

# On-Site and Full-Scale Applications of Phytoremediation to Repair Aquatic Ecosystems with Metal Excess

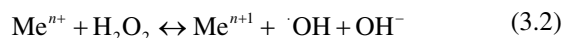
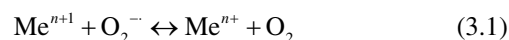
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## 3.1 Introduction

Aquatic ecosystems perform numerous valuable environmental functions. They recycle nutrients, purify water, attenuate floods, augment and maintain streamflow, recharge ground water, and provide habitat for wildlife. Also, these ecosystems provide sources of hydroelectric power, water for municipal, industrial, and agricultural purposes, and sites for people recreation. However, rapid population increases—accompanied by intensified industrial, commercial, and residential development—have led to the pollution of surface waters by metals, fertilizers, insecticides, motor oil, toxic landfill leachates, feedlot waste, industrial and municipal sewage effluents. At the same time, water consumption has also increased, thus reducing the flows available for the dilution of wastes (Committee on Restoration of Aquatic Ecosystems: Science, Technology, and Public Policy; National Research Council 1992). Metals are a group of contaminants of great environmental importance. While many authors support the idea of a segregation of pollutants based on their chemical characteristics (organic or inorganic), its resistance to degradation (biodegradable, persistent or recalcitrant) or its similarities with preexisting biomolecules (biogenic or xenobiotics), others take into account their mechanism of toxic action. Thus, in the environment many metals generate reactive oxygen species (ROS), such as superoxide anion ( $O_2^{\cdot-}$ ), hydrogen peroxide ( $H_2O_2$ ), and in particular hydroxyl radical ( $\cdot OH$ ) (Aravind

and Prasad 2004). In Haber–Weiss cycle (Eqs. 3.1 and 3.2) and Fenton reaction (Eq. 3.2) metals with multiple oxidation states like iron, lead, copper, and chromium catalyze  $\cdot OH$  synthesis from  $H_2O_2$  and  $O_2^{\cdot-}$ .



ROS accomplish a key role regulating growth and development of the biota, thus a change in its delicate balance can lead to necrosis of cells, tissues and eventually death of organisms. Since ROS have the ability to oxidize the four groups of cellular macromolecules (proteins, lipids, polysaccharides, and nucleic acids), and while the degradation of a protein with enzymatic activity can lead to the loss of a metabolic pathway, or a lipid peroxidation can result in damage to the membranes responsible for energy metabolism or structural integrity, DNA damage can also generate both carcinogenic and teratogenic effects on organisms (Leonard et al. 2004).

On the other hand, greater knowledge about the dynamics of metals and their potential effects on the environment questions the “dilution paradigm” as a sustainable remediation strategy. This paradigm shift has been based on ethical and preservation issues, but is also the result of understanding that biogeochemical conditions determine metal mobility, potential dispersion within or between different environmental compartments, and mechanisms of toxic action.

Besides in a similar way to certain soluble organic contaminants, some organometallic compounds such as methylmercury have a high tendency to biomagnify in the food chain and can exert a devastating teratogenic action although initial levels of metal discharges are low (Tadiso et al. 2011; Harmelin-Vivien et al. 2012).

Inland water-bodies are complex systems that have a profound influence on the characteristics and toxicity of contaminants. It is generally considered that aerobic or anaerobic degradation of organic compounds is the only effective way of removal, since produced mineral compounds can be integrated into the cycles of elements. However, the degradation process

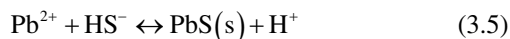
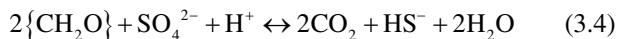
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mainly mediated by microorganisms has the particularity of altering the physicochemical conditions of the environment such as pH and redox potential, generating chemical species able to precipitate metallic ions (Eqs. 3.4 and 3.5), or organic and inorganic ligands that can produce coordination compounds in which heavy metals act as Lewis acids.



Moreover, endogenous or exogenous primary and secondary minerals such as clays behave like chemically reactive surfaces providing high densities of binding sites to retain metals through the formation of outer or inner sphere complexes.

Since a proper understanding of contaminant–environment interactions in aquatic ecosystems requires considering abiotic and biotic factors, it is essential to analyze processes mediated by organisms.

Aquatic plants that have been studied for the remediation of soil and water contaminated by metals include floating species, such as *Salvinia herzogii* (Maine et al. 2004), water hyacinth (*Eichhornia crassipes*) (Mishra et al. 2008), duckweed (including *Lemna polyrrhiza* L., *Lemna minor*, and *Spirodela polyrrhiza* W. Koch) (John et al. 2008; Mishra and Tripathi 2008), mosquito fern (*Azolla pinnata* R. Brown) (Mishra et al. 2008), and water lettuce (*Pistia stratiotes*) (Maine et al. 2004; Mishra et al. 2008), emergent plants such as common cattail (*Typha latifolia*) (Das and Maiti 2008), giant bulrush (*Schoenoplectus californicus*) (Arreghini et al. 2001; Chiodi Boudet et al. 2011), common reed (*Phragmites australis*) (Peruzzi et al. 2011), and submerged plants, such as pondweed (*Potamogeton pectinatus* or *Potamogeton crispus*) (Badr and Fawzy 2008; Mishra et al. 2008), hydrilla (*Hydrilla verticillata*) (Bunluesin et al. 2004; Mishra et al. 2008), and coontail (*Ceratophyllum demersum* L.) (Badr and Fawzy 2008; Bunluesin et al. 2004). Metal–plant interaction depends on metal bioavailability and plant structure involved in absorption. In the case of emergent plants and numerous floating species the preferential uptake structure is the root, where the accumulated metal translocates to other morphological structures, while in the case of submersed plants the root could play an auxiliary role of fixing and the uptake occurs through all the epidermis of the plant. Uptake and mobility of metals in the plant are different for different types and species of macrophytes, also depending on the metal involved (Deng et al. 2004) and its concentration.

While the basic premise for starting any mitigation project is eliminating the source of contamination, this approach is necessary but insufficient. Rivers and their floodplains are so intimately linked that they should be understood, managed, and restored as integral parts of a single ecosystem. The interception of point and nonpoint sources of contamination is

necessary to improve ecosystem attribute. However, the costs of treating nonpoint sources by engineered systems are high. Man-made and natural wetlands have been successful, in some cases, in retaining suspended matter in water flowing through them. Also, the plants remove phosphorus, coliform bacteria, biochemical oxygen demand; and dissolved organic carbon. In situ methods are defined as destruction or transformation of the contaminant, immobilization to reduce bioavailability, and separation of the contaminant from the bulk soil (Reed et al. 1992). In situ techniques are better than the ex-situ techniques due to their low cost and reduced impact on the ecosystem. Wetlands are also highly effective in reducing stream loads of metals.

The aim of this chapter is to discuss several applications of phytoremediation at full scale and on-site for metal excess in aquatic ecosystems using several macrophytes.

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### 3.2 Plants as Promoters of a Better Environment

Preservation of the littoral zone in contaminated environments is crucial, since it contributes in different ways to metal stabilization in sediment. Thus, macrophytes could be a powerful tool in treatment of aquatic ecosystems receiving industrial effluents, municipal wastewater, or agricultural runoff (Rai 2009). The long-term stability that the plants provide in terms of preventing metals from leaving the site means that this technology is often termed phytostabilization. Phytostabilization has a wide application in metal-contaminated vegetated sites.

