Chapter 11
Phytofiltration of Metal(loid)-Contaminated Water: The Potential of Native Aquatic Plants

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11.1 Introduction

All biosphere compartments are vulnerable to pollution, including our freshwater sources—both lentic and lotic. These ecosystems are subjected to constant internal and external changes, both of natural or anthropogenic origin. Anthropogenic influences are often the cause of irreparable damage to some of these ecosystems like mountain streams which are very sensitive. For example, mining activities are well known for their potential deleterious effects on the environment, namely, the

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contamination of soils, sediments, and waters due to uncontrolled runoff, leaching, and/or aeolian deposition. In fact, leading anthropogenic sources of heavy metals and metalloids pollution are mining and milling operations worldwide. Particularly in the case of abandoned mines where there is no control and monitoring. Lead (Pb), copper (Cu), zinc (Zn), uranium (U), and arsenic (As) are some of the metal(loid)s most frequently reported to have the highest impact on organisms.

Water management in mining areas requires a strategic use of technology, since they imply long-term treatment approaches. The high metal(loid)s content, and the pH/Eh variation of the permanent low flow rate seepage waters, creates major difficulties to the design of efficient and affordable remediation projects [1]. However, water remediation techniques, as well as public awareness campaigns about the risks of exposure to toxic heavy metals and metalloids, should be adopted in contaminated areas, especially where the population still uses private wells as a drinking water source.

Contaminated water can be treated by several methods. Currently, preference is being given to in situ and passive methods that are less environmentally disruptive and more economical. In this context, biotechnology offers phytoremediation techniques as a suitable alternative. In this chapter, results of the last two decades of investigations are presented in the light of phytotechnological potential evaluation, incorporating approaches like phytoremediation, phytoextraction, phytofiltration, biosorption, and bioindication, of the Portuguese native aquatic flora found in waters contaminated with metal(loid)s.

11.2 Phytoremediation Technology

Phytoremediation is the use of plants (trees, shrubs, grasses, and aquatic plants) and their associated microorganisms in order to remove, degrade, or isolate toxic substances from the environment (e.g., [2–12]). The word phytoremediation derives from the Greek *phyton*, meaning "plant," and the Latin *remedium*, which means "to remedy" or "to correct." Substances that may be subjected to phytoremediation include metals (Pb, Zn, Cd, Cu, Ni, Hg), metalloids (As, Sb), inorganic compounds (NO_3^-, NH_4^+, PO_4^{3-}), radioactive chemical elements (U, Cs, Sr), petroleum hydrocarbons (BTEX), pesticides and herbicides (atrazine, bentazon, chlorinated, and nitroaromatic compounds), explosives (TNT, DNT), chlorinated solvents (TCE, PCE) and industrial organic wastes (PCPs, PAHs), and others (e.g., [3, 9, 13–19]). Phytoremediation techniques include different modalities, depending on the chemical nature and properties of the contaminant (if it is inert, volatile, or subject to degradation in the plant or in the soil) and the plant characteristics. Thus, phytoremediation essentially comprises six different strategies, though more than one may be used by the plant simultaneously [8].

11.2.1 Phytodegradation (Phytotransformation)

Organic contaminants are degraded (metabolized) or mineralized inside plant cells by specific enzymes that include nitroreductases (degradation of nitroaromatic compounds), dehalogenases (degradation of chlorinated solvents and pesticides), and laccases (degradation of anilines). *Populus* species and *Myriophyllum spicatum* L. are examples of plants that have these enzymatic systems [20, 21].

11.2.2 Phytostabilization (Phytoimmobilization)

Contaminants, organic or inorganic, are incorporated into the lignin of the cell wall of roots cells or into humus. Metals are precipitated as insoluble forms by direct action of root exudates and subsequently trapped in the soil matrix. The main objective is to avoid mobilization of contaminants and limit their diffusion in the soil [5, 22–24]. Species of genera *Haumaniastrum*, *Eragrostis*, *Ascolepis*, *Gladiolus*, and *Alyssum* are examples of plants cultivated for this purpose.

11.2.3 Phytovolatilization

This technique relies on the ability of some plants to absorb and volatilize certain metal(loid)s. Some element ions of the groups IIB, VA, and VIA of the periodic table (specifically Hg, Se, and As) are absorbed by the roots, converted into nontoxic forms, and then released into the atmosphere. As example, the species *Astragalus bisulcatus* (Hook.) A. Gray and *Stanleya pinnata* (Pursh) Britton for Se or transgenic plants (with bacterial genes) of *Arabidopsis thaliana* (L.) Heynh., *Nicotiana tabacum* L., *Liriodendron tulipifera* L., or *Brassica napus* L. for Hg can be mentioned [24–28]. This technique can also be used for organic compounds.

11.2.4 Phytoextraction (Phytoaccumulation, Phytoabsorption, or Phytosequestration)

This involves the absorption of contaminants by roots followed by translocation and accumulation in the aerial parts. It is mainly applied to metals (Cd, Ni, Cu, Zn, Pb) but can also be used for other elements (Se, As) and organic compounds. This technique preferentially uses hyperaccumulator plants that have the ability to store high concentrations of specific metals in their aerial parts (0.01–1 % dry weight, depending on the metal). *Elsholtzia splendens* Nakai ex F. Maek., *Alyssum bertolonii* Desv., *Noccaea caerulescens* (J. Presl & C. Presl) F.K. Mey. (*Thlaspi caerulescens* J. Presl & C. Presl), and *Pteris vittata* L. are known examples of hyperaccumulator plants for Cu, Ni, Zn/Cd, and As, respectively [29–36].

11.2.5 Phytofiltration and Rhizofiltration

When plants absorb, concentrate, and/or precipitate contaminants, particularly heavy metals or radioactive elements, from an aqueous medium through their root system or other submerged organs (e.g., [4, 19, 24, 37–39]). The plants are kept in a hydroponic system, whereby the effluents pass and are "filtered" by the roots (rhizofiltration), or other organs that absorb and concentrate contaminants. Plants with high root biomass, or high absorption surface, with more accumulation capacity (aquatic hyperaccumulators) and tolerance to contaminants achieve the best results. Promising examples include *Helianthus annuus* L.; *Brassica juncea* (L.) Czern.; *Phragmites australis* (Cav.) Trin. ex Steud.; *Eichhornia crassipes* (Mart.) Solms; *Spirodela punctata* (G. Mey.) C.H. Thomps.; *Fontinalis antipyretica* Hedw.; and several species of *Salix*, *Populus*, *Lemna*, and *Callitriche* [5, 40–44].

11.2.6 Rhizodegradation and Phytostimulation

Growing roots promote the proliferation of degrading rhizosphere microorganisms which utilize exudates and metabolites of plants as a source of carbon and energy. In addition, plants may exude biodegrading enzymes themselves. The application of rhizodegradation/phytostimulation is limited to organic contaminants [5, 37]. The microbial community in the rhizosphere is heterogeneous due to variable spatial distribution of nutrients; however, species of the genus *Pseudomonas* are the predominant organisms associated with roots [24, 45, 46].

There are other strategies also, which are considered categories of phytoremediation by some authors, but actually, they are mixed techniques or variations of the earlier mentioned strategies [8].

11.2.7 Hydraulic Barriers

Some large trees, particularly those with deep roots (e.g., *Populus* sp.), remove large quantities of groundwater during transpiration. Contaminants in this water are metabolized by plant enzymes and vaporized together with water or simply sequestered in plant tissues [5, 47].

11.2.8 Vegetation Covers (Vegetative Caps or Phytocovers)

Herbs (usually grasses), eventually shrubs or trees, establish on landfills or tailings, are used to minimize the infiltration of rain water, and contain the spread of pollutants. The roots increase soil aeration thus, promoting biodegradation, evaporation, and transpiration [6, 12, 48–50].

11.2.9 Constructed Wetlands

These are ecosystems consisting of organic soils, microorganisms, algae, and vascular aquatic plants in areas where the water level is at/near the surface, at least part of the year. All the components work together in the treatment of effluents, through the combined actions of filtration, ion exchange, adsorption, and precipitation (e.g., [37, 51–54]). It is the oldest method of wastewater treatment and is not regarded as proper phytoremediation, since it is based on the contributions of the entire system [5, 55]. Depending on how it processes the water circulation, the wetland is classified as horizontal or surface flow and vertical or subsurface flow. In the latter case ensures a greater reactivity of the influent with the substrate. Good cleaning efficiency, low cost of construction along with easy operation and maintenance are the main advantages. It is widely applied in the treatment of domestic, agricultural, and industrial waste water (e.g., [56, 57]) but has proved to be suitable also for treating acid mine drainages (e.g., [58–60]).

11.2.10 Phytodesalination

This is a recently reported [24, 61] emerging technique that utilizes halophytes to remove excess salts from saline soils. The potential of *Suaeda maritima* (L.) Dumort and *Sesuvium portulacastrum* L. in removal and accumulation of NaCl, from highly saline soils, has been demonstrated [62]. Having own peculiarities, this technique is a modality of phytoextraction.

11.3 Phytofiltration of Contaminated Waters

As previously referred, there are two main divisions in the aquatic phytoremediation technology that involve [63, 64] (Fig. 11.1): 1—purely aquatic plants, which remove metals from water by roots, leaves, and stems (***phytofiltration***); 2—submersion of the roots of terrestrial plants in order to remove pollutants from the water (***rhizofiltration***). In addition, we may consider a third division [40]: 3—using young plant seedlings growing in aerated water (aquacultured) to remove toxic metals from water (***blastofiltration***).

