



Comparative performance of trace element bioaccumulation and biomonitoring in the plant species *Typha domingensis*, *Phragmites australis* and *Arundo donax*

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ARTICLE INFO

Article history:

Received 14 May 2013

Received in revised form

12 July 2013

Accepted 15 July 2013

Available online 7 August 2013

Keywords:

Trace elements

Wetlands

Phytoremediation

Biomonitors

Macrophytes

Pollution

ABSTRACT

Toxic levels of trace elements in the environment have been reported worldwide over the last few decades, and their increasing concentrations are of the utmost concern because of the adverse effects on human life and ecosystems. Several plant species are able to accumulate trace elements, and may be used for monitoring and remediation of polluted sites. This study compared the capacity of trace element bioaccumulation in three wetland plants distributed worldwide: *Typha domingensis*, *Phragmites australis* and *Arundo donax*. The aims were to identify which species show better potential for removal and monitoring of these elements: Al, As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn. Results showed that all species may be used as biomonitors of trace element contamination in sediment, but only *P. australis* and *A. donax* showed also a correlation with water. Overall, *T. domingensis* and *P. australis* showed a greater capacity of bioaccumulation as well as a greater efficiency of element removal than *A. donax*. In particular, *T. domingensis* and *P. australis* may be used for Hg phytostabilization, the former acted also as a hyperaccumulator for Hg phytoextraction and as a promising species for As phytostabilization. In contaminated wetlands, the presence of *T. domingensis* and *P. australis* may increase the general retention of trace elements, thus, their introduction is recommended for possible actions of phytoremediation and biomonitoring.

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1. Introduction

Trace elements are a major source of water and soil pollution, present as natural components or as a result of human activity (Ok et al., 2007; Li et al., 2009). Various technologies, including precipitation, reduction, artificial membranes, and ion-exchange have been used for toxic metal removal from contaminated environments (Qdaisa and Moussa, 2004). However, these methods are expensive, unable to remove elements at low concentrations, and may generate a huge amount of waste with inevitable disposal problems. Recently, the plant-based remediation technique known as phytoremediation has emerged as a cost effective, environmentally-friendly method of removing pollutants (e.g., heavy metals, organics) from the environment (Gardea-Torresdey et al., 2005). Phytoremediation, in particular, can be categorized into two different approaches: (1) phytoextraction, which is the removal of pollutants from the environment and their accumulation in the aboveground organs of the plant, and (2) phytostabilization, which is the reduction of pollutants mobility by immobilizing and storing them in belowground organs (Raskin et al., 1997; Garbisu and Alkorta, 2001; Weis and Weis, 2004; Yoon et al., 2006; Antosiewicz et al., 2008; Usman and Mohamed, 2009). In particular,

phytoextraction seems a very promising biotechnology for pollutant removal, and is worldwide considered for commercial use.

To date, numerous scientists have focused on trace elements accumulation in macrophytes (e.g., Ye et al., 1997; Manios et al., 2003; Kamal et al., 2004; Fritioff and Greger, 2006; Mazej and Germ, 2009). In addition, several scholars have also studied macrophytes for phytoremediation of contaminated sediment and water (Hinchman et al., 1998; Gratao et al., 2005; Audet and Charest, 2007). Plants play an important role in wetland geochemistry through their active/passive transport of elements. Plants can absorb metals from soil and sediments through their root/rhizome system which is a common characteristic of phytoremediation (Bose et al., 2008). However, the potential of element uptake largely varies with plant species, metal availability in the system and other environmental conditions.

This study focused on the bioaccumulation capacity of trace elements in three macrophytes distributed worldwide: *Typha domingensis*, *Phragmites australis*, and *Arundo donax*. These species are emergent and perennial herbaceous plants that form dense monospecific stands in natural wetlands characterized by shallow and stagnant water, and muddy sediment. Plants of the *Typha* genus are among the most used species for pollutant removal in constructed wetlands (Merlin et al., 2002; Hadad et al., 2006; Maine et al., 2009). Specifically, southern cattail (*T. domingensis* Pers.) shows a high morphological plasticity that allows it to adapt to different environmental conditions and maintain a significant

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capacity of removal (Hadaad et al., 2010). Similarly, common reed (*P. australis* (Cav.) Trin. ex Steud.) and giant reed (*A. donax* L.) are tolerant species to trace elements, and are used in constructed wetlands and for phytoremediation of contaminated soil and sludge (e.g., Vymazal, 2011; Sagehashi et al., 2011).