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### 3.3 Geophysical and Biochemical Processes of Stabilization

Unvegetated sediments tend to show little aggregation due to the weakening effect of water on the bonds holding sediment particles (Reddy et al. 2000). This makes them more susceptible to weathering, by increasing the contact surface between the solid fraction and the solution phase, and facilitates also their transport through erosional agents. Sedimentation processes combined with oxidation, sorption, and precipitation reactions are effective at removing metals from the system (Bednar et al. 2013).

Natural and anthropogenic events can generate local base levels that decrease the current velocity of rivers and favor sedimentation of the suspended material. Moreover, aquatic vegetation increases resistance to flow and significantly affects sediment transport. In the low-load basin, aquatic plants such as cattail (*Typha* sp.) has a substantial and significant effect on transport capacity since it increase sediment deposition (Brueske and Barrett 1994). Also, riparian vegetation plays an

important role in mitigation and prevention against hydromorphological hazards (flooding, floodplain erosion, protection of river infrastructures), if correctly managed (Kothyari et al. 2009; Cavedon 2012).

The vegetated marsh zones are associated with finer grain particles and exhibit higher metal concentrations in contaminated environment in comparison to the bare mudflats (Daskalakis and O'Connor 1995; Zhang et al. 2001). However, in some cases where there is direct input of contaminants, no clear relationship between the proportion of fine-grained particles and metal concentration has been established (Hosono et al. 2011). Natural events like tidal currents, winds, and storms, and human activities as dredging result in major sediment disturbances, leading to changes in chemical properties that stimulate the mobilization of contaminants from sediment and sediment pore water into the water column (Zhang et al. 2001; Eggleton and Thomas 2004).

Biochemical processes that lead to the formation of a solid phase may involve diverse and complex mechanisms. Chemical precipitation is determined primarily by solubility product of salts ( $K_{ps}$ ), by the concentration of ions forming the precipitate, by the pH and redox potential of the water solution, by the presence of complexing agents and by the ionic strength of the medium. However, the formation of a solid phase requires supersaturated solutions in a stable media rich in precipitation nuclei. Accumulation of organic matter and microorganisms in sediments can provide a high density of nuclei which serves for growth of the precipitates. Both the subsequent aggregation of nuclei in larger particles, leading to decreased surface/volume relationships, and rearrangement of atoms in the crystal lattice of the solid diminish solubility of salts. In this way, organic matter degradation may stimulate the chemical precipitation and consequent stabilization of metals in the solid phase.

Suspended material includes a colloidal fraction constituted by amorphous or crystalline solids of small radius, humic substances, and cellular macromolecules of high molecular weight (Konhauser et al. 2002). Therefore, colloids include a heterogeneous group of compounds characterized by high surface/volume ratio and high density of electric charge. Vegetation release substantial amounts of colloidal material to the water body during its life cycle. These compounds can interact with metals through adsorption phenomena and generation of outer sphere complexes, complexation and generation of inner sphere complexes or eventually through surface precipitation processes (Suteerapataranon et al. 2006). While colloids are stable in aqueous solution and tend to remain in suspension, changes in environmental conditions such as the increase of ionic strength can lead to flocculation and coagulation processes that remove from the solution both colloids as “associated” metals (Suteerapataranon et al. 2006; Ren et al. 2010).

Sediments accumulated by described physical and biochemical processes serve as a substrate for the growth of aquatic vegetation. Emergent plants of the coastal area with high productivity produce a net enrichment of sediments with organic matter (Lenssen et al. 1999). In this way, riparian vegetation contributes to sediment stabilization decreasing risk of contamination of the water column. This enrichment with organic matter is often overlooked by many authors, partly due to the short time span out of most studies—too short for the initial organic matter to be consumed in the chemical processes of removing metals from water (Marchand et al. 2010).

In wetland sediments the organic matter accumulation generates a high oxygen demand. Aerobic microorganisms are replaced by anaerobic ones that use alternative electron acceptors in the process ( $\text{NO}_3^-$ ,  $\text{MnO}_4^-$ ,  $\text{Fe}^{3+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_2$ ), depending on both their relative abundance in the environment and, in the situation when multiple acceptors are present, on the energy yield of redox reactions (Konhauser et al. 2002). Unlike aerobic degradation, where the process can be performed by a single type of organism, anaerobic degradation often requires a consortium of interdependent microorganisms. In this way, and depending on the rate of settleable organic material, net accumulation of reduced forms of sulfur and organic matter represent a significant reserve of binding sites for metals. While some metals such as copper, chromium, and lead have high affinity for the organic matter/sulfides fraction and thus can be immobilized, other metals such as cadmium and zinc are predominantly associated with the exchangeable fraction and iron and manganese oxides, respectively and are comparatively more bioavailable (Tessier et al. 1979). Several authors argue that the less mobile fractions of sediment tend to get rich in metals as time passes from contamination event. Thus although metal shows a greater affinity for a more mobile fraction as exchangeable, the “aging” that occurs in sediment generates a redistribution to thermodynamically more stable phase (McLaren and Clucas 2001; Halim et al. 2003; Evangelou et al. 2007). Peruzzi et al. (2011) have reported that in wetlands vegetated with *Phragmites australis*, built for municipal wastewater treatment, the less available metal-organic fraction increased over time for Cu, Cr, Pb, Ni, Cd, and Zn, thus indicating their lesser availability for plant uptake. Since bioavailability and bioaccumulation of metals in an aquatic ecosystem is mainly dependent on its partitioning behavior or its binding strength to sediment (Eggleton and Thomas 2004) then the input of high quantity of organic matter from aquatic macrophytes as a solid phase with high metal sorption capacity is decisive. Dissolved or weakly adsorbed contaminants are more bioavailable to aquatic biota compared to more structurally complex mineral-bound contaminants (Calmano et al. 1993; Eggleton and Thomas 2004).

In *ex situ* remediation processes, changes in physico-chemical conditions of the environment can lead to a redistribution of metals from “aged” fractions of sediments to more mobile ones, increasing the environmental risk (Rodríguez Salemi et al. 2010).

### 3.4 Tolerant Plants Favor the Settling of Other Species

Metal contamination is a stress factor limiting plant growth and development, which leads to decreased levels of organic matter and nutrients of sediments and negatively affects the establishment of plant. Numerous studies show the recovery of contaminated habitats through revegetation with tolerant species, so implanted areas with wetland plants show an increase in the organic matter content of sediments, a consequent improvement in infiltration and fertility in general, an increase in the N, P, and K available and an improve in water quality (Deng et al. 2004; Mitsch et al. 2005; Lei and Duan 2008; Lottermoser and Ashley 2011; Wang et al. 2012). Although restoration efficiency mainly depends on species selected, colonization by pioneer plants could promote the development of aquatic communities that lead to stabilization of metals and prevent the transfer of environmentally significant contaminants into food-chains.

Metallophytes are species that have evolved biological mechanisms to resist, tolerate, or thrive on toxic metalliferous soils, and are typically endemic of these habitats. Metallophytes are the optimal choice for *in situ* restoration of closed mines, for the rehabilitation of metal-contaminated land (reclamation and rehabilitation) and to provide knowledge for development of environmental technologies such as phytoextraction of metals from soils (Whiting et al. 2004).

Wetland plants growing in contaminated sediments present characteristic patterns of accumulation and translocation of metals, thus findings on terrestrial plants cannot be directly extrapolated. Besides the use of native species in remediation strategies, not always considered in scientific or technical papers and essential to preserve biological diversity, require detailed studies for each natural ecosystem.

