for metal removal and wastewater quality control. Wetlands with their diversified macrophytes are known to retain substances such as metals from water passing through them. Aquatic macrophytes encompassing many common weeds enable cost-effective treatment and remediation technologies for wastewaters contaminated with inorganics and organics.

Constructed wetlands and its assemblage, anoxic lime stone drains (ALD), and successive alkalinity producing systems (SAPS) have produced promising results [198–201] in restoration of acid mine drainage (AMD) in several real-world ecosystems [202,203].

24.6 BIOGEOGENIC CYCLING OF METALS

Metal uptake, translocation and release by *Spartina alterniflora* and *Phragmites australis* association are implicated in phytoremediation and restoration (Figure 24.10) [180]. Salt marsh metallophytes play a potential role in phytoremediation and restoration of metals. Wetland plants and salt marshes function in a similar fashion with regard to metal uptake patterns and in compartmentalizing them in roots. Some species retain more of their metal burden in below-ground structures than other species, which redistribute a greater proportion of metals into above ground tissues, especially leaves. Storage in roots is most beneficial for phytostabilization of the metal contaminants, which are least available when concentrated below ground.

Wetland/aquatic plants and salt marshes may alter the speciation of metals and may also suffer toxic effects depending upon their bioaccumulation coefficient. In certain salt marsh plants, metals in leaves may be excreted through salt glands and thereby returned to the marsh environment. Metal concentrations of leaf and stem litter may become enriched in metals over time, due in part to cation adsorption or to incorporation of fine particles with adsorbed metals.

Several studies suggest that metals in litter are available to deposit feeders and thus can enter estuarine food webs. Marshes, therefore, can be sources as well as sinks for metal contaminants. *Phragmites australis*, an invasive species in the northeastern U.S., sequesters more metals below ground than the native *Spartina alterniflora*, which also releases more via leaf excretion. This information is important for the silting and use of wetlands for phytoremediation as well as for marsh restoration efforts.

Some aquatic plants are used as food and feed. Water spinach, *Ipomea aquatica,* is commonly used as a vegetable and pig food in Thailand. It is very easy to grow, grows fast, and is present in cultivated water, as well as in industrial areas and big cities. It takes up and accumulates heavy metals to such an extent that a threat to human health has been discussed [31,205]. Recent studies have shown that plants collected in Thailand, near Bangkok, contained up to 530, 350, and 123 $\mu g/g\ DW^{-1}$ of Pb, Hg, and Cd, respectively [205]. The biggest problem seems to be Hg. According to FAO, the weekly intake of Hg should not exceed 43 μg per week, which means not more than 250 g of plant per day can be eaten. However, the real problem seems to be the property of this plant to accumulate high levels of CH_3–Hg [205]. This plant has also been tested for removal of metals from wastewaters [37].

When this plant is grown, nutrients are necessary for high biomass production, which in turn is positive for those who grow this plant for their own consumption, as well as for selling. Another positive effect with nutrient addition is that the higher the nutrient concentration is, the lower the uptake of Cd, Pb, and Hg [206]. Sobolewski [170] also showed that adding nutrients prevented toxic effects on the plant, likely due to decreased intrinsic concentration of the metals.

24.7 CONCLUDING REMARKS

The aquatic macrophytes listed earlier have several characteristics — namely, hardiness, ability to survive under adverse environmental conditions, and high productivity (Figure 24.11) together with factors controlling bioaccumulation coefficient (Figure 24.12) that would enable them as potential agents of phytotechnology. Furthermore, the anaerobic environment in the water and sediments renders elements in less oxidized forms. This increases solubility and uptake by aquatic plants and may make it possible to a considerable extent in phytoremediation of wetlands. The partial pressure of oxygen in water is only a small fraction of the 21% oxygen in air; the aquatic environment is a strong defense against free radical formation. Unfortunately, low levels of oxygen also greatly reduce the availability of energy liberated by catabolism. This can hinder growth, particularly in stagnant ponds or other situations lacking natural aeration.

The aquatic environment, especially bottom waters and sediments, often has low oxygen content. Metals in reduced form are more easily taken up by plants. Once in the plant, they may be oxidized and become immobile. Thus, aquatic macrophytes generally have a much higher metal content than terrestrial plants and can be usefully employed in phytoremediation. The reason for higher concentration in submerged than in terrestrial plants is that, comparing leaf uptake, the terrestrial plant leaves have cuticle, which prevents the uptake.