Although several scholars investigated the phytoremediation capacity of trace elements in *T. domingensis*, *P. australis* and *A. donax* (Cardwell et al., 2002; Batty and Younger, 2004; Papazoglou, 2007; Vymazal et al., 2009; Fawzy et al., 2012), to date, few studies have compared the removal efficiency and biomonitoring capacity of these species in a field experiment based on a natural wetland affected by domestic and industrial wastewaters. A direct comparison of these plants may suggest which species best fit the phytoremediation of a given trace element, both in water and sediment, with specific environmental conditions. Indeed, the removal of trace elements by wetland plants can be greatly enhanced by the wise selection of suitable wetland species in suitable places. The criteria of species selection are the type of elements to be removed, the geographical position, environmental circumstances, and the accumulation capability of the species (Zayed et al., 1998). Summing up, this study analyzed the concentrations of Al, As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in *T. domingensis*, *P. australis* and *A. donax* in order to

- 1) identify accumulation patterns in the various organs, namely, root, stem, leaf;
- 2) assess biomonitoring capacity and removal efficiency of trace elements in water and sediment.

2. Materials and methods

2.1. Study area

The study area was the estuary of an urban stream where *T. domingensis*, *P. australis* and *A. donax* grow naturally. It deals with a 6-km long watercourse affected

mainly by municipal wastewater and road run-off, and goes through Catania (300,000 inhabitants), the second largest town of Sicily (Italy) (Fig. 1). The average annual flow is $1 \text{ m}^3 \text{ s}^{-1}$; 622 mm and 19.3°C are the average annual values of rainfall and temperature, respectively. Industrial discharges increase significantly in the final 2 km of stretch where the working of lumber and metal is the predominant activity. Given the low water quality, swimming is forbidden around the mouth area for almost 1 km along the shoreline (Italian Ministry of Health, 2009).

2.2. Sampling

Sampling was conducted in October 2012 according to the protocol described by Bonanno (2012). During sample collection, climatic conditions were stable, in particular, sunny, not windy, and without recent rains. A total of twenty sampling points were randomly chosen, partly in the right side and partly in the left one of the stream, along a spatial gradient 1 km upstream from the mouth. In each point, the following samples were collected: 2 L of water, 1 kg of sediment, four plant individuals. The basic plant sample consisted of the mixture of individuals from the same species, collected in one sampling point. In particular, species with similar height (on average 2 m) were collected from $5 \text{ m} \times 5 \text{ m}$ plots bordering the river bankline. Plants from the same sampling point were submerged at the same height which ranged from 30 to 80 cm. Only one plot was considered in each sampling point. Plant species were uprooted by using stainless-steel tools to avoid contamination. In particular, once roots were delicately shaken to remove coarse particles of sediment, plant samples were put in sterilized plastic bags. No plant sample was washed in the stream. Water samples were collected through a 2-L clean polyethylene bottle at a distance of 0.5–1 m from the bankline and at a depth of 20–50 cm (average water depth 1 m), whereas sediment collection was conducted at 1–3 m from the banks and within the plot. In particular, sediment samples were collected at a variable depth of 10–30 cm through stainless-steel tools, and put in glass containers. The basic sediment sample consisted of the mixture of randomly collected sediments within the plot until reaching a total weight of 1 kg. Samples were transported in a cool box ($5 \pm 2^\circ \text{C}$) to the laboratory the same day of the collection.

2.3. Chemical analysis

Sample preparation and chemical analysis were performed according to Bonanno (2012). Plant samples were preliminarily dissected in roots, stems and leaves in the laboratory. The basic root sample consisted of the mixture of root parts from all plants collected in one plot, in particular, root samples included both roots sensu stricto and rhizomes. The basic stem sample was instead prepared by