In the present study dealing with phytofiltration potential of the Portuguese native aquatic flora, the term phytofiltration is used to describe the remediation of metal(loid)-contaminated water through uptake and bioaccumulation of metal(loid) s into organs of aquatic plants. Freshwater vascular plants (or simply aquatic plants) comprise mainly angiosperms with a few fern species, when combined with macroscopic algae are known collectively as macrophytes [63]. By definition, aquatic plants are those that complete their biological life cycle in aquatic environments and

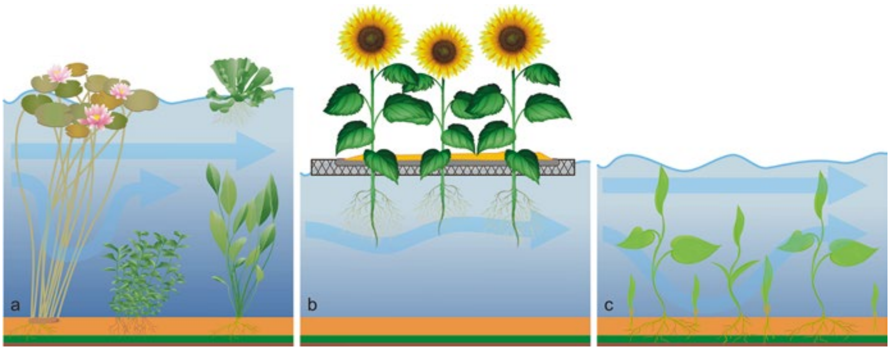

Fig. 11.1 Schematic representation of aquatic phytoremediation strategies: (**a**) phytofiltration, (**b**) rhizofiltration, and (**c**) blastofiltration

include diversified forms such as free-floating, submerged, and emergent life forms [38, 65, 66]. In a more specific way, the aquatic macrophytes can be classified as follows [57, 63, 67–70] (Fig. 11.2).

11.3.1 Rooted Emergent Plants

These macrophytes are rooted in bottom sediments/submerged soils or in aerial soils at which the water table is about 0.5 m below the soil. These are sometimes referred as semiaquatic plants. They are generally rhizomatous or cormous perennials (e.g., *Typha* spp., *Phragmites* spp., *Scirpus* spp.).

11.3.2 Rooted Submerged Plants

These are rooted in bottom sediments and with leaves under water (e.g., *Potamogeton pectinatus* L., *Myriophyllum spicatum* L., *Chara* spp.).

11.3.3 Rooted Floating-Leaved Plants

These are rooted in bottom sediments at water depths from about 0.5 to 3 m but with floating leaves. In heterophyllous species submerged leaves accompany the floating leaves. Floating leaves are on short petioles from long ascending stems (e.g., *Potamogeton natans* L.), or with long and flexible petioles (e.g., *Nymphaea* spp.) and reproductive organs are floating or aerial.

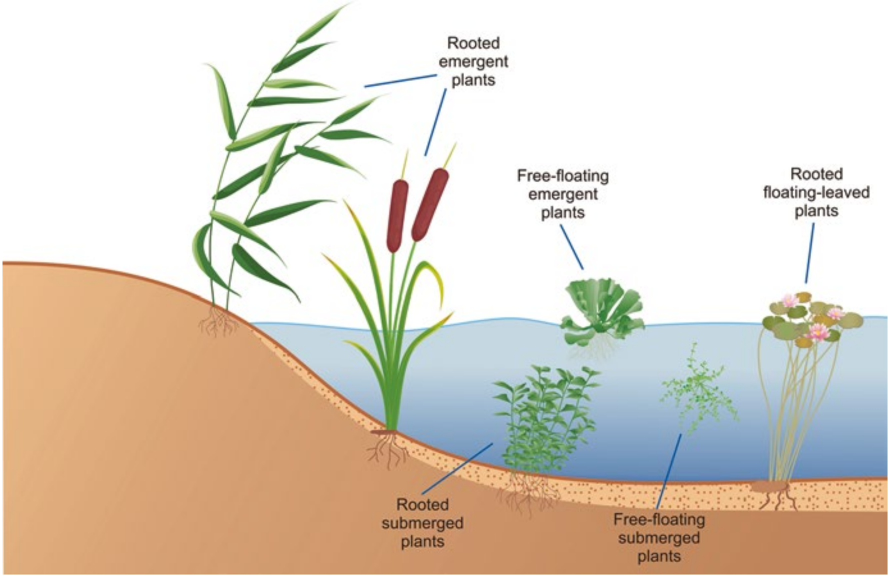

Fig. 11.2 Five major groups of aquatic macrophyte types

11.3.4 Free-Floating Emergent Plants

These are not rooted in sediments but live unattached in water. Forming a highly varied group, they range from long plants with rosettes of aerial and floating leaves and well-developed submerged roots (e.g., *Eichhornia crassipes*, *Pistia stratiotes* L.) to minute surface floating plants with few or no roots (e.g., *Lemna* spp., *Azolla* spp., *Salvinia* spp.).

11.3.5 Free-Floating Submerged Plants

These are submerged, nonrooted aquatic plants (e.g., *Ceratophyllum demersum* L., *Utricularia vulgaris* L., *Utricularia intermedia* Hayne, *Utricularia gibba* L.).

The first extensive review on the ability of aquatic plants to accumulate chemical elements from the aquatic environment was carried out by Hutchinson [71]. The author reported a set of aquatic plant species with the ability to accumulate cadmium (Cd), lead (Pb), and mercury (Hg) in concentrations that are many higher than the ambient environment. Since then, the number of studies involving aquatic macrophyte communities have been on the rise as a consequence of the growing importance of the water management. Phytofiltration of metal(loid)-contaminated waters involves both abiotic (water and sediments) and biotic (organisms living in the contaminated environment), and the specific process of phytofiltration depends not only

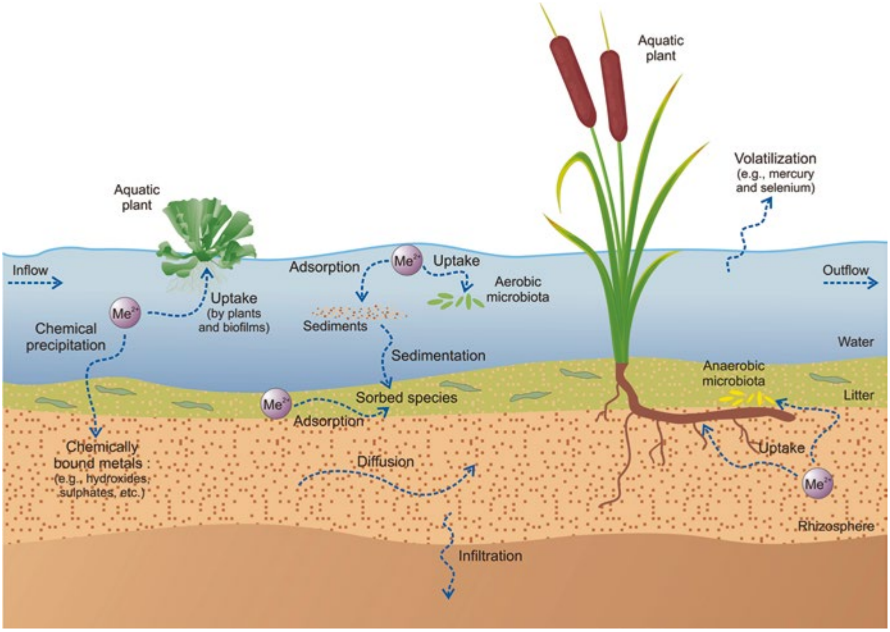

Fig. 11.3 Mechanisms of metal(loid)s removal in aquatic environments

on plant traits but also on certain physicochemical and geochemical processes. At natural sites, metal(loid)s removal also depends on factors that include microbial biofilms on abiotic substrates and the growth of periphyton [72–77]. Thus, the metal(loid)s removal from water in natural aquatic environments involves integrated physical, chemical, and biological processes, such as those reported by Hedin et al. [78], Sobolewski [58], and ITRC [51] in wetlands, namely the following (Fig. 11.3).

11.3.6 Filtration of Suspended Solids

Including adsorbed metal(loid)s.

11.3.7 Sorption onto Organic Matter

Several metals have a high affinity to bind to organic matter forming stable complexes.

11.3.8 Oxidation and Hydrolysis

Al, Fe, and Mn can form insoluble compounds—oxides, oxyhydroxides, and hydroxides—through hydrolysis and/or oxidation.

11.3.9 Formation of Carbonates

Some metals can form carbonates when concentrations of bicarbonate in water are high.

11.3.10 Formation of Insoluble Sulfides

Anaerobic conditions promote the growth of sulfate-reducing bacteria, which convert sulfates into hydrogen sulfide; metal(loid)s such Ag, As, Cd, Cu, Hg, Pb, and Zn react with hydrogen sulfide to form highly insoluble sulfides.

11.3.11 Binding to Iron and Manganese Oxides

Several metal(loid)s have a high affinity to bind to Fe and Mn oxides through the adsorption or coprecipitation phenomena.

11.3.12 Reduction to Nonmobile Forms by Bacterial Activity

Metal(loid)s such as Cr, Cu, Se, and U can be reduced into nonmobile forms—e.g., metallic forms—through processes governed by bacterial activity or physicochemical factors such as Eh–pH and hydrogen sulfide concentrations.

11.3.13 Biological Methylation and Volatilization

Some metal(loid)s (e.g., Hg, Se, and As) may be converted into nontoxic forms and then released into the atmosphere through volatilization by direct release from plants or by microbial or chemical activity in the water and sediments. These elements can also be biomethylated by plant roots and microorganisms — e.g., under anaerobic sediment conditions, Hg ions are biomethylated by anaerobic microorganisms to methyl mercury; methylation processes made these metal(loid)s highly toxic and available to the entire food chain through biomagnification, creating additional environmental problems.

11.3.14 Plant Uptake

Metal(loid)s are absorbed from water and/or sediment by roots or other submerged organs followed by translocation and accumulation in the tissues.

Metal(loid) uptake by aquatic plants depends on the type of plant, with direct absorption from the water column to the plant surface followed by passive or active transport across membranes and, to a lesser extent, root uptake [63, 79, 80]. These processes have been observed not only in submerged species (with poorly developed root systems) but also in free-floating plants [63]. However, root uptake in plants with developed root systems can also be effective, as endorsed by *Eleocharis dulcis* (Burm.f.) Trin. ex Hensch. with higher U levels in roots compared to stems. It has been suggested that the low accumulation in stems has an important advantage because metal cycling and resuspension following the decay of stems are minimized [81]. In another study, Entry et al. [82] demonstrated sunflower (*Helianthus annuus*) seems to be very effective in recovering U from contaminated water. Uranium accumulated mainly in the roots, with concentrations 5000–10,000 times greater than that of the ambient water.