### 3.5 Metal Accumulation in Plants as an Avoidance Strategy

#### 3.5.1 Emergent Macrophytes

Although high levels of metals reported in wetland sediments, their low bioavailability and limited transfer into the water column determine that macrophytes of the littoral zone typically exhibit relatively low concentrations of these contaminants. Whereas it was observed that in the same environment

submerged and floating plants exhibit higher concentrations of metals in their organs than emergent ones, there are no reported hyperaccumulators in wetland habitats (Cardwell et al. 2002). Thus, despite its great development in biomass, the amount of metals accumulated by emerging plants represents only a small fraction of the total content in sediments, so they cannot be considered as a metal sink (Lee and Scholz 2007; Marchand et al. 2010).

Although it is recognized that the particular properties of wetland sediments (organic matter content, pH, redox potential, levels of P and N) influence the bioavailability of metals, there are contrasting observations regarding the role played by each environmental factor.

Organic matter content of sediment can be negatively correlated with chromium uptake by the roots, as this metal can form inner-sphere complexes with organic matter and oxides making it less available to plants (Iorio et al. 2007; Valea 2011). Moreover, association of metals with amino groups ( $-NH_2$ ) of humic compounds (Bargiela 2009) favors solubilization and increases their bioavailability.

McGrath (1995) and Vicari Mellis et al. (2004) argue that Ni sorption to sediment is maximum with high pH and high content of organic matter, so acidic pH and negative redox potential found in highly contaminated sites could facilitate solubilization of essential and nonessential metals and uptake by plants. Armstrong (1967) reports that oxidation of immediate root environment promote the uptake of essential elements and prevent the internalization of toxic components. Metals mobilized from the reduced sediments can precipitate with Fe and Mn (oxy)hydroxides on the root surface (“root plaque”) (Gries et al. 1990), resulting in high rhizoconcentrations on a small scale or even in elevated concentrations in bulk sediments from a vegetated marsh compared to non-vegetated sediments (Teuchies et al. 2013).

Some authors emphasize the antagonistic relationship between P and metals since chemical reactions in the rhizosphere produce highly insoluble precipitates (Kabata-Pendias 2011; Olsen 1991; Deng et al. 2004), although others report increases in bioavailability in the presence of soluble P (Kidd et al. 2007). Therefore, depending on the nature of the phosphorus compounds and the heavy metal species, metal bioavailability can be favored or disadvantaged (Bolan et al. 2003).

Lambert et al. (1979) and Taiz and Zeiger (2002) state that mycorrhizal associations produce a remarkable increase in P, Zn, and Cu uptake by terrestrial plants, yet not in common symbiosis studies with aquatic plants exposed to high levels of nonessential metals. Another factor than can affect the accumulation of metals in wetland plants is the presence of microbial symbionts such as rhizosphere bacteria. Mycorrhizae provide an interface between the roots and the soil increasing the absorptive surface area and are effective at assimilating metals that may be present at toxic concentrations in the soil (Meharg and Cairney 2000). However, Khan

et al. (2000) suggested that they play a protective role, restricting the uptake of metals by plants by immobilizing the metals in the fungal tissue.

Wetlands are complex ecosystems, so availability and uptake of metals by emergent plants is the result of interactions between biotic and abiotic compartments that create conditions for immobilization or release of contaminants.

Plant metal uptake can be measured through different indexes. One of the most used is bioconcentration factor, BCF, obtained as metal concentration ratio of plant root to sediment. There is great variation among the reported BCF values for the different species of emergent macrophytes and heavy metals, especially related to its essentiality (Tables 3.1 and 3.2). Thus, the species indicated in Table 3.2 shows similar behavior in the uptake of Zn and Cu. For example, *Schoenoplectus californicus*, *Scirpus sylvaticus*, *Cyperus esculentum*, *Cyperus alternifolius*, *Sagittaria montevidensis*,

*Equisetum arvense*, *Hydrocotyle americana*, and *Phragmites australis* have always BCF values close to or less than unity over a wide range of sediment concentrations, from 28.5 to 5,400  $\mu\text{g Zn/g}$  and from 5 to 2,100  $\mu\text{g Cu/g}$ . *Cyperus eragrostis* and *Equisetum fluviatile* have high BCF values (close to 4 for Zn, and between 7 and 16 for Cu) at levels of these metals that do not exceed the LEL (lowest effect level) level in sediment. *Schoenoplectus validus*, *Typha domingensis*, *Typha orientalis*, *Typha latifolia*, and *Eleocharis equisetina* present high values of BCF at Zn or Cu sediment levels between LEL and SEL (severe effect level). For Ni, almost all species reported showed BCF values near or less than 1 especially at sediment levels above LEL, except *T. domingensis* and *T. latifolia* whose BCF values are between 2 and 10 at levels of Ni slightly above LEL (Table 3.2). For nonessential metals Pb, Cd, and Cr the BCF values reported are generally lower than those for essential ones. *Cyperus*

**Table 3.1** List of emergent and floating macrophyte species grown in natural and contaminated environments with their scientific name, common name, authors, and location of different studies

| Code                   | Species name                       | Common name        | Study | Authors                       | Location      |
|------------------------|------------------------------------|--------------------|-------|-------------------------------|---------------|
| <b>Emergent plants</b> |                                    |                    |       |                               |               |
| <i>Sch cal</i>         | <i>Schoenoplectus californicus</i> | Giant bulrush      | 1     | Chiodi Boudet et al. (2011)   | South America |
|                        |                                    |                    | 2     | Valea (2011)                  | South America |
| <i>Sch val</i>         | <i>Schoenoplectus validus</i>      | River bulrush      | 3     | Cardwell et al. (2002)        | Oceania       |
| <i>Sci syl</i>         | <i>Scirpus sylvaticus</i>          | Sylvan bulrush     | 4     | Hozhina et al. (2001)         | Europe        |
| <i>Cyp esc</i>         | <i>Cyperus esculentum</i>          | Yellow nutsedge    | 5     | Yoon et al. (2006)            | North America |
| <i>Cyp era</i>         | <i>Cyperus eragrostis</i>          | Tall flatsedge     | 3     |                               |               |
| <i>Cyp alt</i>         | <i>Cyperus alternifolius</i>       | Umbrella sedge     | 6     | Yang et al. (2010)            | Asia          |
| <i>Ele equ</i>         | <i>Eleocharis equisetina</i>       |                    | 7     | Lottermoser and Ashley (2011) | Oceania       |
| <i>Typ dom</i>         | <i>Typha domingensis</i>           | Southern cattail   | 8     | Maine et al. (2006)           | South America |
|                        |                                    |                    | 3     |                               |               |
|                        |                                    |                    | 9     | Kamel (2013)                  | Africa        |
| <i>Typ lat</i>         | <i>Typha latifolia</i>             | Broadleaf cattail  | 13    | Bonanno (2013)                | Europe        |
|                        |                                    |                    | 4     |                               |               |
|                        |                                    |                    | 11    | Klink et al. (2013)           | Europe        |
| <i>Typ ori</i>         | <i>Typha orientalis</i>            | Cumbungi cattail   | 12    | Sasmaz et al. (2008)          | Africa        |
|                        |                                    |                    | 3     |                               |               |
| <i>Phr aus</i>         | <i>Phragmites australis</i>        | Common reed        | 10    | Sawidis et al. (1995)         | Europe        |
|                        |                                    |                    | 9     |                               |               |
| <i>Hyd ame</i>         | <i>Hydrocotyle americana</i>       | American pennywort | 13    | Bonanno (2013)                | Europe        |
|                        |                                    |                    | 5     |                               |               |
| <i>Sag mon</i>         | <i>Sagittaria montevidensis</i>    | Giant arrowhead    | 2     |                               |               |
| <i>Equ arv</i>         | <i>Equisetum arvense</i>           | Field horsetail    | 5     |                               |               |
| <i>Equ flu</i>         | <i>Equisetum fluviatile</i>        | Fluvial horsetail  | 4     |                               |               |
| <b>Floating plants</b> |                                    |                    |       |                               |               |
| <i>E crass</i>         | <i>Eichhornia crassipes</i>        | Water hyacinth     | 8     |                               |               |
|                        |                                    |                    | 14    | Kumar et al. (2012)           | Asia          |
|                        |                                    |                    | 9     |                               |               |
|                        |                                    |                    | 15    | Agunbiade et al. (2009)       | Africa        |
| <i>L gibb</i>          | <i>Lemna gibba</i>                 | Duckweed           | 16    | Kumar et al. (2008)           | Asia          |
|                        |                                    |                    | 9     |                               |               |
| <i>M min</i>           | <i>Marsilea minuta</i>             | Dwarf waterclover  | 14    |                               |               |
| <i>S mol</i>           | <i>Salvinia molesta</i>            | Kariba weed        | 17    | Ashraf et al. (2011)          | Asia          |