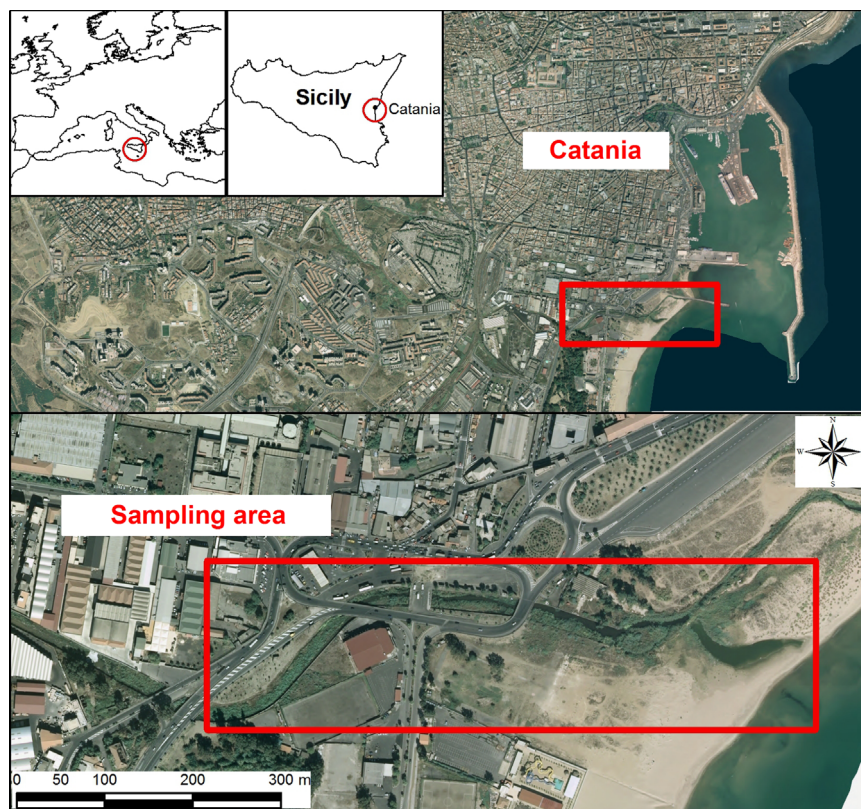


Fig. 1. Study area.

mixing twenty 10-cm long pieces of stem (five per plant), randomly cut from the plant individuals of one plot. Root and stem parts were cut off with stainless steel scissors, and put in glass containers. Regarding the leaves of *P. australis* and *A. donax*, the basic sample contained a mixture of a relatively constant number of leaves (30–35), manually removed from the top final 0.5 m of the species. The mean number of leaves of *Typha* per sample was instead lower than the other species, on average ten, because of the morphology of *Typha* itself. Plant samples had an average weight of 0.30–0.50 kg, and were washed to remove superficial impurities with tap water and then rinsed with deionized water.

Plant samples were dried at 30 °C for 48 h, and homogenized to a fine powder in an agate mortar to ensure uniform element distribution. Regarding sediment, dried samples were passed through a 2-mm diameter sieve. Plant and sediment samples followed the same procedures of digestion and analysis: an amount of 125 mg of homogenized sample was digested in a MW oven at 180 °C for 10 min with 10 mL of concentrated HNO₃. After cooling at room temperature, the digestate was filtered, centrifuged, and then diluted in distilled water. The concentrations of Hg and the other elements were respectively analyzed by AA FIAS and ICP-AES. Element concentrations in plant and sediment were calculated on a dry weight basis. Blank samples were digested in the same manner. Analytical accuracy was checked by analyzing the Standard Reference Material CTA-VTL-2 “tobacco leaves”. Recoveries were within 10% of the certified values.

Water samples were firstly passed through Whatman glass microfiber filters (grade GF/C: 1.2 µm). After filtration, water samples were acidified with HNO₃ to a pH < 2, to stabilize cations. To determine trace elements in water, except for Hg, a 45-mL aliquot of homogenized sample was transferred into an appropriate vessel where 5 ± 0.1 mL of concentrated HNO₃ was added. The vessel was then sealed, placed in a microwave system, and heated to 170 ± 5 °C for 20 min. At the end of the microwave program, the vessels were cooled for a minimum of 5 min before removing them from the microwave system, followed by venting the microwave containers in a fume hood before uncapping, to avoid a rush of acid vapor in the headspace. The sample was then transferred into an acid-cleaned bottle, diluted, and analyzed by ICP-AES. For Hg determination in water, a 100-mL aliquot of the water sample was transferred into a suitable closed container where 5 mL of H₂SO₄ and 2.5 mL of HNO₃ were added. The water sample was then digested in diluted solutions with 15 mL of KMnO₄ and 8 mL of K₂S₂O₈, and oxidized for 2 h at 95 °C. Sample containers were cooled to room temperature, and 6 mL of NaCl-(NH₂OH)₂·H₂SO₄ were added to reduce the excess of KMnO₄. Finally, Hg was reduced with 5 mL of SnCl₂ to elemental Hg, and measured by CV-AAS. The analysis of all samples was conducted in triplicate.