Plants growing near mining sites or in trace element-rich substrates are able to accumulate or exclude toxic metal(loid)s and can therefore tolerate the imposed stress. Some of these accumulating plant species reveal the mineral composition of those substrates, for example, in the soil, sediment, and water. This ability can be used in mineral prospecting, in contamination bioindication or, if the biomass and bioproductivity are high, in phytoremediation. Certain aquatic plants, such as algae, bryophytes, and angiosperms, are considered to be indicators of trace element pollution and have been successfully used as diagnostic tools for monitoring environmental pollution [83, 84]. In fact, the ability of plants to accumulate metal(loid)s from water, which may not be essential for their growth and development, has been observed in several studies performed in natural wetlands where the metal(loid) concentration in aquatic plants is manifold higher than the ambient water. This evidence has led to the generalized idea that metal(loid) hyperaccumulation in aquatic plants is not as rare as in terrestrial plants and that suitable and sustainable remediation strategies could be developed based on this characteristic [63, 79, 80, 85, 86]. This function is of considerable significance in the emerging areas of wastewater treatment and in the establishment of constructed treatment wetlands (e.g., [70]). In recent years, several studies have been performed on metal(loid)s accumulation by aquatic plants, including possible phytofiltration applications.

The accumulation of metal(loid)s in aquatic plants may occur due to absorption, adsorption, and/or other retention mechanisms. Holistically, these physicochemical processes generally fall under the term “bioaccumulation”, when performed by living organisms. Another term, “biosorption”, is used to describe the set of mechanisms for the removal of substances from solution by biological materials (living or dead biomass), including absorption, adsorption, ion exchange, surface complexation, and precipitation (e.g., [64, 87–96]). However, some of these authors only consider the term “biosorption” in the case of dead biomass.

Several studies have shown that many factors affect the “bioaccumulation” and/or “biosorption” of metals in aquatic ecosystems. Among the physicochemical factors, pH is possibly the most important (e.g., [93, 97–101]). This can be attributed to the influence of pH on the solution chemistry of metals and the activity of the functional groups of the biomass [102]. Phytofiltration and rhizofiltration efficiencies are determined by the ability of plants to accumulate metal(loid)s and the biomass production. Thus, phytofiltration and rhizofiltration potential can be estimated by calculation of bioconcentration factor (or biological absorption coefficient) and translocation factor. The bioconcentration factor (BCF), defined as the ratio of the total concentration of elements in the plant tissue (C_{plant}) to its concentration in the water in which the plant was growing (C_{water}), is calculated as follows (e.g., [103–105]):

$$\text{BCF} = \frac{C_{\text{plant}}}{C_{\text{water}}}$$

Translocation factor (TF), defined as the ratio of the total concentration of elements in the aerial parts of the plant (C_{shoot}) to the concentration in the root (C_{root}), is calculated as follows (e.g., [104, 106]):

$$\text{TF} = \frac{C_{\text{shoot}}}{C_{\text{root}}}$$

Using both the BCF and the TF it is possible to assess the phytofiltration or rhizofiltration capacity of the plants. A high root-to-shoot translocation (TF) of metal(loid)s is a fundamental characteristic for a plants to be classified as effectively used in rhizofiltration. The commercial efficiency of phytofiltration and rhizofiltration can be estimated by the rate of metal(loid) accumulation and biomass production. After harvesting, biomass may be processed for extraction and recovery of metals with commercial value—phytomining [48, 49, 107, 108]. The commercial value of metals such as Ni, Zn, Cu, or Co may encourage the phytoremediation process. Alternatively, thermal, physical, chemical, or microbiological processes can be used to reduce the volume/weight of biomass.

The earlier referred metal(loid)s removal processes naturally occurring in aquatic ecosystems, constitute a form of natural attenuation of contamination (e.g., [109]). The natural attenuation can be defined as the natural processes of dilution, dispersion, precipitation, sorption, biodegradation, bioaccumulation, volatilization, and/or chemical and biochemical stabilization of contaminants occurring in aquatic environments that effectively reduce contaminant mobility, bioavailability, toxicity, or concentration to levels that are not too harmful on the human health and ecosystems

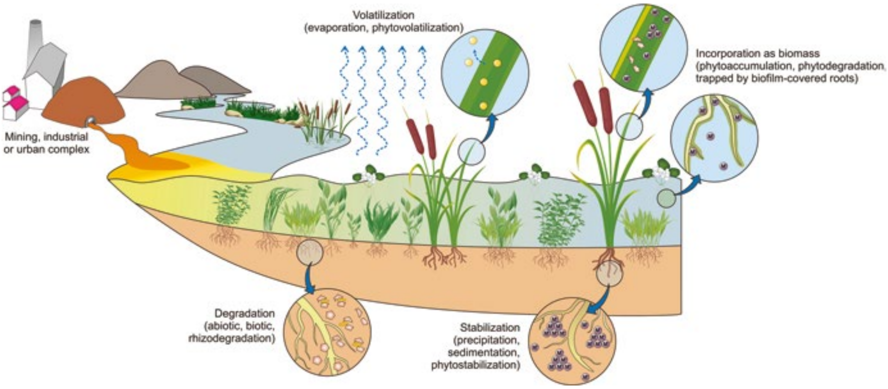

Fig. 11.4 Schematic representation of mechanisms of natural attenuation of contamination (including phytoremediation) in aquatic environments

(Fig. 11.4). Thus, human intervention to remediate waters and sediments and restoring aquatic ecosystems can be based on these natural processes. These processes can be replicated in a more complex manner in constructed wetlands, or in a more simply way in phytofiltration and rhizofiltration systems.

11.4 Phytofiltration Potential of Aquatic Plants

The ability of aquatic plants to accumulate metal(loid)s from water and/or from water–sediment interface has been observed in several studies performed both in field or laboratory conditions (e.g., [63, 80, 85, 86, 110–119]). It has been generally observed that the metal concentration in aquatic plants is several times higher than the concentration in surrounding water. Thus, several aquatic plant species have been identified as accumulators of metal(loid)s and as a result they might prove useful in biomonitoring and phytofiltration.

11.4.1 Natural Phytofiltration of Metal(loid)-Contaminated Water in Portugal

A few studies to assess the indigenous aquatic plant species of diverse contaminated areas and evaluate their potential for phytofiltration have been performed in Portugal (e.g., [41, 42, 112, 120–129]). In this chapter, important findings have been presented from several studies to evaluate the phytofiltration potential of native aquatic flora grown in waters enriched with metal(loid)s in distinct areas of Portugal.

11.4.1.1 Study Areas

The studied areas are located in Portugal (South Western Europe), including the uraniferous regions of Nisa (Southern Portugal), Beiras (Central Portugal), and Horta da Vilariça (Northern Portugal). Uraniferous deposits are located in the hercynian granites, in the metasediment enclaves and in the metamorphism contact haloes. In the Beiras region, several deposits have been exploited either by underground or surface mining. The main mineral processing method used was lixiviation, especially during the last active working phase (the last mine closed in 2001). Many of the sites were left in different stages of degradation. However, several programs for the environmental restoration of some of these old mines have been developed. Nisa and Horta da Vilariça regions were recognized for uranium deposits. However, these deposits have never been target for mining.

11.4.1.2 Material and Methods

Both plant and water samples were collected from selected sites in the vicinity of the uranium mineralized areas. The plants included submerged, free-floating, and rooted emergent species. Plant material was washed thoroughly with fresh water to remove sediment and other foreign objects. The preparation of plant material included, where appropriate, separation into roots and aerial tissues. After drying in an oven at 60 °C for 72 h, plant samples were ground into a homogeneous powder for further analysis. Water pH was determined using a pH meter (WQC-24, DKK-TOA) in the field. HCO_3 concentrations were also measured in situ using the titration method. The water samples were filtered through 0.45 μm Millipore cellulose membrane filters and cooled to 4 °C immediately after collection. For determination of metals and As, samples were acidified to $pH<2$ with 65 % HNO_3 (V/V).

To define the chemical characteristics of the stream water as well as the occurrence of heavy metal and other elemental contamination, several parameters were measured using current analytical methods, including Atomic Absorption Spectrometry (AAS, SOLAAR M Series equipment from Thermo–Unicam) for Ca, Mg, Na, and K; coupled graphite furnace AAS for Fe, Mn, Cu, Zn, Cd, Co, Ni, Bi, Cr, Pb, and As; and the High Performance Anion Exchange Chromatography method for Cl^-, NO_3^-, and PO_4^{3-}. Plants were prepared by microwave digestion with an HNO_3–H_2O_2 mixture in closed Teflon vessels (Multiwave 3000, Anton Paar). The analysis was performed in the same way as stated for water. Fluorometry was adopted for the determination of the U content in the water and plants using a "Fluorat-02-2 Manalyzer" (Lumex, Russia).

Water data quality control was performed by inserting reagent blanks and duplicate samples into each batch. Analytical precision, defined as the percent relative variation at the 95 % confidence level, ranged from 2 to 6 %, depending on the concentration levels. Certified reference material from the National Water Research Institute of Canada (reference TMDA-62) was also used to validate the results. For the plants, the analytical methods were assessed using a Polish certified reference material, Virginia Tobacco Leaves (CTA-VTL-2), which was included in the triplicate analyses. The agreement between the certified reference values and the values determined by the analytical method was in the range of 85.5–110.2 %.

11.4.1.3 Phytofiltration of Arsenic-Contaminated Water

Arsenic (As) is a metalloid that is ubiquitous in nature and is found in minerals and rocks, soils, natural waters, the atmosphere, and organisms (e.g., [130–132]). More than 245 minerals contain As, and the principal source of As is geological. However, human activities such as mining, pesticide application, and burning of fossil fuels also cause As pollution (e.g., [132]). Arsenic can occur in the environment in a variety of chemical forms with different mobility, bioavailability, and toxicity. Arsenic exists in inorganic and organic complexes such as arsenate [As(V)], arsenite [As(III)], monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), trimethylarsine (TMA), arsenocholine (AsC), arsenobetaine (AsB), arsenosugars, and others, and can occur in four oxidation states: +V (arsenate), +III (arsenite), 0 (arsenic), and −III (arsine) (e.g., [104]). However, in natural waters, As is found mostly in the inorganic form as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)] (e.g., [131, 132]). These forms, which are also the most biologically important species, are interchangeable depending on the redox status of the environment [104].

In the natural environment, redox potential (Eh) and pH are the most important factors controlling As speciation. Under oxidizing conditions (high Eh values), $H_2AsO_4^-$ is dominant at low pH (less than approximately pH 6.9), while at higher pH, $HAsO_4^{2-}$ becomes dominant. In the pH range from 2 to 11, both $H_2AsO_4^-$ and $HAsO_4^{2-}$ species exist. The species $H_3AsO_4^0$ and AsO_4^{3-} may be present under extremely acidic and alkaline conditions, respectively. Under reducing conditions (low Eh values), H_3AsO_3 is the predominant inorganic As species (e.g., [131, 132]).