**Table 3.2** Metal sediment concentration ( $\mu\text{g/g}$ ); Bioconcentration factor (BCF) and translocation factor (TF) of different emergent macrophytes

| Species name   | Study <sup>a</sup> | Zn     |                   |                   | Cu    |                   |                   | Pb    |                   |                   |
|----------------|--------------------|--------|-------------------|-------------------|-------|-------------------|-------------------|-------|-------------------|-------------------|
|                |                    | Sed    | BCF               | TF                | Sed   | BCF               | TF                | Sed   | BCF               | TF                |
| <i>Sch cal</i> | 1                  | 28.5   | 1.22              | 0.66 <sup>b</sup> | 9.2   | 0.97              | 0.61 <sup>b</sup> | –     | –                 | –                 |
|                | 1                  | 28.5   | 0.58              | 1.69 <sup>b</sup> | 13.5  | 0.88              | 0.22 <sup>b</sup> | –     | –                 | –                 |
|                | 1                  | 54.5   | 0.65              | 0.46 <sup>b</sup> | 21.9  | 0.55              | 0.14 <sup>b</sup> | –     | –                 | –                 |
|                | 2                  | 95     | 0.48 <sup>b</sup> | 0.26 <sup>b</sup> | 23    | 0.32 <sup>b</sup> | 0.26 <sup>b</sup> | –     | –                 | –                 |
|                | 2                  | 99     | 0.77 <sup>b</sup> | 0.22 <sup>b</sup> | 28    | 0.50 <sup>b</sup> | 0.41 <sup>b</sup> | –     | –                 | –                 |
|                | 2                  | 404    | 0.36 <sup>b</sup> | 0.20 <sup>b</sup> | 143   | 0.15 <sup>b</sup> | 0.29 <sup>b</sup> | –     | –                 | –                 |
| <i>Sch val</i> | 3                  | 514    | 3.05              | 0.03 <sup>c</sup> | 38.3  | 2.00              | 0.04 <sup>c</sup> | 72.5  | 1.74              | 0.03 <sup>c</sup> |
| <i>Sci syl</i> | 4                  | 40     | 1.00              | 2.10              | 15    | 0.80              | 0.83              | 25    | 0.92              | –                 |
|                | 4                  | 5,400  | 0.03              | 2.73              | 2,100 | 0.02              | 0.57              | 3,000 | 0.01              | 0.84              |
| <i>Cyp esc</i> | 5                  | 195    | 0.83              | 1.02              | 20    | 0.80              | 0.63              | 90    | 0.31              | 0.64              |
|                | 5                  | 200    | 0.86              | 0.47              | 21    | 0.48              | 2.80              | 143   | 0.11              | 1.64              |
|                | 5                  | 572    | 0.45              | 1.12              | 300   | 0.50              | 0.13              | 1,451 | 0.29              | 0.06              |
| <i>Cyp era</i> | 3                  | 93.4   | 2.14              | –                 | 17.6  | 1.68              | –                 | 12.9  | 2.84              | –                 |
|                | 3                  | 128    | 4.55              | –                 | 36.6  | 7.19              | –                 | 77.2  | 1.63              | –                 |
| <i>Cyp alt</i> | 6                  | 62     | 0.71              | 0.68              | –     | –                 | –                 | 29    | 0.20              | –                 |
|                | 6                  | 580    | 0.27              | 0.24              | –     | –                 | –                 | 711   | 0.25              | 0.01              |
| <i>Ele equ</i> | 7                  | 174    | 2.37              | 0.67              | 84    | 2.67              | 0.32              | 59    | 0.49              | 0.09              |
|                | 7                  | 282    | 1.21              | 0.67              | 331   | 2.12              | 0.10              | 222   | 0.21              | 0.11              |
| <i>Typ dom</i> | 8                  | 60     | 2.15              | 0.14 <sup>c</sup> | –     | –                 | –                 | –     | –                 | –                 |
|                | 3                  | 93.4   | 3.81              | 0.06 <sup>c</sup> | 17.6  | 4.65              | 0.04 <sup>c</sup> | 12.9  | 1.64              | 0.07 <sup>c</sup> |
|                | 3                  | 128    | 3.88              | 0.17 <sup>c</sup> | 36.6  | 3.48              | 0.12 <sup>c</sup> | 72.5  | 1.81              | 0.03 <sup>c</sup> |
|                | 13                 | 294    | 0.29              | 0.27 <sup>c</sup> | 115   | 0.14              | 0.15 <sup>c</sup> | 64.2  | 0.12              | 0.09 <sup>c</sup> |
|                | 3                  | 514    | 2.00              | 0.07 <sup>c</sup> | 38.3  | 1.40              | 0.16 <sup>c</sup> | 77.2  | 2.61              | 0.01 <sup>c</sup> |
|                | 9                  | 1,201  | 0.30 <sup>b</sup> | 0.60 <sup>c</sup> | 52.7  | 1.00 <sup>b</sup> | 1.00 <sup>c</sup> | 12.2  | 0.77 <sup>b</sup> | 0.87 <sup>c</sup> |
| <i>Typ lat</i> | 4                  | 40     | 0.78              | 1.65              | 15    | 1.33              | 0.24              | 25    | 0.8               | –                 |
|                | 11                 | 62.2   | 6.00              | 0.10 <sup>d</sup> | 4.98  | 1.73              | 0.43 <sup>d</sup> | 10.0  | 1.21              | 0.34 <sup>d</sup> |
|                | 12                 | 70.0   | 4.80              | 0.69 <sup>c</sup> | 45.0  | 1.27              | 0.61 <sup>c</sup> | 10.0  | 1.51              | 0.56 <sup>c</sup> |
|                | 4                  | 2,700  | 0.16              | 0.08              | 1,600 | 0.02              | 0.18              | 900   | 0.05              | –                 |
|                | 4                  | 5,400  | 0.09              | 0.41              | 2,100 | 0.04              | 0.23              | 3,000 | 0.03              | –                 |
|                | 4                  | 7,800  | 0.06              | 0.09              | 2,200 | 0.26              | 0.17              | 4,900 | 0.49              | –                 |
|                | 4                  | 8,000  | 0.18              | 0.29              | 2,600 | 0.05              | 0.26              | 5,400 | 0.02              | –                 |
|                | 4                  | 19,000 | 0.23              | 0.08              | 2,600 | 0.06              | 0.19              | 5,400 | 0.11              | –                 |
| <i>Typ ori</i> | 3                  | 29.7   | 0.45              | 1.52 <sup>c</sup> | 5.1   | 0.80              | 0.58 <sup>c</sup> | 14.9  | 0.01              | 0.35 <sup>c</sup> |
| <i>Phr aus</i> | 10                 | 70     | 1.55 <sup>c</sup> | 0.15 <sup>c</sup> | 20.3  | 1.56 <sup>c</sup> | 1.08 <sup>c</sup> | 16.3  | 0.15 <sup>c</sup> | 0.08 <sup>c</sup> |
|                | 9                  | 1,201  | 0.06 <sup>b</sup> | 4.84 <sup>c</sup> | 52.7  | 0.92 <sup>b</sup> | 0.91 <sup>c</sup> | 12.8  | 1.49 <sup>b</sup> | 0.70 <sup>c</sup> |
|                | 13                 | 294    | 0.44              | 0.19 <sup>c</sup> | 115   | 0.14              | 0.40 <sup>c</sup> | 64.2  | 0.15              | 0.12 <sup>c</sup> |
| <i>Hyd ame</i> | 5                  | 572    | 0.47              | 0.19              | 26    | 0.81              | 0.76              | 1,451 | 0.07              | 0.08              |
|                | 5                  | 720    | 0.09              | 0.58              | 300   | 0.11              | 0.41              | –     | –                 | –                 |
| <i>Sag mon</i> | 2                  | 241    | 0.57 <sup>b</sup> | 0.53 <sup>b</sup> | 87    | 0.46 <sup>b</sup> | 0.31 <sup>b</sup> | –     | –                 | –                 |
|                | 2                  | 1,138  | 0.45 <sup>b</sup> | 0.24 <sup>b</sup> | 365   | 0.25 <sup>b</sup> | 0.46 <sup>b</sup> | –     | –                 | –                 |
| <i>Equ arv</i> | 5                  | 2,200  | 0.11              | 0.65              | 990   | 0.11              | 0.21              | 4,100 | 0.07              | 0.13              |
| <i>Equ flu</i> | 4                  | 40     | 16.8              | 0.04              | 15    | 16.7              | 0.16              | 25    | 4.00              | 0.01              |
|                | 4                  | 19,000 | 0.25              | 0.25              | 2,600 | 0.22              | 0.12              | 5,400 | 0.04              | 0.12              |
| ISQG           |                    | 123    |                   |                   | 35.7  |                   |                   | 35    |                   |                   |
| LEL            |                    | 129    |                   |                   | 13    |                   |                   | 19    |                   |                   |
| SEL            |                    | 1,300  |                   |                   | 85    |                   |                   | 167   |                   |                   |