2.4. Statistical analysis

Statistical analysis was performed according to Bonanno (2012). The element concentrations of plant samples were statistically processed through a fixed-effects model of one-way ANOVA ($\alpha=0.05$) where the concentration of the generic element was the experimental factor, and trace values in root, stem, and leaf were the three different balanced treatments (levels), each of them composed of $N=20$ observations. The generic observation of a treatment referred to the chemical concentration of a given element in a plant organ collected in one plot (sampling point). Statistical analysis of trace concentrations in plant samples aimed to ascertain whether the various organs of a given species (roots, stems, and leaves) accumulate significantly different quantities of trace elements. Normality was preliminarily ascertained through the Shapiro-Wilk test according to which no log-transformation was necessary to normalize data; after that, Bartlett's test was applied to test homogeneity of variance. The significant difference of means was ascertained by performing a multiple sample contrasts with Bonferroni's correction. A possible linear correlation between plant organs and water/sediment was verified through Pearson correlation coefficient (r). All statistical calculi were

performed through the software SPSS version 19 (IBM Corporation). Plant ability to take up elements from growth media, and element translocation within the plant were respectively evaluated by applying the bioaccumulation factor (BAF) and the translocation factor (TF)

$$\text{BAF} = [\text{trace element}]_{\text{root}} / [\text{trace element}]_{\text{sediment}}$$

$$\text{TF} = [\text{trace element}]_{\text{organ}} / [\text{trace element}]_{\text{root}}$$

3. Results

Trace element concentrations and transfer factors are reported in Tables 1 and 2, respectively. Water showed the highest number of undetected elements whereas only one element (Hg) was below detection limit in sediment. As and Cd showed undetected values in plant organs, except for As in roots of *T. domingensis*. Hg was below detection limit only in *A. donax*. Element concentrations showed the highest values in sediment except for Hg and Ni. Regarding organs, the highest concentrations were generally found in roots, with the exception of *T. domingensis* for Cr and Ni, which showed similar values in root and stem, and for Hg and Zn, which showed the highest values in stem. *T. domingensis* showed significant correlations only with sediment, *P. australis* and *A. donax* also with water, especially the former. *T. domingensis* and *P. australis* showed a higher bioaccumulation capacity than *A. donax*. In particular, *T. domingensis* and *P. australis* proved hyperaccumulators of Hg. A different bioaccumulation trend was found in the macrophytes: root > stem > leaf in *T. domingensis*, and root > leaf > stem in *P. australis* and *A. donax*. The decreasing trends of the various samples were (undetected elements not shown):

- water: Cu > As > Zn > Ni
- sediment: Al > Mn > Zn > Cu > Pb > Cr > Ni > As > Cd
- *T. domingensis*_(root): Al > Mn > Zn > Ni > Cu > Pb > Cr > Hg > As
- *T. domingensis*_(stem): Al > Zn > Ni > Mn > Hg > Cu > Cr
- *T. domingensis*_(leaf): Al > Mn > Zn > Ni > Cu > Cr > Hg > Pb
- *P. australis*_(root): Al > Mn > Zn > Cu > Pb > Ni > Cr > Hg
- *P. australis*_(stem): Al > Mn > Zn > Cu > Pb > Hg > Cr > Ni
- *P. australis*_(leaf): Al > Mn > Zn > Cu > Ni > Hg > Pb > Cr
- *A. donax*_(root): Al > Mn > Cu > Zn > Ni > Pb > Cr
- *A. donax*_(stem): Al > Mn > Zn > Cu > Ni > Cr
- *A. donax*_(leaf): Al > Mn > Cu > Zn > Ni > Cr

4. Discussion

Most elements occur at trace levels in natural waters. Being trace elements in natural waters does not necessarily qualify them as trace elements in rocks. For example, aluminum is one of the

Table 1
Trace element concentrations in water [µg L⁻¹], sediment [mg kg⁻¹] and plant organs [mg kg⁻¹].