Concentrations of As in unpolluted surface water and groundwater typically vary from 1 to 10 μg/L (e.g., [132]). The highest concentrations of As are found in groundwater as a result of water–rock interactions and the tendency for favorable physical and geochemical conditions for As mobilization and accumulation (e.g., [131]). In fresh water, the variation is in the range of 0.15–0.45 μg/L [132] or 0.1–0.8 μg/L but can range up to 2 μg/L [131]. In this oxic water, arsenate is the predominant species, and both arsenate and arsenite are bioavailable to the plants in aquatic systems (e.g., [133]).

Although no evidence exists that As is essential for plant nutrition, As is naturally present in plants but in concentrations that rarely exceed 1 mg/kg (e.g., [130]). However, plants vary considerably in their tolerance of As and in the amount of As that they can take up from soils and water.

In the context of constructed wetlands, García et al. [134] reported that the direct uptake and accumulation of As in plants appears to play insignificant role in As removal. Similar findings were drawn by Singhakant et al. [135], who reported that only 0.5–1 % of the total As input was accumulated in plant tissues. There are also studies indicating that wetland plants have a remarkable effect on As retention [136, 137]. Several studies have shown that roots accumulate more As than shoots (e.g., [138, 139]). Except in hyperaccumulator plants, the typical ratios of shoot to root As concentrations are <1. The As distribution, in general, decreases from root to stem and leaf to fruit [130]. Different reasons may explain why As remains mostly in plant roots, such as limited translocation of As from roots to shoots (e.g., [140]), the presence of Fe and S (e.g., [141]), the effect of As speciation in the mechanism of translocation and its relationship to the phosphate transporter (e.g., [142]), and the formation of As(III)-phytochelation (PC) complexes in roots and subsequent sequestration in root vacuoles (e.g.,[105]). Arsenic speciation appears to play an important role in the uptake mechanism and further translocation. Due to the chemical similarity between arsenate and phosphate, arsenate is presumed to be taken up by the same transporters of phosphate in the roots. However, the form of As that is translocated to shoots is not known nor is how this translocation occurs [142, 143].

Reay [144] reported that the species *Ceratophyllum demersum*, a free-floating submergent plant, has been shown to accumulate As with a 20,000-fold concentration factor. Meanwhile, several studies have identified aquatic plants with high As content: *Lagarosiphon major* (Ridl.) Moss (300 mg/kg, in dry weight, DW [63]), *Egeria densa* Planch. (>1000 mg/kg DW [145]), *C. demersum* (>1000 mg/kg DW [145]), and *Lemna gibba* L. (1021.7 ± 250.8 mg/kg DW [146]). Some species of submerged macrophytes such as *Callitriche stagnalis* Scop. and *Myriophyllum propinquum* A. Cunn. have revealed high potential to accumulate As and therefore show potential for phytofiltration of As-contaminated water [147]. Other plants reported to accumulate As with some potential for phytofiltration of As-contaminated water are as follows: *Lepidium sativum* L. [148], *Rorippa nasturtium-aquaticum* (L.) Hayek [147], *Spirodela polyrrhiza* (L.) Schleid. [133], *Eichhornia crassipes* (Mart.) Solms and *Lemna minor* L. [149], *Hydrilla verticillata* (L.f.) Royle [105], *Eleocharis acicularis* (L.) Roem. & Schult. [103], and *Arundo donax* L. [104], *Callitriche lusitanica* Schotsman [42], *Micranthemum umbrosum* (J.F. Gmel.) S.F. Blake [150]; *Pistia stratiotes* [151], and *Vallisneria natans* (Lour.) H. Hara. [152].

The pH may affect the bioavailability of As and the consequent uptake by plants. For example, Wells and Richardson [153] reported a decrease in arsenate uptake in the moss *Hylocomium splendens* (Hedw.) Schimp. with increasing pH. In this moss, arsenate uptake was optimal at pH 5, where $H_2AsO_4^-$ was the dominant form in solution. As the pH increased to pH 8, where $HAsO_4^{2-}$ was the dominant anion, arsenate uptake decreased. Maximum As uptake rates occurring at pH 6.5 was observed by Mukherjee and Kumar [154] in aquatic plant *Pistia stratiotes*. The accumulation of As therefore depends on the type of plant (e.g., [141, 143]). The potential of some aquatic plants to accumulate As has been well demonstrated, and thus strongly supports their possible use in phytofiltration of As-contaminated water (e.g., [105, 155]).

In the studied areas As was detected in the surface waters at a range of concentrations between 0.15 and 40.2 μg/L (Fig. 11.5). The pH of the water ranged between 4.9 and 8.6. According to Smedley and Kinniburgh [131] and Sharma and Sohn [132], under oxidizing conditions, both $H_2AsO_4^-$ and $HAsO_4^{2-}$ inorganic As species

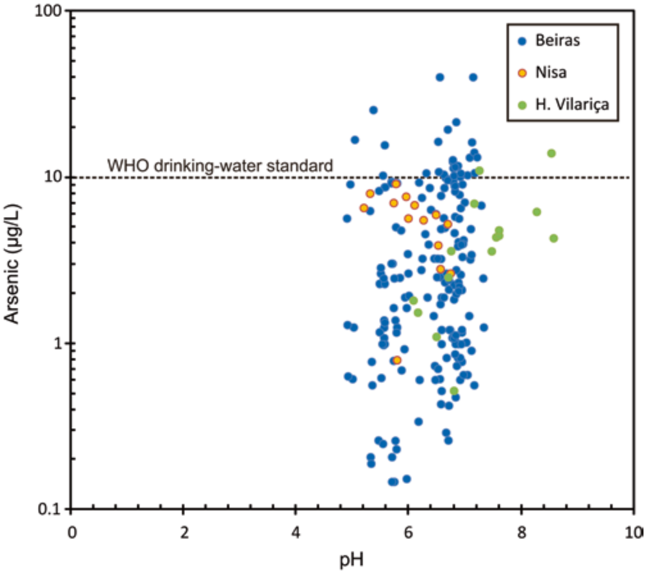

Fig. 11.5 Arsenic concentration relative to pH for stream waters of the studied areas. The World Health Organization [156] drinking-water provisional guideline value of 10 µg/L is indicated for reference

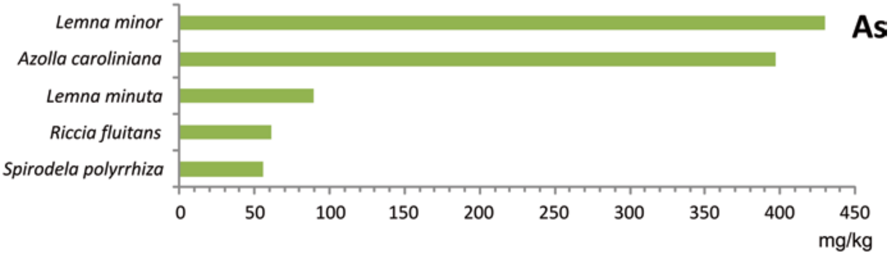

Fig. 11.6 Maximum As content in free-floating aquatic plants (mg/kg DW) of the studied areas

exist in the pH range found in the waters that were studied, although the form $H_2AsO_4^-$ may be predominant. At 28 of the sites sampled, the As concentration exceeded the limit (10 µg/L) established by the World Health Organization [156] for drinking water (Fig. 11.5).

The results of the chemical analysis of As on the most representative aquatic plant species in the studied areas revealed that As is highly accumulated by some species (Figs. 11.6, 11.7 and 11.8). High bioaccumulation levels were observed in several species at a magnitude much higher than the concentration in the surrounding water. The highest concentrations of As were found in the submerged species (Fig. 11.7) *Callitriche lusitanica* (2346 mg/kg, in dry weight, DW), *Ranunculus tripartitus* DC. (1463 mg/kg DW), *Callitriche brutia* Petagna (523 mg/kg DW),

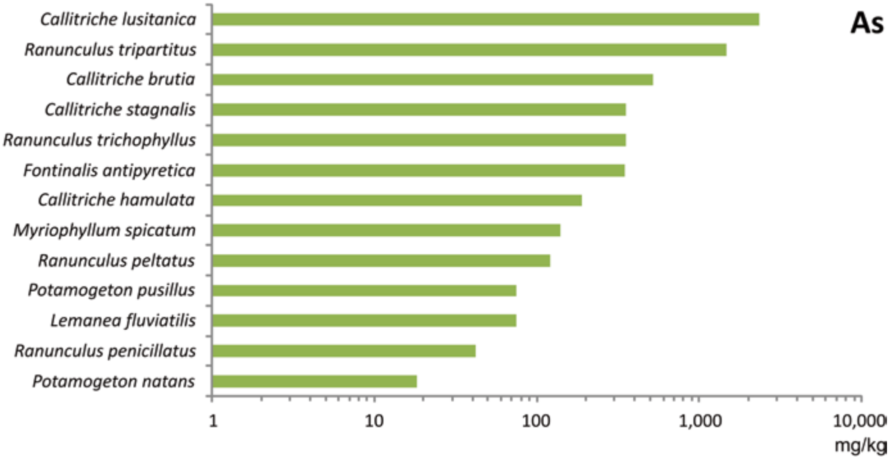

Fig. 11.7 Maximum As content in submerged aquatic plants (mg/kg DW) of the studied areas

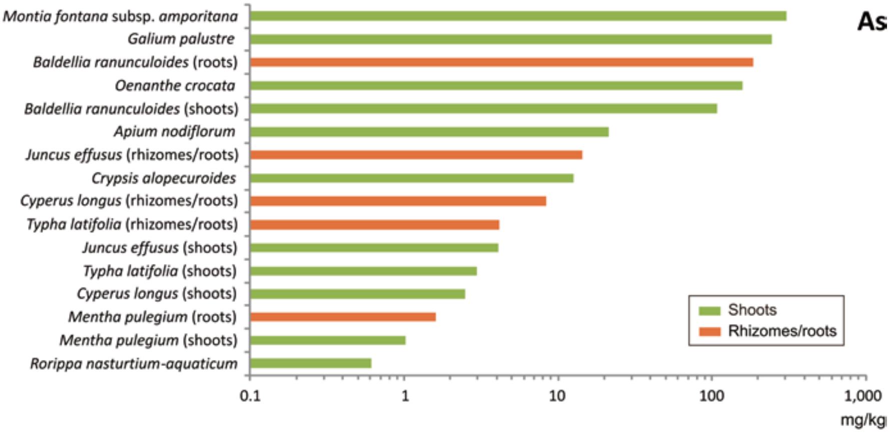

Fig. 11.8 Maximum As content in rooted emergent aquatic plants (mg/kg DW) of the studied areas

Callitriche stagnalis (354 mg/kg DW), *Ranunculus trichophyllus* Chaix ex Vill. (354 mg/kg DW), *Callitriche hamulata* Kütz. ex W.D.J. Koch (190 mg/kg DW), *Ranunculus peltatus* subsp. *saniculifolius* (Viv.) C.D.K. Cook (120 mg/kg DW), in the free-floating species (Fig. 11.6) *Lemna minor* (430 mg/kg DW), *Azolla caroliniana* Willd. (397 mg/kg DW), in the bryophyte *Fontinalis antipyretica* (346 mg/kg DW), and in the rooted emergent species (Fig. 11.8) *Montia fontana* L. (305 mg/kg DW), *Galium palustre* L. (247 mg/kg DW), and *Oenanthe crocata* L. (158 mg/kg DW). The measured concentrations in the remaining rooted emergent plants, such as *Apium nodiflorum* (L.) Lag., *Typha latifolia* L., and *Juncus effusus* L. were significantly lower when compared with the previous species, even in the rhizomes/roots.