ISQG Canadian interim sediment quality guideline ( $\mu\text{g/g}$ ) from CCME (2002), LEL lowest effect level ( $\mu\text{g/g}$ ), SEL severe effect level ( $\mu\text{g/g}$ ) (de Deckere et al. 2011)

<sup>a</sup>Study number from Table 3.1

<sup>b</sup>BCF and TF values from corresponding studies, no calculated

<sup>c</sup>TF obtained from ratio metal concentration leaf/root

<sup>d</sup>TF obtained from ratio metal concentration low part of leaf/root

*esculentum*, *C. alternifolius*, *S. sylvaticus*, *E. equisetina*, *T. orientalis*, *E. arvense*, *H. americana*, and *P. australis* have always BCF values of Pb below unity over a wide range of concentrations in the sediment (from 10 to 4,100  $\mu\text{g Pb/g}$ ). Although *C. eragrostis*, *E. fluviatile*, *S. validus*, *T. domingensis*, and *T. latifolia* show similar behavior for Pb to that of Zn and Cu, its BCF values are well below of the others.

The BCF values for Cr and Cd reported were below 0.7 in a broad range of sediment concentrations (from 26 to 881  $\mu\text{g Cr/g}$ , and from 0.22 to 84  $\mu\text{g Cd/g}$ ), with some exceptions; *T. domingensis* and *T. latifolia* have chromium BCF values near to 5 at sediment levels below or near LEL (Maine et al. 2006; Klink et al. 2013), and *T. domingensis*, *T. orientalis*, *T. latifolia*, *E. fluviatile*, *E. equisetina*, and *S. sylvaticus* show high values for Cd (up to 21) at levels in sediment lower than LEL. *Phragmites australis* and *S. validus* have cadmium BCF values of 2.4 and 3.8 respectively at levels in sediment between LEL and SEL.

Plants have developed a defense system to deal with metals and can resist environmental toxic concentrations, implementing avoidance or tolerance strategies (Levitt 1980). Avoidance includes a set of mechanisms that prevent the access of metals to sites of toxic action, thereby limiting its adverse effects on plant metabolism (i.e., immobilization in the rhizosphere by organic chelators, cell wall retention, endocytosis of metal transporters to prevent uptake). Low rates of metal accumulation estimated from the BCF ratio could be explained by the action of plant avoidance strategies in an environment that also behaves as a strong metal immobilizer. On the other hand, when plants are unable to completely prevent metal uptake, mechanisms to limit their toxic action are implemented. The efficiency of this response will determine the tolerance of the species or ecotype studied to toxic metal concentrations. Tolerance strategies can be divided in three major groups: those oriented to neutralize nonessential metals (i.e., molecular chaperons that prevent substitution of essential metals by nonessential ones in metalloenzymes); those directed to neutralize the adverse effects produced by some metals (i.e., enzymatic and non-enzymatic response to reactive oxygen species generated by metals with redox activity) and those directed to retain metals in extra-cytoplasmic compartments such as the vacuole or the cell wall (Clemens et al. 2002; Carroll et al. 2004; Hall 2002; Shanker et al. 2005; Krämer et al. 2007). In emergent aquatic plants the uptake of metals occurs primarily through the root, so it is expected that tolerance strategies involve an accumulation of contaminants in belowground biomass thus preventing transport to photosynthetic structures.

It is essential to understand the distribution of the metal adsorbed onto the surface in relation to the metal accumulated inside the cell, in order to understand the predominant removal mechanisms and to make decisions of the viability of the recovery of the adsorbed metals (Olguín and Sánchez-Galván 2012).

The primary cell wall is composed of an amorphous matrix of polysaccharides (hemicellulose and pectin), plus a small amount of structural proteins that bind cellulose fibers with varying degree of crystallization by covalent and non-covalent bonds (Taiz and Zeiger 2002; Caffall and Mohnen 2009).

Polysaccharides play a significant role in the immobilization of metals, particularly those containing high amount of carboxyl groups are able to bind divalent and trivalent metal ions. These groups have a high metal binding capacity by forming inner sphere complexes through the inclusion of divalent and trivalent metals in place of calcium ions, which mostly pectins stabilize (Krzyszowska 2011).

Several authors (Khotimchenko et al. 2007; Colzi et al. 2011; Krzyszowska 2011) suggest that both acetylation and methylation of the carboxyl groups of pectins diminish its affinity for heavy metals, favoring and increasing their toxicity, while others suggest that the methylation level would not be constant but may vary response to the metal abundance in the environment, this being a characteristic of the tolerant species or ecotypes (Krzyszowska 2011).

Emergent macrophytes generally show metal accumulation in belowground biomass as tolerance strategy. Metal mobility within the plant measured by the translocation factor (TF, ratio of metal concentration leaf/root) differs among metals and plant species, generally following a decreasing order  $\text{Ni} > \text{Cr} > \text{Cd} = \text{Zn} = \text{Cu} > \text{Pb}$  (from the median of the data reported in Table 3.2). Cardwell et al. (2002) indicated that *T. domingensis* translocates essential metals such as zinc and copper much more easily than nonessential such as lead and cadmium. Despite this, generally the concentrations of metals at roots are greater than in the aerial parts (Cheng et al. 2002).