Element	Water	Sediment	<i>T. domingensis</i>			<i>P. australis</i>			<i>A. donax</i>		
			root	stem	leaf	root	stem	leaf	root	stem	leaf
Al	< 0.50	25,460 ± 3,240	1711 ± 230 ^b	358 ± 41.6 ^b	44.7 ± 3.31 ^b	2570 ± 420 ^b	86.6 ± 10.3 ^b	345 ± 29.8 ^b	77.4 ± 6.45 ^b	15.5 ± 2.02 ^b	21.2 ± 2.83 ^b
As	5.62 ± 0.44	7.86 ± 0.62	2.50 ± 0.15 ^b	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Cd	< 0.50	0.44 ± 0.05	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
Cr	< 0.50	25.7 ± 1.88	4.58 ± 0.64 ^{b,*}	5.44 ± 0.62 ^{b,*}	0.89 ± 0.06	4.12 ± 0.65 ^b	0.89 ± 0.09 ^b	1.12 ± 0.14 ^b	2.15 ± 0.26 ^b	0.52 ± 0.05	1.13 ± 0.13 ^b
Cu	22.7 ± 3.45	115 ± 17.6	16.4 ± 1.07 ^b	10.4 ± 1.45 ^b	2.41 ± 0.37 ^b	15.7 ± 2.02 ^{a,b}	3.16 ± 0.41 ^{a,b}	6.23 ± 0.75 ^{a,b}	7.42 ± 0.88 ^{a,b}	1.88 ± 0.15 ^b	3.06 ± 0.41 ^{a,b}
Hg	< 0.50	< 0.05	3.53 ± 0.22	11.4 ± 0.88	0.87 ± 0.05	3.06 ± 0.55	0.97 ± 0.04	1.84 ± 0.21	< 0.10	< 0.10	< 0.10
Mn	< 0.50	920 ± 104	108 ± 16.2 ^b	37.4 ± 5.13 ^b	26.2 ± 3.15 ^b	246 ± 21.5 ^b	28.4 ± 1.95 ^b	168 ± 21.7 ^b	19.7 ± 2.15 ^b	4.78 ± 0.68 ^b	10.2 ± 1.67 ^b
Ni	1.19 ± 0.15	19.3 ± 2.15	47.1 ± 6.51 [*]	48.4 ± 6.21 [*]	8.86 ± 1.05	8.36 ± 0.98 ^{a,b}	0.79 ± 0.06 ^{a,b}	2.21 ± 0.36 ^{a,b}	3.11 ± 0.45 ^{a,b}	0.97 ± 0.08	1.89 ± 0.21 ^b
Pb	< 1.00	64.2 ± 8.16	7.59 ± 1.02 ^b	< 0.10	0.71 ± 0.05	9.65 ± 1.32 ^b	1.08 ± 0.15 ^{a,b}	1.15 ± 0.10 ^{a,b}	2.46 ± 0.21 ^b	< 0.10	< 0.10
Zn	1.68 ± 0.26	294 ± 23.6	85.7 ± 12.4 ^b	126 ± 18.9 ^b	23.4 ± 2.78 ^b	128 ± 15.3 ^{a,b}	13.4 ± 1.87 ^{a,b}	24.8 ± 3.21 ^{a,b}	3.34 ± 0.29 ^{a,b}	1.93 ± 0.23 ^b	2.69 ± 0.32 ^{a,b}

^a Indicates a significant correlation between water and organ ($p < 0.05$).

^b Indicates a significant correlation between sediment and organ ($p < 0.05$).

^{*} Indicates similar values between organs of the same plant ($p < 0.05$).

Table 2Bioaccumulation and translocation factors (BAF and TF) in *T. domingensis*, *P. australis* and *A. donax*.

Element	<i>T. domingensis</i>			<i>P. australis</i>			<i>A. donax</i>		
	BAF		TF	BAF		TF	BAF		TF
	root/sediment	stem/root	leaf/root	root/sediment	stem/root	leaf/root	root/sediment	stem/root	leaf/root
Al	0.07	0.21	0.03	0.10	0.03	0.13	< 0.01	0.20	0.27
As	0.32	–	–	–	–	–	–	–	–
Cd	–	–	–	–	–	–	–	–	–
Cr	0.18	1.19	0.19	0.16	0.22	0.27	0.08	0.24	0.53
Cu	0.14	0.63	0.15	0.14	0.20	0.40	0.06	0.25	0.41
Hg	> 70.6	3.23	0.25	> 61.2	0.32	0.60	–	–	–
Mn	0.12	0.35	0.24	0.27	0.12	0.68	0.02	0.24	0.52
Ni	2.44	1.03	0.19	0.43	0.09	0.26	0.16	0.31	0.61
Pb	0.12	–	0.09	0.15	0.11	0.12	0.04	–	–
Zn	0.29	1.47	0.27	0.44	0.10	0.19	0.01	0.58	0.81

Factors were not calculated in case of concentrations below detection limits in plant organs (–).

major elements in rocks, but it occurs as a trace element in waters, due to its low mobility at Earth's surface (Gaillardet et al., 2003). In aquatic systems, metal ions are generally associated with particulate matter, and settle and accumulate in the bottom sediments which in turn become important sinks and sources of heavy metal pollution (Wang et al., 2009). In this study, trace elements in water showed a significant correlation with *P. australis* and *A. donax* for some elements. Rooted macrophytes, indeed, are generally influenced by element concentrations in sediment more than by those in water (Mucha et al., 2008), as a result, bioaccumulation is greater when sediment is highly contaminated.