The species *Callitriche stagnalis* and *Callitriche lusitanica* showed average BCFs of 1.1×10^4 and 1.8×10^4, respectively [42], revealing a great phytofiltration ability. The highest concentrations of As were therefore found in the plants from the Callitrichaceae family. Similar behavior was reported by Robinson et al. [147] in the Taupo Volcanic Zone of New Zealand, where As concentrations of 4215 mg/kg (DW) in *Callitriche stagnalis* and 422 mg/kg (DW) in *Callitriche petriei* R. Mason was found in waters with high As concentration (mean of 90 μg/L). The submerged species *Ranunculus trichophyllus* and *Ranunculus peltatus* subsp. *saniculifolius* also showed a high BCF, with averages of 7.5×10^3 and 1.1×10^4, respectively [42], and showed a very highly significant ($P < 0.001$) positive correlation with the As present in the water [42]. Therefore, this species may serve as an indicator of As pollution.

The free-floating species *Lemna minor* and *Azolla caroliniana* showed good ability to accumulate As in a similar way with average BCFs of 6.1×10^3 and 5.5×10^3 [42]. They therefore have a great potential for As accumulation in fresh waters. *Lemna minor* also showed a very significant ($P < 0.001$) positive correlation with the As present in the waters [42]. Therefore, this species may serve as a good indicator of As pollution. The bryophyte *Fontinalis antipyretica* showed a strong ability to accumulate large amounts of As, displaying a high BCF of approximately 1.2×10^4 [42]. In general, bryophytes have a great potential for rapid accumulation and exhibit seasonal fluctuations depending upon the environmental contaminants [84]. As this species does not have a root system, uptake occurs through the rhizoids as an ionic exchange between the environment and the basal portion of the plant.

The rooted emergent species *Montia fontana*, *Galium palustre,* and *Oenanthe crocata* also showed a significant As accumulation in their aerial organs and high BCF (with averages of 5.2×10^4, 1.4×10^4, and 4×10^4, respectively [42]). The remaining rooted emergent species *Apium nodiflorum*, *Typha latifolia*, and *Juncus effusus*, in spite of their high biomass and bioproductivity, did not show a significant As accumulation in their aerial organs. In these species, only the leaves of *Juncus effusus* showed a very highly significant ($P < 0.001$) positive correlation with the As found in the water [42]. Among the studied rooted emergent species, only in *Typha latifolia* and *Juncus effusus* the aerial parts (leaves) and the underground parts (rhizomes/roots) were separated. The As concentrations are significantly higher in the underground parts, and, in general, the TF values are below 1 [42]. Further studies on the rooted emergent species are therefore needed to investigate the mechanism of As uptake, translocation, and accumulation, considering both the water and the sediment and taking into account the relationship with Fe, S, and phosphate and determining the As species present.

11.4.1.4 Phytofiltration of Uranium-Contaminated Water

In the natural environment, U occurs almost entirely as ^{238}U in its hexavalent state (U^{6+}), and in minor quantities as ^{235}U, and in trace quantities as ^{234}U. In aqueous systems U reacts with oxygen to form uranyl ion UO_2^{2+} which is highly stable and soluble, which determines its toxicity [157–160]. Other soluble forms are UF_6, $UO_2(NO_3)_2$, UO_2Cl_2, UO_2F_2, uranyl acetates, sulfates, and carbonates [161]. Several physicochemical and biological variables may influence the U speciation, bioavailability, uptake, and toxicity in fresh surface waters, including pH, water hardness, natural organic matter, and microbial activity [94, 98, 102, 162–164]. The average global concentration of U in river water is ~0.3 μg/L [165], which is within the range 0.2–0.6 μg/L suggested by Palmer and Edmond [166].

The potential of some aquatic plants to accumulate U has been well demonstrated, supporting their possible use in phytofiltration of U-contaminated water. Among aquatic plants, algae are of considerable interest to ecological engineers due to their ability to sequester U as evidenced by the fact that many algae can survive in abundance under extreme environmental conditions (e.g., [119, 158]). Algae grow in a wide spectrum of contaminated waters from alkaline environments (*Chara*, *Nitella*) to acidic mine drainage wastewaters (*Mougeotia*, *Ulothrix*). Therefore, Kalin et al. [158] suggested that algae could provide a simple and long-term solution for removing U in waste streams through the combined processes of adsorption, reduction, and transformation.

Pettersson et al. [167] identified the water lily (*Nymphaea violacea* Lehm.) as an accumulator of several radionuclides when they observed high levels of U and Th series radionuclides in plant roots, rhizomes, and foliage in the vicinity of the Ranger Uranium Mine (Australia). At the same mine, an attempt to phytoremediate mine runoff water was tested using *Eleocharis dulcis* [81]. Members of Lemnacea are the most favored plants for phytoremediation and have been intensively described in literature as duck weeds including *Lemna*, *Spirodella*, *Wolffia*, and *Wolffiella* [133, 168]. *Lemna gibba* (612.36 ± 143.6 mg/kg DW) is an example of a U accumulator plant [169]. Other aquatic plants suggested as U accumulators are *Zostera japonica* Ascherson & Graebner and *Zostera marina* L. [170], *Phragmites australis* (Cav.) Trin ex. Steud. [171, 172], *Hydrilla verticillata* (L.f.) Royle [94], *Callitriche stagnalis* and *Fontinalis antipyretica* [41, 129], and *Spirodela punctata* [44].

Many microbial organisms, including bacteria, lichens, fungi, and algae, have been studied for their U-binding capacity, and the maximum U uptake was most frequently observed between pH 4 and 5 [98, 102, 173]. Similar results have been found in several other plant materials, such as dried roots [174] or coir pith [175]. Srivastava et al. [94] also observed in the aquatic plant *Hydrilla verticillata* that the maximum U uptake rates occurred at pH 5. Pratas et al. [41] found a very highly significant ($P < 0.001$) negative correlation between water pH and U concentration in *Callitriche stagnalis*.

The results of chemical analysis of the stream water samples at the studied sites show that U was detected in the surface waters at concentrations ranging from 0.23 to 1217 μg/L (Fig. 11.9). From a geographical interpretation of the sampling locations, it was clear that mine effluents contributed significantly to aquatic U contamination. Mean U concentration was higher in streams directly fed by mine drainage due to two locations with high concentrations, near Cunha Baixa and Urgeiriça mine sites [129].

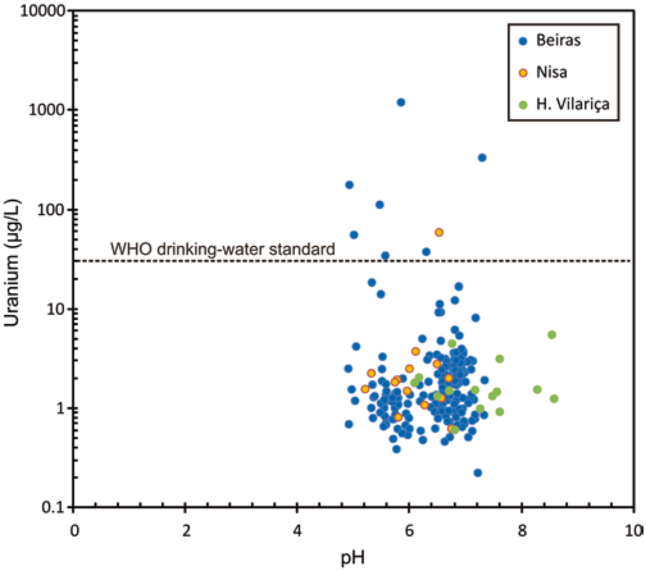

Fig. 11.9 Uranium concentration relative to pH for stream waters of the studied areas. The World Health Organization [156] drinking-water provisional guideline value of 30 µg/L is indicated for reference

According to Wang et al. [102], in an acidic environment (pH < 4.0), U(VI) occurs predominately as UO_2^{2+}, whereas at higher pH ranges (4.0 < pH < 7.0) composite hydrolyzed ionic species yield compounds such as UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)^{5+}$. When the pH is above 7.0, U(VI) precipitates easily. The pH of water samples ranged between 4.9 and 8.6 and reveals a complex behavior due to the wide hydrochemical variability. The mean U concentration (11.1 µg/L) is significantly higher than the range values estimated by Palmer and Edmond [166] as global riverine U flux. At 9 of the sites sampled, the U concentration exceeded the provisional guideline value (30 µg/L) indicated by the World Health Organization [156] for drinking water (Fig. 11.9). At these points, U concentrations could be directly linked to mining activities since these streams were directly fed by mine drainage.