All species reported in Table 3.2 showed TF values near or less than 1 for all metals, and generally lower than the respective values of BCF, except for Zn in *S. sylvaticus* and *P. australis* whose TF value are 2.8 and 4.8 respectively (Hozhina et al. 2001; Kamel 2013) at elevated sediment levels, although in both cases BCF values were very low (less than 0.05). Metal translocation into shoots appears to be very restricted in all wetland plants so that harvesting plants will not be an effective source of metal removal in a wetland system. However, in the view of toxicology, this could be a desirable property, as metals would not pass into the food chain via herbivores, and thus avoid potential risk to the environment (Deng et al. 2004).

### 3.5.2 Submersed Macrophytes

Rooted submersed plants have a great importance owing to the fact that their roots, rhizomes, and stolon can facilitate the colonization of bacteria, algae and other microorganisms that help in phytoremediation process. Submersed aquatic macrophytes have got ability to extract metals from the sediments

via their root systems and directly from the surrounding water. Plant uptake of trace elements by leaves of submersed macrophytes becomes more important when the trace element concentrations in the surrounding environment are high (Guilizzoni 1991).

Most studies were conducted in laboratory or greenhouse settings using metal-enriched nutrient solutions (Bunluesin et al. 2004; John et al. 2008; Maine et al. 2004; Mishra and Tripathi 2008). Results from these studies were usually very impressive with high metal uptake or accumulation (Mishra and Tripathi 2008). However, it may be entirely different when these aquatic plants are applied to field condition such as lakes, reservoirs, and estuaries where both metals and nutrients are of much lower concentrations and other environmental factors are far less favorable. On the other hand, the performance of aquatic plants in natural water bodies is more meaningful as degradation of natural aquatic ecosystem is a worldwide concern and yet conventional physical or chemical treatments are not cost-effective due to the nature of non-point source pollution. Investigations have been conducted in natural water bodies such as lakes (Kamel 2013; Badr and Fawzy 2008; Vardanyan and Ingole 2006), rivers (Borisova et al. 2014), reservoirs (Mishra et al. 2008; Molisani et al. 2006), estuaries (Almeida et al. 2006), and stormwater in detention plants (Lu 2009).

Borisova et al. (2014) examined the uptake of five metals (Cu, Fe, Ni, Zn, and Mn) in *Ceratophyllum demersum* L. (hornwort) and *Potamogeton alpinus* Balb. (pondweed) from Iset' river, Ural region, Russia. Differential accumulation pattern was noted for metals. Higher amounts of metals were accumulated in *C. demersum* compared to *P. alpinus*. Also it was shown that in leaves of *C. demersum* there were high amount of total phosphorus, nitrogen, organics acids, and ash.

Kamel (2013) assessed heavy metal concentration in water and sediment of a polluted lake in Egypt along with two native submersed macrophytes *Ceratophyllum demersum* and *Myriophyllum spicatum*. The mean values of the six investigated metals in the selected aquatic macrophytes were  $Zn > Pb > Cu > Ni > Co > Cd$ . Regarding the mean values of the metal concentrations among the submersed plants it showed the following pattern *Ceratophyllum demersum* > *Myriophyllum spicatum*. The BCF (bioconcentration factor) value for each individual heavy metal was *Ceratophyllum demersum* > *Myriophyllum spicatum*. The highest BCF values were estimated for Zn in *C. demersum* (903.3). Translocation factors were low for both species.

Another submersed plant, *Vallisneria spiralis*, was promising for chromium accumulation in different parts of plant from chromium containing solutions and tannery effluents. *Vallisneria spiralis* also tolerates high chromium concentration, thus the plant resulted highly suitable for phytoremediation of chromium-polluted wastewater (Vajpayee et al. 2001).

*Potamogeton pectinatus* is a submersed aquatic plant that can survive in metal-polluted lakes and can accumulate significant amounts of cadmium (266.3 µg/g). However, the adverse effect of cadmium was reported on loss in photosynthetic pigment. *P. pectinatus* showed cadmium tolerance through increased levels of cysteine, non-protein thiol, and carotenoids and an increase of protein content (Rai et al. 2003).

Lead concentrations in plant tissue were found to be 1,621 and 1,327 times those in the external solution for *C. demersum* and *C. caroliniana*, respectively (Fonkou et al. 2005).

*Ceratophyllum demersum* and *Hydrilla verticillata* showed high cadmium accumulation (7,381 and 7,942 mg Cd/Kg) and a high BCF (>2,500) at 1 mg/L. There was significant growth decrease in both species with increasing metal concentration. But cadmium was less toxic to *H. verticillata* and its cadmium accumulation capacity was higher (Bunluesin et al. 2004).

Mazej and Germ (2009) determined trace elements in sediment of Velenjsko Jezero Lake and their concentrations were found to be above the European background concentration. Given their low concentrations in the water of lake they concluded that the trace elements found in above-ground parts is predominantly the result of their translocation from roots to stems and leaves. Entirely submersed species (*Najas marina* and *Potamogeton lucens*) have been shown to accumulate relatively large amounts of trace elements than the studied floating species. Essential metals as Zn and Cu appear to be more readily translocated from roots to shoots than other elements in submersed and floating plants. Cr accumulation in roots and translocation from roots to shoots were very low. Kähkönen et al. (1997) affirmed that there is usually no mobility of Cr from roots to shoots and leaves due to barriers or lack of transport mechanisms. The concentration of Pb was the lowest of all the trace elements in roots probably due to its strong binding to organic matter and other components and to the roots. Also, Pb mobility was low. Translocation factors from roots to stem or leaves were very low in *N. marina* (0.05), and *P. lucens* (0.1).

With regard to the uptake ability of submersed plants, *C. demersum* seems to be a promising species for remediation of sediments contaminated with metals mainly essential metals. Denny and Wilkins (1987) observed that tendency to use shoots as sites of metal uptake instead of roots increases with progression towards submergence and simplicity of shoot structure. However, translocation factors were low and metal uptake by leaves from the surrounding water is negligible in submersed plants because element concentrations in water are generally low. Most of the metals in the aquatic phase pass to bottom sediments in natural or artificial water bodies and become particulate, complexed, or chelated complex practically not bioavailable.



### 3.5.3 Floating Macrophytes

Different plant species have different allocation patterns of metals. With the purpose of evaluating strategies for the remediation, we selected four species of floating macrophytes studied in natural or artificial contaminated water bodies. Metal concentrations in water, roots and leaves of selected floating macrophytes, metal bioconcentration factor (BCF), and translocation factor (TF) are presented in Tables 3.1 and 3.3.