According to the US Environmental Protection Agency (1996), trace element concentrations in sediment passed the ecotoxicological threshold in three cases: Cu (115 versus 34 mg kg⁻¹), Pb (64.2 versus 47 mg kg⁻¹), and Zn (294 versus 150 mg kg⁻¹). Cu and Zn contamination is likely due to adjacent metallurgic industries, whereas the high values of Pb should be mainly correlated with the spill of lubricating oils from nearby machine shops. Once released into the aquatic environment, a part of heavy metals is transferred to sediments by the processes of adsorption onto suspended matter and sedimentation (Zwolsman et al., 1993). Sedimentation of polluted particles results in high metal content in the soil of wetlands, which act generally as a sink of trace elements (Hart, 1982). The fact that the trace content of all studied plants is generally correlated with sediment, points out the role of sediment as the primary source of trace elements for rooted macrophytes, in agreement with literature data (e.g., Priju and Narayana, 2007; Mucha et al., 2008). Roots are the main pathway of trace elements to plants (Kumar et al., 2006). In this study, the highest element concentrations were generally found in roots, in line with most studies reporting that elements are largely retained in belowground organs (Stoltz and Greger, 2002; Weis and Weis, 2004; Obarska-Pempkowiak et al., 2005). Cell walls of the roots may prove suitable sites of accumulation and hence may be the reason of higher concentrations of trace elements in roots compared to other organs (Mishra et al., 2008). Metal tolerance is generally a function of plant phenology, vigor and growth as well as metal speciation and aquatic chemistry. Some species have been also found to develop tolerant ecotypes that either are able to survive higher concentrations of metals accumulated in their tissues, or have developed more efficient mechanisms to exclude metal ions from their tissues (Dunbabin and Bowmer, 1992).

Metal uptake by plants can be influenced by many factors including soil pH, cation exchange capacity, clay content, organic matter content and the presence of other ions (Kabata-Pendias, 2001). Plant communities respond differently to heavy metal

contaminated soils also depending on their ability to accumulate and detoxify various heavy metals (Usman et al., 2012). The plant species of this study showed a different capacity of trace element bioaccumulation. In particular, *T. domingensis* and *P. australis* showed similar values of trace element concentrations, significantly greater than *A. donax*. Therefore, *T. domingensis* and *P. australis* seem more suitable for trace element phytoremediation. A different translocation pattern was also found among the various species. The stem/root translocation factor showed higher values in *T. domingensis* as compared to *P. australis* and *A. donax*. This implied a different bioaccumulation trend in the various organs, namely, root > stem > leaf in *T. domingensis* (for most elements), and root > leaf > stem in *P. australis* and *A. donax*. Compartmentalization was also found in this study, in particular, the plants can restrict element translocation in root to shoot without showing any toxic effect, as a likely consequence of an internal detoxification capacity (Kabata-Pendias, 2001). These results are in general agreement with numerous studies according to which belowground organs of rooted macrophytes accumulate greater trace concentrations than shoots (e.g., Zurayk et al., 2002; Weis et al., 2004). In particular, several authors showed that element concentrations decrease in the order of root > leaf > stem in many macrophytes such as *P. australis* (Vymazal et al., 2009). In turn, the trend root > stem > leaf in *T. domingensis* seems relatively frequent within *Typha* genus as found for instance in *T. latifolia* by Carranza-Álvarez et al. (2008). The element by element analysis is discussed below.

Al was the most abundant element in sediment and macrophytes, whereas negligible values were found in water. In particular, Al concentrations in roots of *T. domingensis* and *P. australis* showed phytotoxic levels (1000–3000 mg kg⁻¹) according to Kabata-Pendias (2001). Al content in roots of *A. donax* was instead one order of magnitude lower than the other two species. This may suggest that the plants of this study adopt different strategies of tolerance to toxicity: the higher BAF of *T. domingensis* and *P. australis* implies a dominant bioaccumulation process based on high concentrations in belowground organs, whereas *A. donax* seems to follow metal exclusion mechanisms (BAF < 0.01). Despite the highest concentrations in plant organs as compared to the other elements, Al showed the lowest values of BAF and TF, thus proving the least mobile element. The physiological function of Al in plants is not clear, although there is some evidence that low levels of Al may have beneficial effects on plant growth (Kabata-Pendias, 2001). This may explain why the translocation is low from root to stem and leaf, as found in previous studies according to which elements like Al and Fe are mainly immobilized in the roots of metallophytes (Baker et al. 1994).