The analysis of plants from the studied areas revealed high U bioaccumulation levels in several species and in magnitudes much higher than the ambient water concentrations (Figs. 11.10, 11.11 and 11.12). However, the water samples represent a "snapshot" while the U in the plant tissue may reflect more of an average of the U over time as the water U content could change after a rainfall or prolonged drought. In general, highest concentrations of U were observed in the submerged species and the lowest in the free-floating species. Among the submerged species highest concentrations of U were found in *Fontinalis antipyretica* (4979 mg/kg, DW), *Callitriche stagnalis* (1963 mg/kg DW) followed by *Callitriche hamulata* (379 mg/kg DW), *Ranunculus peltatus* subsp. *saniculifolius* (243 mg/kg DW), *Callitriche lusitanica* (218 mg/kg DW), and Ranunculus trichophyllus (65.8 mg/kgDW) (Fig. 11.11).

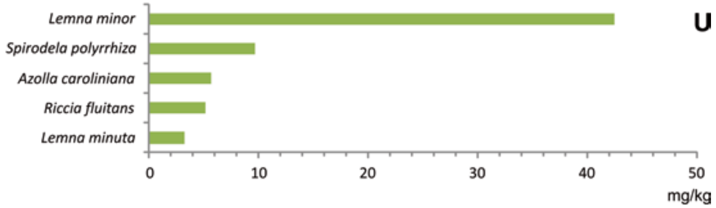

Fig. 11.10 Maximum U content in free-floating aquatic plants (mg/kg DW) of the studied areas

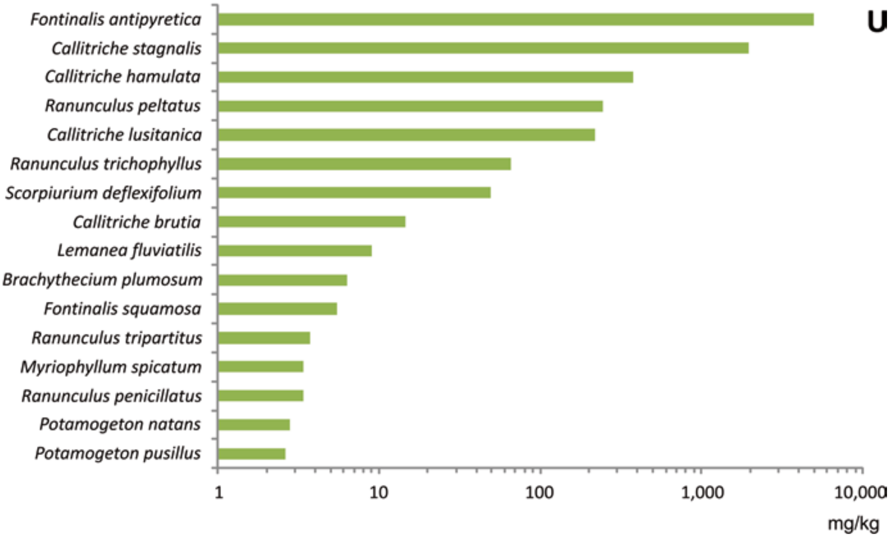

Fig. 11.11 Maximum U content in submerged aquatic plants (mg/kg DW) of the studied areas

The hydrophyte moss *Fontinalis antipyretica* showed a strong ability to accumulate large amounts of U, displaying a high mean BCF of approximately 1.0×10^4 [129] and a highly significant ($P < 0.001$) positive correlation with the U present in water [129]. Therefore, this species may serve as an indicator of U pollution. Accumulation of other metal(loid)s has also been demonstrated in *Fontinalis antipyretica*, such as As, Se, Cd, Cr, Cu, Pb, and Zn (e.g., [42, 176–185]). The species *Callitriche stagnalis*, *Callitriche hamulata*, and *Callitriche lusitanica* showed average BCFs of 3.0×10^3, 7.5×10^3, and 5.9×10^3, respectively [129], revealing a great phytofiltration ability. Furthermore, *Callitriche stagnalis* showed a highly significant ($P < 0.001$) positive correlation with the U present in the water [129]. Therefore, this species also serves as an excellent indicator of U pollution. High BCFs were also seen in *Ranunculus peltatus* subsp. *saniculifolius* and *Ranunculus trichophyllus*, with averages of 1.6×10^4 and 3.2×10^3, respectively [129].

Among the free-floating species (Fig. 11.10), *Lemna minor* showed good ability to accumulate U (42.5 mg/kg DW) as previously observed in *Lemna gibba* [169], with average BCF of 1.4×10^3 [129]. This plant belongs to the Lemnaceae family

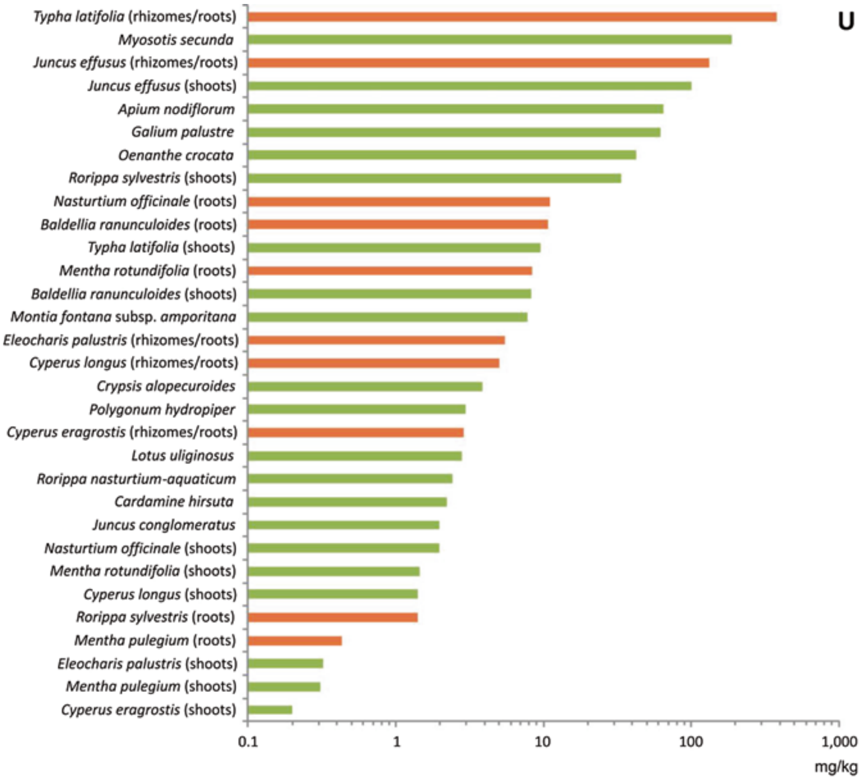

Fig. 11.12 Maximum U content in rooted emergent aquatic plants (mg/kg DW) of the studied areas

much studied in phytoremediation (e.g., [41, 128, 133, 149, 168, 186]). According to these studies, the fast growth rate, widespread distribution in natural wetlands, total independence from sediment, and adaptation to stress conditions like mine waters, makes such species a good option for water treatment technologies, in spite of the constant need for biomass removal. *Lemna minor* also showed a very significant ($P<0.001$) positive correlation with the U present in the waters [129]. However, the U contents in free-floating plants probably cannot reflect their corresponding water U concentrations as they are moved with running river water. Nevertheless, *Lemna minor* also showed a very significant ($P<0.001$) positive correlation with the U present in the standing water [41]. Therefore, this species may serve as a good indicator of U pollution.

Among the rooted emergent species high U concentrations were observed in rhizomes/roots of *Typha latifolia* (380 mg/kg DW), and *Juncus effusus* (132 mg/kg DW), and in the aerial parts of *Myosotis secunda* Al. Murray (188 mg/kg DW), *Juncus effusus* (99.9 mg/kg DW), *Apium nodiflorum* (64.5 mg/kg DW), *Galium palustre* (62.4 mg/kg DW), *Oenanthe crocata* (42.2 mg/kg DW), and *Rorippa sylvestris* (L.) Besser (33.8 mg/kg DW) (Fig. 11.12). *Myosotis secunda*, *Rorippa* *sylvestris*, *Juncus effusus*, *Apium nodiflorum*, *Galium palustre*, and *Oenanthe crocata* also showed high BCFs (mean BCF: 2.2×10^4, 4.8×10^3, 2.6×10^3, 3.6×10^3, 6.6×10^3, and 1.1×10^3, respectively) [129]. Only *Rorippa nasturtium-aquaticum* showed a significant ($P<0.05$) positive correlation with the U content of water. More studies are therefore needed on these emergent species taking into consideration the mechanism of U uptake and accumulation, partitioning of U between stems and roots, water column, and sediment.

Among the species studied, U concentrations are higher in the underground parts (significantly more in *Juncus effusus* and *Typha latifolia*), except for *Baldellia ranunculoides* (L.) Parl., *Cyperus eragrostis* Lam., *Mentha pulegium* L., and *Rorippa sylvestris*. In these species the mean TF values are above 1 suggesting better partitioning in the aerial parts. Pettersson et al. [167] identified the water lily, *Nymphaea violacea*, as an accumulator of several radionuclides when they observed high levels of ^{234}U, ^{238}U, ^{228}Th, ^{230}Th, ^{232}Th, ^{226}Ra, ^{210}Pb, and ^{210}Po in the plant, waters, and sediments in the vicinity of the Ranger Uranium mine (Australia). Higher levels of these contaminants were detected in the roots and rhizomes suggesting root uptake from sediment as the main uptake mechanism.

Preferential partitioning of U in roots may be attributed to the effect of U speciation in the mechanism of translocation and its complexation with phosphate. Studies have shown that among the physicochemical factors, pH is possibly the most important contributing factor [162, 163]. This can be attributed to the influence of pH on the speciation and bioavailability of metals and the activity of the functional groups of the biomass [102]. Other physicochemical variables which may influence the U speciation, bioavailability, and toxicity in fresh surface waters are water hardness, alkalinity, and natural organic matter [164]. In the studied areas, water pH varied from 4.9 to 8.6; this range favors the occurrence of U composite hydrolyzed ionic species. Variation in pH and the effect on U speciation may have affected the results. Only the species *Myosotis secunda* had a significant ($P<0.05$) negative correlation with the pH of the water. On the other hand, the species *Azolla caroliniana* showed a significant ($P<0.05$) positive correlation with the U present in the water [129]. Species with high U uptake, such as *Fontinalis antipyretica*, *Callitriche hamulata*, *Ranunculus peltatus* subsp. *saniculifolius*, *Callitriche lusitanica*, *Typha latifolia* (rhizomes/roots), *Juncus effusus*, and *Myosotis secunda*, may also be used in phytofiltration devices either in monoculture systems or in combined systems resembling the natural systems.