*Eichhornia crassipes* (water hyacinth) has been listed as most troublesome weed in aquatic system. It is a floating aquatic plant, found abundantly throughout the year in very large amounts. It originated in tropical South America, but has become naturalized in many warm areas of the world: Central America, North America (California and southern states),

Africa, Asia, and Australia. It is one of the most commonly used plants in constructed wetlands because of its fast growth rate and large uptake of nutrients and contaminants. While there are numerous references relating to the capabilities of heavy metal removal by *E. crassipes* in laboratory experiments (e.g.: Mishra and Tripathi 2008; Maine et al. 2001), this is not true for on-site and full-scale applications. There are also limited data on the capacity of *E. crassipes* to remediate a broad spectrum of metals particularly the highly toxic ones. *Eichhornia crassipes* absorbs and translocates essential metals Cu, Ni, and Zn (Table 3.3) and nonessential metals Cr, Pb, and Cd (Table 3.3). However, water hyacinth generally locates the elements into the roots which imply that the plant has a high capacity to absorb the metals and reveals its ability to serve as rhizofiltration plant in phytoremediation technology. The concentrations of essential metals (Zn, Cu, and Ni) in

**Table 3.3** Metal water concentration (mg/L); metal root and leaf concentration (mg/kg); Bioconcentration factor (BCF) and translocation factor (TF) of different macrophytes

| Species name       | <i>E. crass</i> |       |       |       |        | <i>L. gibb</i>         | <i>M. min</i> | <i>S. mol</i> | Normal range in plants <sup>a</sup> |           |
|--------------------|-----------------|-------|-------|-------|--------|------------------------|---------------|---------------|-------------------------------------|-----------|
| Study <sup>b</sup> | 8               | 14    | 9     | 15    | 16     | 16                     | 14            | 19            |                                     |           |
| Zn                 | Water           | ND    | –     | 340   | 3.28   | 1,600                  | 340           | –             | –                                   |           |
|                    | Root            | 24    | –     | 604.5 | 131.88 | 7.09 × 10 <sup>5</sup> | 252.4         | –             | 128.31                              | 1–400     |
|                    | Leaf            | 15    | –     | 492   | 223    | –                      | 93            | –             | 223                                 |           |
|                    | BCF             | –     | –     | 1.78  | 40     | 443                    | 0.74          | –             | –                                   |           |
|                    | TF              | 0.62  | –     | 0.81  | 1.69   | –                      | 0.36          | –             | 1.73                                |           |
| Ni                 | Water           | 0.017 | 0.080 | –     | 0.062  | 10.13                  | –             | 0.080         | –                                   |           |
|                    | Root            | 42    | 16.5  | 48.7  | 0.72   | 2.8 × 10 <sup>4</sup>  | 14.31         | 5.5           | –                                   | 0.89–2.04 |
|                    | Leaf            | 21    | 8.5   | 40.4  | 1.41   | –                      | 2.4           | 1             | –                                   |           |
|                    | BCF             | 2,471 | 206   | –     | 11.6   | 2,764                  | –             | 69            | –                                   |           |
|                    | TF              | 0.5   | 0.51  | 0.83  | 1.96   | –                      | 0.16          | 0.18          | –                                   |           |
| Cu                 | Water           | –     | 0.260 | –     | 0.044  | 19.670                 | –             | 0.260         | –                                   |           |
|                    | Root            | –     | 4.25  | 22.5  | 31.40  | 4.4 × 10 <sup>4</sup>  | 16.8          | 2.3           | 680.91                              | 7.53–8.44 |
|                    | Leaf            | –     | 2.8   | 14.5  | 56.58  | –                      | 8.2           | 0.8           | 91.40                               |           |
|                    | BCF             | –     | 16.3  | –     | 714    | 2,237                  | –             | 8.8           | –                                   |           |
|                    | TF              | –     | 0.66  | 0.64  | 1.80   | –                      | 0.49          | 3.83          | 0.13                                |           |
| Cr                 | Water           | 0.022 | 4.670 | –     | 1.330  | –                      | –             | 4.670         | –                                   |           |
|                    | Roots           | 78    | 16.85 | –     | 5.05   | –                      | –             | 0.2           | –                                   |           |
|                    | Leaf            | 9     | 28    | –     | 10.12  | –                      | –             | 10            | –                                   |           |
|                    | BCF             | 3,546 | 3.6   | –     | 3.8    | –                      | –             | 0.04          | –                                   |           |
|                    | TF              | 0.11  | 1.67  | –     | 2      | –                      | 0.49          | 3.83          | –                                   |           |
| Pb                 | Water           | –     | 0.04  | 18.27 | 0.018  | 6.11                   | 18.27         | 0.04          | –                                   |           |
|                    | Roots           | –     | 2.8   | 16.8  | 0.39   | 9,800                  | 52.1          | 2.4           | 162.72                              | 0.2–2.0   |
|                    | Leaf            | –     | 1.4   | 11.3  | 0.65   | –                      | 13.5          | 1             | 367                                 |           |
|                    | BCF             | –     | 70.0  | 0.9   | 21.4   | 1,604                  | 2.9           | 60.0          | –                                   |           |
|                    | TF              | –     | 0.53  | 0.67  | 1.67   | –                      | 0.26          | 0.42          | 2.25                                |           |
| Cd                 | Water           | –     | –     | 20.9  | 0.01   | 0.74                   | 20.9          | –             | –                                   |           |
|                    | Root            | –     | –     | 0.8   | 0.19   | 790                    | 0.62          | –             | –                                   | 0.1–2.4   |
|                    | Leaf            | –     | –     | 0.52  | 0.50   | –                      | 0.16          | –             | –                                   |           |
|                    | BCF             | –     | –     | 0.04  | 17.3   | 1,067                  | 0.030         | –             | –                                   |           |
|                    | TF              | –     | –     | 0.65  | 2.63   | –                      | 0.26          | –             | –                                   |           |

<sup>a</sup>Kabata-Pendias (2011)

<sup>b</sup>Study number from Table 3.1

*E. crassipes* (Kumar et al. 2008) were higher than standard normal ranges for plants, defined by Kabata-Pendias (2011) associated with high levels of metals detected in water reservoir.

The relatively low leaf metal contents indicated the presence of a prevention mechanism to inhibit uptake until drastic conditions. However, Agunbiade et al. (2009) (Table 3.3) detected translocation factor above 1 for essential and non-essential metals in coastal water at optimum removal conditions (pH: 5.5–6.5; salinity below 2 ‰ and dissolved oxygen above 6 mg/L). Water hyacinth plants had high bioconcentration factor with low water concentrations of the six elements. Also, water hyacinth has a high tolerance to toxic contaminants. This shows that water hyacinth can be a promising candidate to remove heavy metals. *E. crassipes* could be eaten by humans and animals. Then, harvesting of biomass must be considered in restoration or mitigation plans for specific contaminated sites.

Duckweed commonly refers to a group of floating, flowering plants of the family Lemnaceae. It is fast-growing and adapts easily to various aquatic conditions. The different species (*Lemna*, *Spirodela*, *Wolffia*, and *Wolffiella*) are worldwide distributed in wetlands, ponds, and some effluent lagoons. The plants can grow at temperature ranging from 5 to 35 °C with optimum growth between 20 and 31 °C and across a wide range of pH (3.5–10.5) (Cayuela et al. 2007). Wetlands and ponds are the most common sites to find duckweed. The capacity of aquatic plant such as duckweed (*Lemna* sp.) to remove toxic metals from water are well documented through laboratory experiences (e.g., Sharma and Gaur 1995; Tripathi and Chandra 1991, Lahive et al. 2011). *Spirodela intermedia* W. Koch (duckweed) and *Lemna minor* L. (duckweed) present a high growth rate and have been used for the removal of Cd, Cr, and Pb from water column (Maine et al. 2001; Cardwell et al. 2002).

Kamel (2013) examined ability of *Lemna gibba* to remove cadmium, copper, nickel, lead, and zinc in a contaminated lake in Egypt. The species was tolerant to high metal concentrations, although copper, nickel, and lead concentrations in roots were higher than normal range in plants according Kabata-Pendias (2011). In general, concentration factors were low. Like the rest of the macrophytes chosen, its translocation factors were also low.