As and Cd showed concentrations below detection limit ($< 0.10 \text{ mg kg}^{-1}$) in all macrophytes with the only exception of As in the roots of *T. domingensis* (2.50 mg kg^{-1}). These values are in line with concentrations of As in plants growing on uncontaminated soils according to Kabata-Pendias (2001). Several studies showed that, in case of high contamination, rooted macrophytes can accumulate great quantities of As without showing symptoms of toxicity, as found by Mirza et al. (2010) in *A. donax*. The negligible concentrations of As in *P. australis* and *A. donax* may thus reflect the poor presence of this element in water and sediment. However, the relatively high content of As in the roots of *T. domingensis* but negligible root to shoot translocation, suggests that this plant has potentials for As phytostabilization. In general, plant species with higher BAF combined with lower TF can be suitable for phytostabilization of soils contaminated with heavy metals (Yoon et al., 2006; Padmavathiamma and Li, 2007). Cd is a toxic and non-essential element for metabolic processes. However, Cd did not show hazardous values in the study area because the concentrations of Cd in all plant species were lower than 0.10 mg kg^{-1} , and fell within the range of $0.01\text{--}0.30 \text{ mg kg}^{-1}$ found by Allen (1989) for plants in unpolluted environments. In case of Cd contamination, several studies showed that *Typha* spp., *P. australis* and *A. donax* are Cd-tolerant species, able to accumulate massive concentrations, whose strategy of defense should be correlated with increased antioxidant enzyme activities (e.g., Ederli et al., 2004; Carranza-Álvarez et al., 2008; Sagehashi et al., 2011).

Cr is considered as a toxic element for plants because an excess quantity may cause poor protein formation resulting from the disruption of N metabolism (Chatterjee and Chatterjee, 2000). The macrophytes of this study showed toxic levels of Cr in all organs ($> 0.50 \text{ mg kg}^{-1}$) according to Allen (1989). However, Pais and Jones (2000) reported that there is some evidence of toxic effects on plants for Cr concentrations higher than 10 mg kg^{-1} . Cr concentration in plants is mainly dependent on the soluble Cr fraction of soil. However, although most soils contain high levels of Cr, its availability to plants is significantly limited, probably because root tissues are not able to stimulate the reduction of Cr^{3+} to readily soluble Cr^{2+} (Kabata-Pendias, 2001). The ability of phytoremediation has commonly been characterized by a TF defined as the ratio of the metal concentration in the shoots to that in the roots (e.g. Baker, 1981; Yoon et al., 2006). In particular, plants with TF values > 1 are classified as high-efficiency plants for metal translocation from the roots to shoots (Ma et al., 2001). This study showed that *T. domingensis* has thus the potential for Cr phytoextraction.

Cu plays an important role in plant nutrition at low concentrations but becomes toxic at higher levels (Xu et al., 2006; Fairbrother et al., 2007). Kabata-Pendias (2001) reported that Cu levels of various plants from unpolluted regions in different countries do not exceed 8.40 mg kg^{-1} . In this study, *T. domingensis* and *P. australis* showed high levels of Cu, the former in roots and stems, the latter only in roots, thus reflecting Cu contamination in sediment better than *A. donax*. However, Cu concentrations in all macrophytes were below the phytotoxic range of $25\text{--}40 \text{ mg kg}^{-1}$ (Chaney, 1989). A greater bioaccumulation capacity of Cu in *T. domingensis* and *P. australis* is also supported by several studies (e.g., Cardwell et al., 2002; Vymazal et al., 2007).

Hg is a metal whose biological functions are currently not very clear, and although rare in water and soil, it can prove toxic for biota if its solubility increases (Bargagli, 1998). A remarkable result of this study is the high accumulation of Hg in the roots of *T. domingensis* and *P. australis* whose BAF values were greater than 70.6 and 61.2, respectively. When BAF is greater than 1, a species is a potential candidate for element phytostabilization of contaminated soils (Usman et al., 2012). Both species thus acted as efficient Hg bioaccumulators and their application is recommended for Hg phytostabilization. Depending on the ability of plants used as a phytoremediation medium to absorb, accumulate and tolerate

heavy metals, plant species are generally classified into three categories: hyperaccumulators, indicators and excluders (Ghosh and Singh, 2005). Specifically, hyperaccumulators comprise plant species that are tolerant to extreme levels of heavy metals, and can accumulate $> 10 \text{ mg kg}^{-1}$ in the case of Hg (Baker and Brooks, 1989). This study showed that *T. domingensis* acted as a hyperaccumulator of Hg with 11.40 mg kg^{-1} in the stem, thus proving a suitable species also for Hg phytoextraction. In particular, the stem/root TF of *T. domingensis* was 3.23, and Wei and Chen (2006) suggested that plant species with TF values > 1 , actively take up metals from the soil and accumulate them in their aboveground parts, therefore, can be good phytoremediators.