11.4.1.5 Phytofiltration of Lead-, Copper-, and Zinc-Contaminated Water

Among heavy metals, Pb is one of the most hazardous pollutants, due to its impact on human health and environment (e.g., [113]). The main sources of Pb pollution are mining and smelting, industrial effluents, fertilizers, pesticides, and municipal sewage sludge (e.g., [113, 187]). In plants, Pb toxicity leads to reduction in cell division and inhibition of photosynthesis [188], decreases in seed germination, as well as growth, dry biomass of roots and shoots, and disruption of mineral nutrition

[187]. Lead bioaccumulation potential and the effect of Pb stress have been studied recently in various aquatic plant species, including *Fontinalis antipyretica* [180], *Ceratophyllum demersum* L. [79, 189], *Potamogeton pectinatus* L. and *Potamogeton malaianus* Miq. [190], *Wolffia arrhiza* (L.) Horkel ex. Wimm. [191], *Lemna minor* [117, 186], *Lemna gibba* [117], *Najas indica* (Willd.) Cham. [192], *Typha latifolia* [193, 194], *Eichhornia crassipes* (Mart.) Solms [113, 195], and *Callitriche cophocarpa* Sendtn. [196].

In contrast to the Pb, certain heavy metals are required for the metabolic processes in plants. However, despite this, some of these metals, including Cu and Zn, become toxic at elevated levels (e.g., [197, 198]). Several aquatic plant species have been identified as accumulators of multi metals, including Cu and Zn, and as a result they might prove useful in phytofiltration technique. Some examples are as follows: *Ceratophyllum demersum* L. for Cu, Cr, Fe, and Mn [79]; *Fontinalis antipyretica* for Zn, Cu, and Cd [180, 181]; *Callitriche palustris* L. for Cu [199]; *Myriophyllum aquaticum* (Vell.) Verdc., *Ludwigina palustris* (L.) Ell., and *Mentha aquatica* L. for Cu, Fe, Hg, and Zn [200]; *Lemna minor* for Cu, Cd, Pb, and Zn [117, 201]; *Potamogeton pectinatus* L. and *Potamogeton malaianus* Miq. for Cd, Mn, Zn, and Cu [190]; *Lemna gibba* for Cu, Pb, and Zn [117, 202]; *Elodea canadensis* Michx. and *Elodea nuttallii* (Planch.) H. St. John for Cd, Cr, Cu, Mn, Ni, Pb, Zn, and Fe [203]; *Eichhornia crassipes* (Mart.) Solms for Cu, Zn, Cd, and Cr [195, 204–206]; and *Callitriche cophocarpa* Sendtn. for Tl, Cd, Zn, and Cr [196]. In the studied areas Pb, Cu, and Zn were detected in the surface waters at a concentration ranges of 0.1–13.4 μg/L, 0.45–125 μg/L, and 1.00–441 μg/L, respectively (Figs. 11.13, 11.14, and 11.15). Only at two of the sites sampled the Pb concentration exceeded the provisional guideline value (10 μg/L) indicated by the World Health Organization [156] for drinking water (Fig. 11.13).

The analytical results on the most representative aquatic plant species in the studied areas revealed the following significative uptake patterns: Pb from 90.5 to 1104 mg/kg in *Ranunculus trichophyllus*; rhizomes/roots of *Typha latifolia*, *Lemna minor*, *Spirodela polyrrhiza* (L.) Schleid.; and *Myriophyllum spicatum* (Figs. 11.16, 11.17, and 11.18); Cu from 81.8 to 161 mg/kg in *Callitriche lusitanica*, *Callitriche hamulata*, *Ranunculus trichophyllus*, and *Callitriche stagnalis* (Figs. 11.19, 11.20 and 11.21); and Zn from 900 to 34,162 mg/kg in *Lemna minor*, *Lemanea fluviatilis*, *Callitriche lusitanica*, *Callitriche brutia*, *Ranunculus trichophyllus*, *Fontinalis antipyretica*, and *Callitriche stagnalis* (Figs. 11.22, 11.23, and 11.24).

11.5 Conclusion

The studied aquatic plant species exhibited ability to accumulate several metal(loid) s, namely As, U, Pb, Cu, and Zn, in concentrations that are orders of magnitude higher than the surrounding water. This ability, reveled by several species, confirmed their high potential for the phytofiltration of contaminated waters. In general, submerged plants exhibited higher metal(loid) content. The highest U

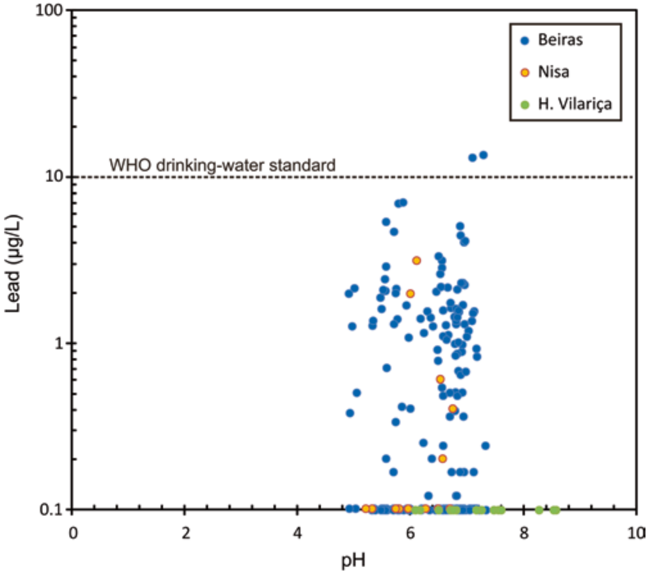

Fig. 11.13 Lead concentration relative to pH for stream waters of the studied areas. The World Health Organization [156] drinking-water provisional guideline value of 10 µg/L is indicated for reference

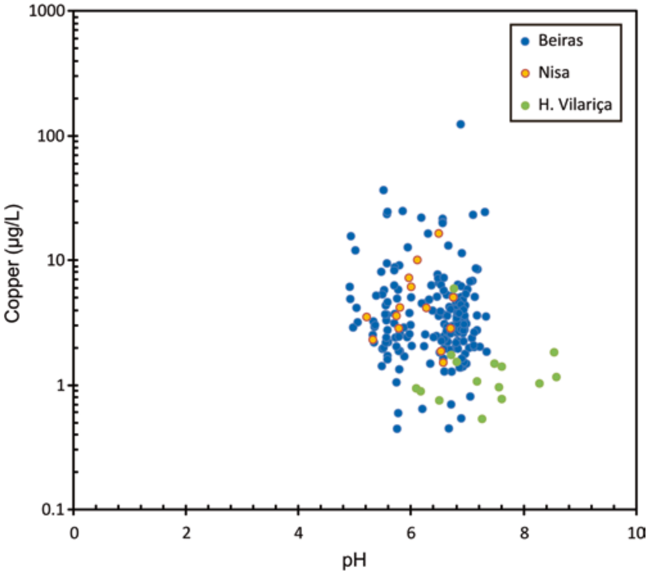

Fig. 11.14 Copper concentration relative to pH for stream waters of the studied areas

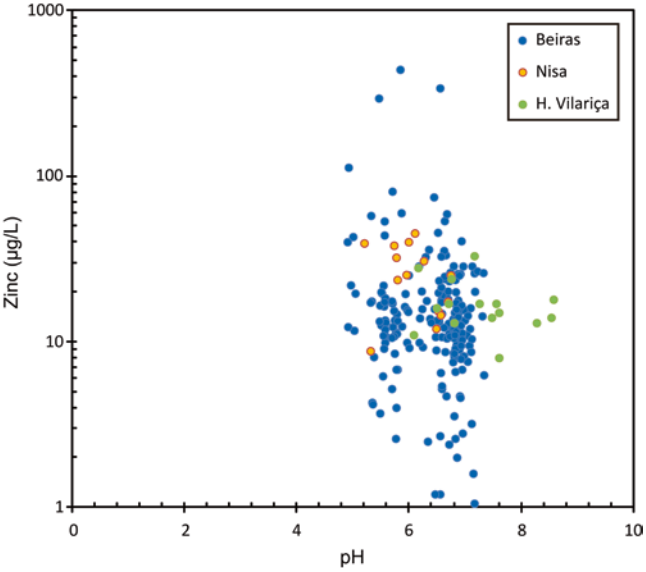

Fig. 11.15 Zinc concentration relative to pH for stream waters of the studied areas

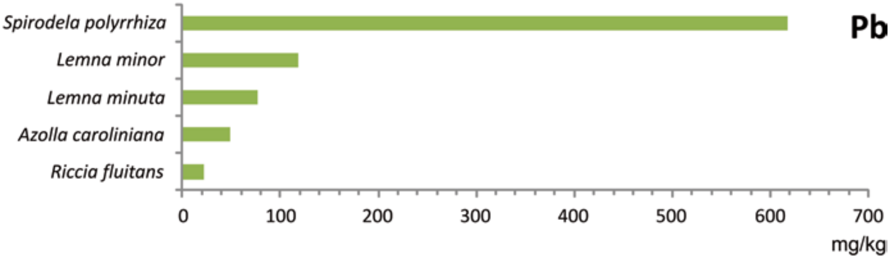

Fig. 11.16 Maximum Pb content in free-floating aquatic plants (mg/kg DW) of the studied areas

concentrations were observed in the bryophyte *Fontinalis antipyretica* and members of the monogeneric family Callitrichaceae. In the rooted emergent species, U seemed to be preferentially partitioned in rhizome/roots; maximum U content was observed in *Typha latifolia* rhizomes. The highest concentrations of As were found in the representatives of Callitrichaceae family. Other species with high As concentrations were *Lemna minor*, *Azolla caroliniana*, *Ranunculus trichophyllus*, *Fontinalis antipyretica*, *Montia fontana*, and *Galium palustre*.