Kumar et al. (2012) assessed accumulation potential in native macrophytes growing naturally in a drain receiving tannery effluent. *Marsilea minuta* accumulated lead from the water mainly in roots. Lead concentration in roots was higher than normal concentration for plants (Kabata-Pendias 2011). Nickel showed the same behavior. BCF and TF were elevated for copper, associated with low metal concentrations in the tissue, below the normal range for plants. Cr accumulation from the environment was low. It is known that in many plant species the mobility of Cr is low due to the fact that

there are barriers or lack of transport mechanism suitable for Cr transport from roots to shoots (Kähkönen et al. 1997). In *Spirodela polyrhiza*, the Cr presence decreases growth rate inhibiting photosynthesis (Appenroth et al. 2001). However, chromium translocation factor in *M. minuta* was higher than 1.

*Salvinia molesta* is an aquatic fern, native to south-eastern Brazil and is widely distributed in tropical and subtropical areas. It has a fast growing rate, and is tolerant to pollution, favorable properties in species to be used in phytoremediation. *Salvinia minima* (Olguín et al. 2002 and Casares 2013) can accumulate chromium, lead, cadmium, copper, and zinc in bioassays performed in laboratory conditions. Ashraf et al. (2011) investigated polluted soils that surround mining slag pile and the potential remediation ability of *S. molesta* among others native macrophytes growing in the area. Concentrations of copper and lead in pseudoroots and leaves were higher than defined toxic levels for plants (Deng et al. 2004). Also, the plants translocated lead and zinc. *S. molesta* can tolerate the adverse environmental conditions, colonize the waterbodies in tailings areas and accumulate toxic metals.

According to Baker and Brooks (1989) and Srivastava et al. (2006), a plant can be considered as hyperaccumulator when the metal concentration in the shoots (stems or leaves) is 10,000 µg/g for Zn; above 1,000 µg/g dry mass for As, Pb, Cu, Ni, and Co and 100 µg/g for Cd. Then, the selected plants cannot be considered hyperaccumulators in natural or artificial environments. Also, translocation (Baker and Brooks 1989) and bioconcentration factors (Weiss et al. 2006) should be higher than 1. In most of study cases, these factors were lower than 1. BCF were recorded only greater than 1 in the case of extremely high or low water metal concentrations (Kumar et al. 2008 and Maine et al. 2006) (Table 3.3). The differences in TF indicate the preferential accumulation–uptake pattern of metals. TF was typically lower than 1 in all selected study cases (Table 3.3). However, in Agunbiade et al. (2009) and Ashraf et al. (2011), *E. crassipes* and *S. molesta* effectively transported metals from root to shoot (TF > 1) due to efficient metal transporter system and probably sequestration of metals in vacuoles and apoplast (Lasat et al. 1998). Also, Agunbiade et al. (2009) metal concentrations in plants respect to water concentrations were low (BCF < 1), revealing an excluder strategy to transport of metals from abiotic environment to macrophytes. Both roots and aboveground biomass have a kind of natural controlling mechanism regarding the quantity of metals taken from the environment.

The general trend shows that the root tissues accumulate significantly greater concentrations of metals than shoots, indicating plant availability of metals as well as its limited mobility once inside the plant. The exclusion of metals from aboveground tissues has been suggested as a metal tolerant strategy in many plants (Deng et al. 2004). This strategy allows plant photosynthetic machine preservation.

Metal tolerant strategy is widely evolved and exists in wetland plant species when they grow in metal-contaminated areas. As Deng et al. (2004) said for wetland emergent plants that can colonize heavily metal-polluted areas, the floating plants can tolerate metals mainly by their metal exclusion ability. However, the higher-than-toxic level of metal concentrations in leaves indicates that internal detoxification metal tolerance mechanisms might also exist.

Therefore floating macrophytes might have developed internal exclusion strategies whereby the toxic metal is prevented from damaging the cell. Also, studies on metal compartmentalization in floating macrophyte bioassays (Casares 2013; Mouvet and Claveri 1999; Vazquez et al. 1999) showed that the removal by adsorption extracellular compartment was higher than intracellular accumulation. Plant species with a high capacity for removing heavy metals in solution have cell walls or membranes with abundant carboxyl, sulfhydryl, amino, and phosphate groups and a large specific surface enabling greater metal biosorption (Bates et al. 1982).

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### 3.6 Decomposition of Plant Biomass and Release of Metals into the Environment

Wetland plants behave as transient reservoirs of nutrients, metals, and metalloids, so litter decomposition represents a pathway for the release of contaminants from plant biomass into water bodies (Eid et al. 2012; Schaller et al. 2011). During the primary stage of the decomposition process, microorganisms and exudates form a heterotrophic biofilm on plant litter (Kominkova et al. 2000) where bacteria and fungi can accumulate high amounts of contaminants. Molecular oxygen is usually considered as a primary electron acceptor in organic matter degradation. However, since dissolution of gases in water is a relatively slow process from a kinetic perspective and also considering that in metal-contaminated sediments, biofilms and organic matter content may limit oxygen diffusion. Oxygen depletion leads to changes in the decomposers communities, from aerobic to anaerobic and then less efficient microorganisms.

Organic matter accumulation in sediments will be favored by high sedimentation rates and high proportion of organic compounds in the settleable material. In the early stages of decomposition process, the labile organic compounds with low C:N:P ratios are preferentially degraded. At the advanced stages of decomposition, the residual compounds (waxes, polyphenols) with high C:N:P ratios are degraded at lower rates. Several authors argue that the sink/source behavior of plant litter depends on the metal content and the plant accumulation organ. Thus, plants which translocate metals to photosynthetic structures, will produce litter with high levels of pollutants and in this case the more appropriate management

strategy would be harvesting, in order to phytoextract metals. However, as stated previously, metal hyperaccumulation and high rates of translocation are not widespread among aquatic macrophytes in contaminated environments. Therefore, if accumulation exists probably involve to belowground biomass. In situ decomposition in anaerobic habitats will contribute to form litter with high tendency to immobilize metals. Thus, at the same time that metals are released during the decomposition by mineralization, generating new binding sites could immobilize them again.

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### 3.7 Concluding Remarks

With regard to the metal uptake capacity of aquatic plants at full scale and on-site treatments, concentration factors found to be low and the exclusion strategy seems to be more widespread among aquatic plants. This strategy was shared with other plants tolerant to stress by toxic excess. Both bioconcentration factors such as translocation were lower than those calculated in bioassays conducted under laboratory conditions. There have been no hyperaccumulators among the studied plants, but there are accumulator species under certain conditions of pH, dissolved oxygen, and metal concentrations. Furthermore, translocation factors were in most cases less than 1. However, regarding the capacity of accumulation of metals in the standing crop, the floating plants are most effective, followed by submersed species and then emergent species. The metal concentrations in leaves of various floating species were higher than tolerable levels for other macrophytes. Therefore floating macrophytes might have developed internal exclusion strategies whereby the toxic metal is prevented from damaging the cell. Also, removal by adsorption extracellular compartment was higher than intracellular accumulation in floating plants.

The application of phytoremediation at full scale and on-site for metal excess in aquatic ecosystems using several macrophytes is limited mainly to the immobilization of toxics in the sediments and rhizosphere-root system. The low translocation to the aboveground tissues main advantage is to avoid the dispersion of pollutants into the food chain. Moreover, in situ decomposition of the macrophytes used in phytoremediation is a valid strategy since the contribution of detritus favors the input of organic matter in sediment and in turn the complexation of metal ions in the bottom of water bodies contaminated. Since floating plants are those that can occasionally translocate, harvesting is advisable in these cases. On the other hand, the emergent plants are more effective for phytostabilization. In situ decomposition in anaerobic habitats will contribute to form litter with high tendency to immobilize metals. The metals released during the decomposition could be further retained by the new binding sites generated in bottom sediment.

The use of native species in remediation projects, not always considered in scientific or technical papers is essential to preserve biological diversity and, requires more detailed studies for each natural ecosystem.

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