Mn is an essential element for plants and plays an important role in many redox enzymatic processes and in photosynthesis (Carranza-Álvarez et al., 2008). After Al, Mn was the most abundant element in the plant species of this study, in line with macrophytes growing in anthropogenic sites (Samecka-Cymerman and Kempers, 2001). In particular, Mn concentrations fell within the range of $50\text{--}500 \text{ mg kg}^{-1}$ which is considered toxic to plants according to Allen (1989). However, no plant species showed symptoms of toxicity. This study showed that *P. australis* performed better than the other species in terms of BAF and TF, thus its use should be preferred for possible actions of phytoremediation.

Ni is one of the most toxic elements and may cause growth reduction, yield depression and disorder in plant metabolism and physiology (Papazoglou et al., 2007). In this study, *T. domingensis* showed a better performance in terms of bioaccumulation and translocation. A BAF value of > 1 indicates indeed high efficacy in the phytostabilization of metal-contaminated soils (Usman et al., 2012), but a TF value of > 1 indicates also the possibility of phytoextraction for soil cleaning up. Ni concentrations in *T. domingensis* and in the roots of *P. australis* exceed the level of 5 mg kg^{-1} which is toxic to most plants (Allen, 1989), but also *A. donax* is able to tolerate Ni stresses thanks to a very effective antioxidant system protecting chloroplast and stomatal function (Papazoglou et al., 2007).

Pb is not an essential element for plant metabolism and can prove toxic. The content of Pb in macrophytes was in line with Pb natural values of plants, namely $0.05\text{--}3.0 \text{ mg kg}^{-1}$ (Kabata-Pendias, 2001), with the exception of the roots of *T. domingensis* and *P. australis* whose high concentrations reflect Pb contamination in sediment. Pb is also rather immobile in soil and tends to accumulate in roots, with a low translocation into the aboveground organs (Siedlecka et al., 2001; Carranza-Álvarez et al., 2008). Although *P. australis* showed higher concentrations than the other species, its values of BAF and TF were relatively low.

Zn is an important element for plants with essential functions regarding metabolism. Zn concentrations in all macrophytes were significantly below the phytotoxic range of $500\text{--}1500 \text{ mg kg}^{-1}$ (Chaney, 1989), and *A. donax* was the species with the lowest bioaccumulation capacity. *P. australis* showed high concentrations of Zn in roots but a significant action of phytostabilization should be excluded ($\text{BAF} < 1$). In turn, *T. domingensis* seems more suitable for phytoextraction given a value of stem/root TF > 1 .

The ability of some plant species to accumulate high concentrations of trace elements in their tissues, is an important strategy for the remediation of polluted sites. This methodology, known as phytoremediation, is a safe, eco-friendly and relatively inexpensive alternative. Macrophytes used for water treatment or soil phytoremediation, should have basic characteristics such as fast growth, high biomass production, and efficiency to accumulate high concentrations of nutrients and heavy metals over a long time exposure. In particular, this study showed that *T. domingensis* and *P. australis* outperformed *A. donax* in terms of trace element bioaccumulation. However, *T. domingensis* showed a better performance of bioaccumulation for some elements whereas *P. australis*

for others, thus, their combined use is recommended for optimizing the results of phytoremediation. The chemical alteration of the environment is a growing issue and the application of suitable bioaccumulator species may thus mitigate the consequences of polluting processes.

5. Conclusions

Multiple benefits can be derived from the application of plant species to human needs. In particular, *T. domingensis* and *P. australis* proved particularly suitable for trace element phytoremediation because they showed a higher efficiency to uptake the bio-available elements as compared to *A. donax*. These findings indicate that phytoremediation may provide a sustainable option to remediate heavy metal contaminated soils, but the proper selection of plant species for specific target metals must be achieved before implementing phytoremediation technique. Future studies are necessary not only to evaluate the phytoremediation efficacy of plant species against various trace elements in water and sediment, but also to investigate the mechanisms of phytostabilization and phytoextraction of these elements.

Acknowledgments

The author wishes to thank all the people involved in the sampling, and that provided scientific support. This study was partially financed by the Italian Ministry of University and Scientific Research (PRA no. 20104001098/2010).

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