The accumulation patterns of U and As of some of the aforementioned plants may also make them potential tools as bioindicators for trace elements in limnetic environment. Any adverse ecological impact in the aquatic food chain of these metal(loid)s by studied aquatic plants would be considered for future research. The abundance of *Fontinalis antipyretica* and Callitrichaceae family members, their biomass, relatively high bioproductivity, and ability to accumu-

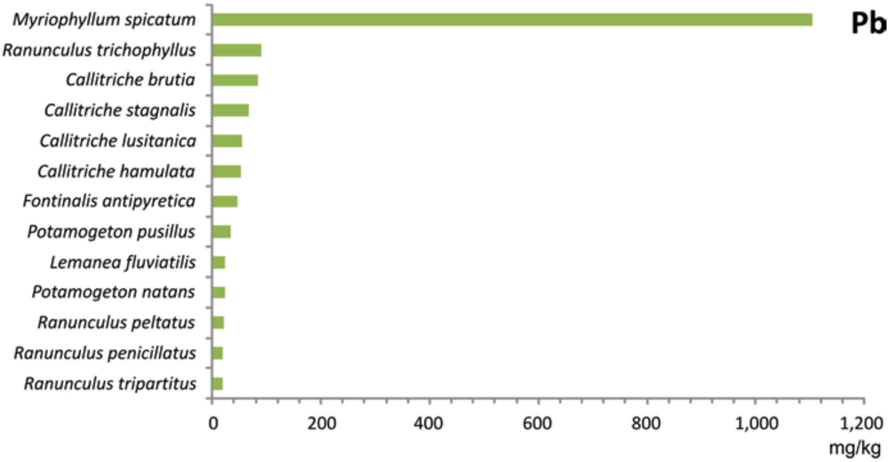

Fig. 11.17 Maximum Pb content in submerged aquatic plants (mg/kg DW) of the studied areas

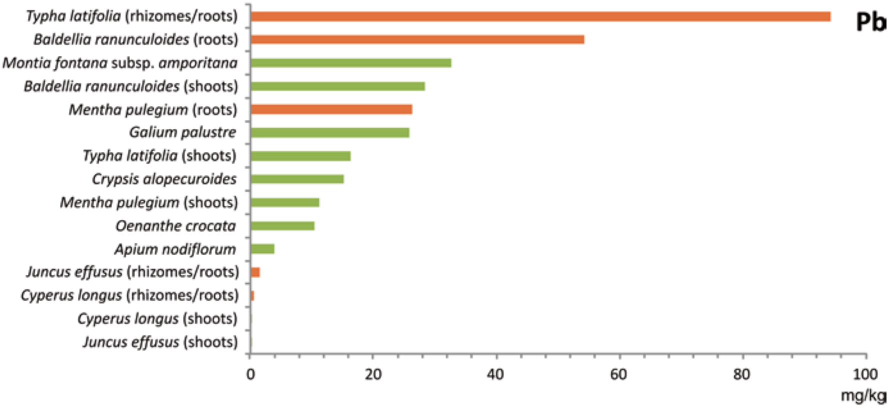

Fig. 11.18 Maximum Pb content in rooted emergent aquatic plants (mg/kg DW) of the studied areas

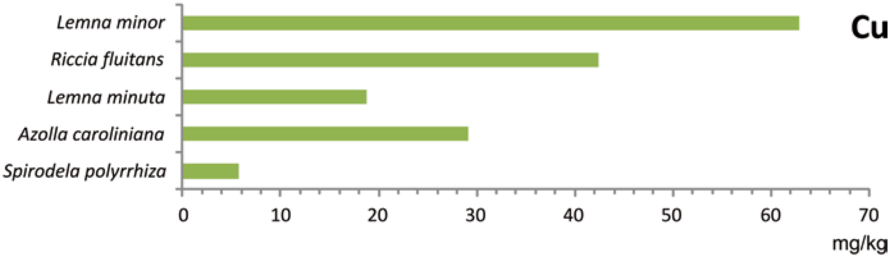

Fig. 11.19 Maximum Cu content in free-floating aquatic plants (mg/kg DW) of the studied areas

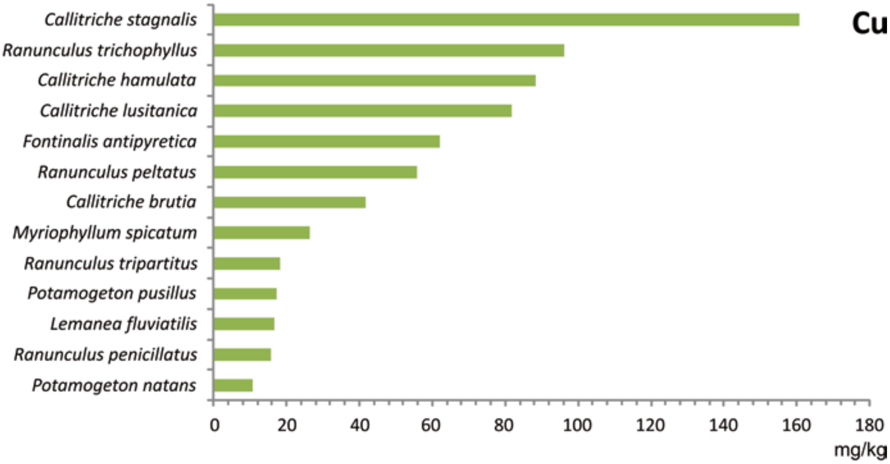

Fig. 11.20 Maximum Cu content in submerged aquatic plants (mg/kg DW) of the studied areas

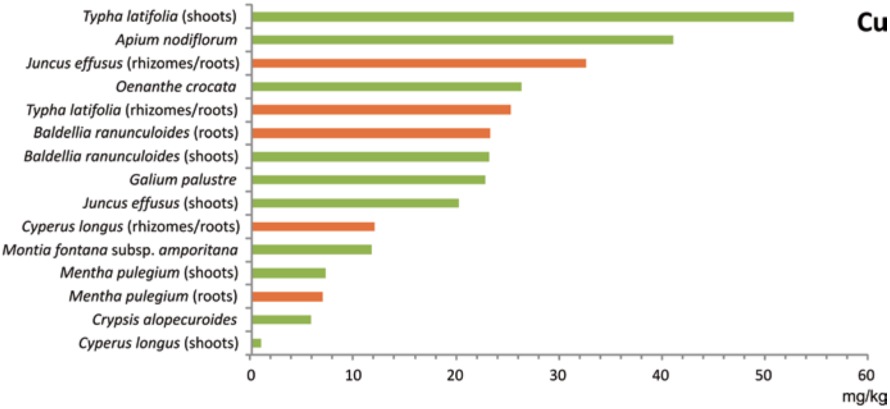

Fig. 11.21 Maximum Cu content in rooted emergent aquatic plants (mg/kg DW) of the studied areas

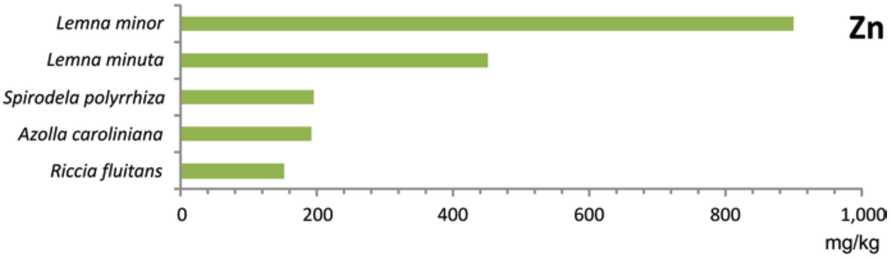

Fig. 11.22 Maximum Zn content in free-floating aquatic plants (mg/kg DW) of the studied areas

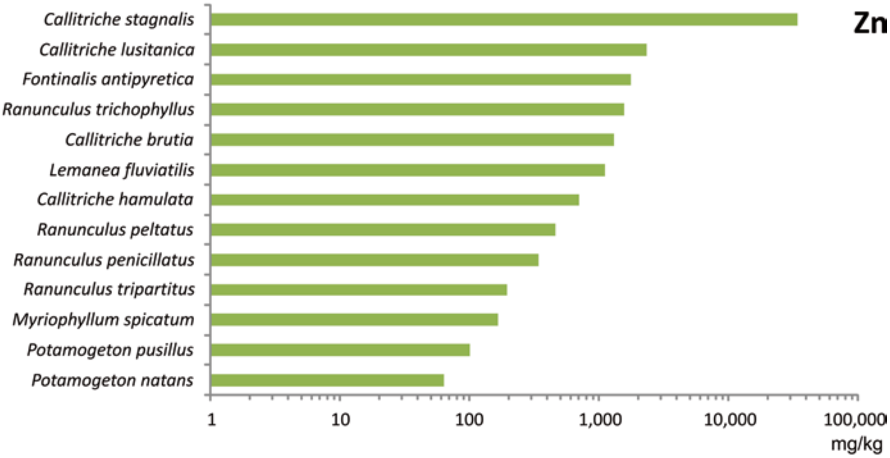

Fig. 11.23 Maximum Zn content in submerged aquatic plants (mg/kg DW) of the studied areas

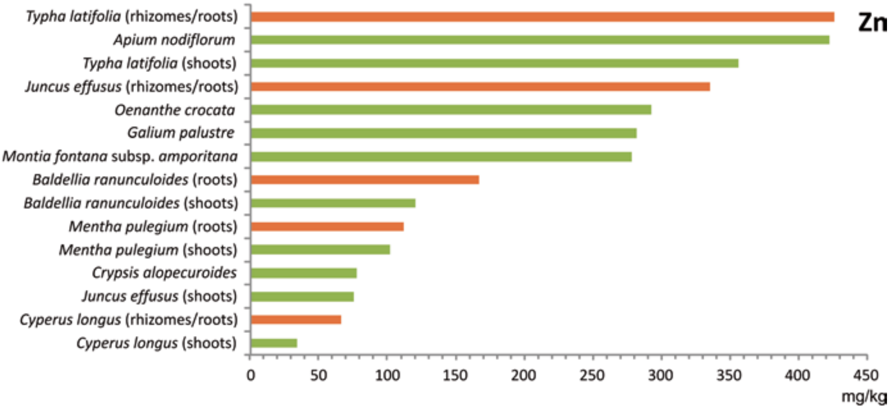

Fig. 11.24 Maximum Zn content in rooted emergent aquatic plants (mg/kg DW) of the studied areas

late several toxic elements at the same time make them promising candidates for the development of phytofiltration methodologies. Other species with high metal(loid) uptake such as *Lemna minor*, *Azolla caroliniana*, *Ranunculus trichophyllus*, *Montia fontana*, and *Galium palustre* can also be used in phytofiltration applications either in monoculture systems or in a combined systems representing the natural systems.

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