Furthermore, most uptake is via roots in terrestrial plants, as well as emergent plants, and the translocation is often low — approximately up to 10% — because the metals bind in the root cell walls due to the negative charge. Submerged plants take up metals via roots to a lesser extent because their roots, at least in most aquatic plants, are few and root biomass is low compared to the shoot part. Aquatic macrophytes serve as accumulators and indicators of pollution and also mitigate metal pollution to a considerable extent [47,93,107,138,207–213].

Macrophytes bioconcentrate metals from water and sediments, resulting in an internal concentration several fold greater than their surroundings. The submerged plants in polluted water bodies are reported to accumulate trace metals to the tune of 10^3 to 10^4 and also reduce the water velocity, facilitating rapid sedimentation of the suspended fine particulates containing trace metals; otherwise,

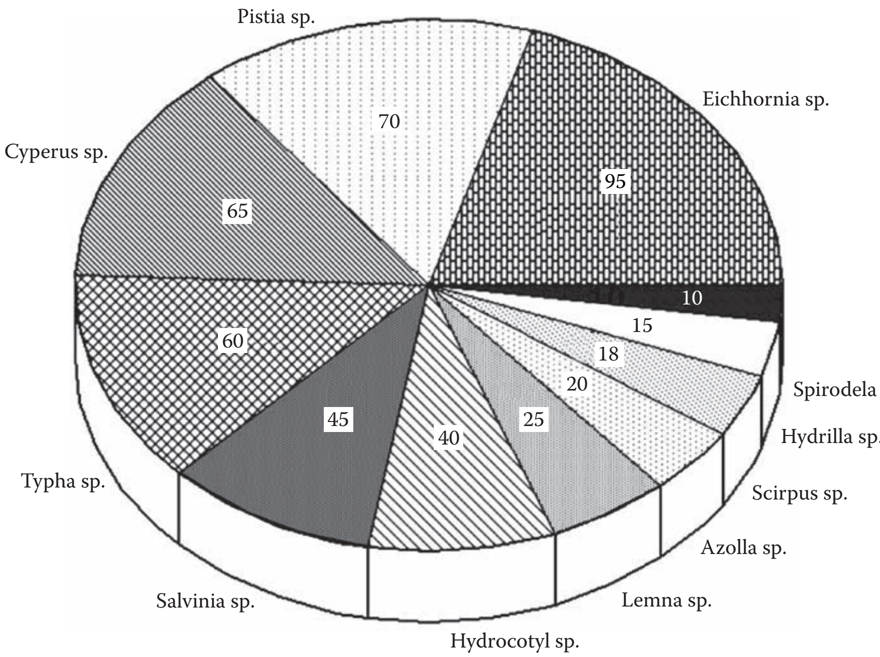

FIGURE 24.11 Bioproductivity (t ha $^{-1}$ yr $^{-1}$) of selected aquatic and wetland macrophytes under specific conditions enable them to act as potential agents in phytotechnology.

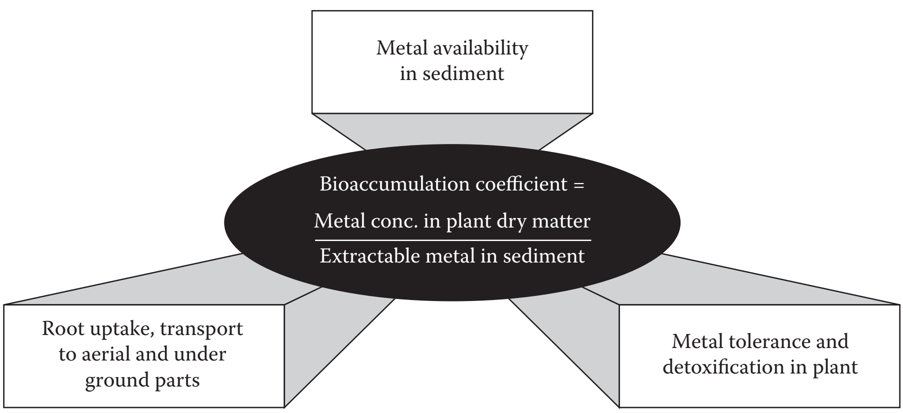

FIGURE 24.12 Factors determining the bioaccumulation coefficient in aquatic/wetland ecosystems.

these are toxic to the biota when present in the interstitial waters in available form [7,8]. Thus, they play a major role in biogeochemical cycling of trace metals.

The reedbed technology developed for bioremediation of organic and inorganic pollutants has attained global significance. Aquatic macrophyte-based phytotechnology for bioremediation has limitations in addition to vast scope. The notable limitations are

- Invasive species could harm the ecosystem.
- Tropical wetlands are rapidly changing.
- Evapotranspiration losses are too high.

Therefore, the future development, potential, and implementation of these systems should be investigated in detail, considering the advancements in biotechnology and molecular biology.

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