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Hg, Cu, Pb, Cd, and Zn Accumulation in Macrophytes Growing in Tropical Wetlands

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Abstract The concentrations of Hg, Cu, Pb, Cd, and Zn accumulated by regional macrophytes were investigated in three tropical wetlands in Colombia. The studied wetlands presented different degrees of metal contamination. Cu and Zn presented the highest concentrations in sediment. Metal accumulation by plants differed among species, sites, and tissues. Metals accumulated in macrophytes were mostly accumulated in root tissues, suggesting an exclusion strategy for metal tolerance. An exception was Hg, which was accumulated mainly in leaves. The ranges of mean metal concentrations were 0.035–0.953 mg g^{-1} Hg, 6.5–250.3 mg g^{-1} Cu, 0.059–0.245 mg g^{-1} Pb, 0.004–0.066 mg g^{-1} Cd, and 31.8−363.1 mg g^{-1} Zn in roots and 0.033–0.888 mg g^{-1} Hg, 2.2–70.7 mg g^{-1} Cu, 0.005–0.086 mg g^{-1} Pb, 0.001–0.03 mg g^{-1} Cd, and 12.6–140.4 mg g^{-1} Zn in leaves. The scarce correlations registered between metal concentration in sediment and plant tissues indicate that metal concentrations in plants depend on several factors rather than on sediment concentration only. However, when Cu and Zn sediment concentrations increased, these metal concentrations in tissues also increased in *Eichhornia crassipes*, *Ludwigia helminthorriza*, and *Polygonum punctatum*. These species could be proposed as Cu and Zn phytoremediators. Even though macrophytes are important metal accumulators in wetlands, sediment is the main metal compartment due to the fact that its total mass is greater than the corresponding plant biomass in a given area.

Keywords Heavy metals · Wetlands · Macrophytes · Sediment

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1 Introduction

Tropical wetlands are ecosystems of a high biodiversity, being frequently impacted by metal contamination caused by human activities such as industrial, rural, and mining exploitation. Wetland plants play an important role in metal accumulation via filtration, adsorption, cation exchange, and through plant-induced chemical changes in the rhizosphere (Dunbabin and Bowmer 1992; Wright and Otte 1999). The accumulation of metals in sediment and different macrophyte species growing in contaminated sites has been studied all over the world (Cardwell et al. 2002; Coelho et al. 2009; Demirezen and Aksoy 2004;

Deng et al. 2004; Kumar et al. 2006; Ye et al. 1997). These investigations identified potential threats to natural aquatic ecosystems and also provide information as to which locally growing aquatic plant species might be of use in constructed treatment wetlands (Cardwell et al. 2002).

Wetland plants vary greatly in their degree of metal uptake (Deng et al. 2004; Hadad et al. 2006; Maine et al. 2006). Ellis et al. (1994) reported that the Zn concentration in *Typha latifolia* roots growing in a natural wetland utilized for storm water treatment in London was 0.700 mg g^{-1} dry weight. Cardwell et al. (2002) investigated 15 macrophytes in southeast Queensland, Australia, and found that the highest Cu concentration in leaves of emergent plants was approximately 34 μg g^{-1} and in roots was 1,571 μg g^{-1}. The range of Cd concentrations found in contaminated plants was 5–30 μg g^{-1} (Kabata-Pendias and Pendias 2000) and the value of uncontaminated plants is 1.9 μg g^{-1} (Outridge and Noller 1991). The range of Pb concentrations reported by Outridge and Noller (1991) for uncontaminated freshwater plants is 6.3–9.9 mg kg^{-1}.

Metal accumulation by wetland plants is affected by many factors (Yu and Gu 2007a, b, 2008a). In general, the variations in plant species, the growth stage of the plants, and element characteristics control absorption, accumulation, and translocation of metals (Deng et al. 2004; Yu and Gu 2008b). Metal uptake processes by macrophytes involve two stages: a fast one and a slow one (Maine et al. 2004; Suñé et al. 2007; Hadad et al. 2009). The fast stage, virtually instantaneous, occurs during the first hours of contact. This fast stage might also include the processes of chemical sorption (absorption) as chelation (Dushenkov et al. 1995; Schneider and Rubio 1999) and ion exchange (Lyon et al. 1969). Root-mediated precipitation and biological processes as intracellular uptake (transported through the plasmalemma into the cells) were probably responsible for the slower stage of metal removal from water.

The metal bioaccumulation capacity of the macrophytes grown in three tropical wetlands located in Colombia was determined. The studied wetlands are located in rural zones. Contamination sources in the area are rural small villages and mining exploitation sites. The objectives of the research were: (1) to determine the capacity of different macrophytes to uptake Hg, Pb, Zn, Cu, and Cd in three natural wetlands impacted by human activities; (2) to compare the metal concentration in plant tissues with the metal concentration in the surrounding water or sediment; and (3) to determine suitable macrophyte species for their use in constructed wetlands or as biomonitors.

2 Materials and Methods

2.1 Sampling and Analysis

Three natural wetlands were sampled in Córdoba state, Colombia (Fig. 1). Ayapel wetland is different from the other sampled wetlands because it presents gravel sediment. In the area, there are vast cultivation lands where agrochemicals are applied. Many poor houses were built on the margins of the wetlands. Nautical sports are practiced in these water bodies. The depths of the studied wetlands were found in the ranges of 0.5–1.5 m for Ayapel, 0.6–1.3 m for Betanci, and 0.4–1.4 m for Lorica.

Water, macrophytes, and sediment were collected at each sampling point. Samples were taken during a transitional period of low water level in winter (January–February of 2008). Water samples for chemical analyses were taken from the surface, by triplicate, kept cold, and sent to the lab. Water temperature and conductivity were measured in situ using a YSI portable conductivity meter. Dissolved oxygen (DO) was measured with a Horiba OM-14 portable meter. pH was determined in situ using an Orion portable meter. Chemical analyses were performed following APHA (1998). For the determination of metals in water, samples were treated according to EPA method 200.2 (USEPA 1991a, b) and analyzed by atomic absorption spectrometry (APHA 1998).

Sediment was sampled with an Eckman dredge and the upper 10 cm was collected. Redox potential (E_h) and pH of the bulk sediment layers were measured in situ with an Orion pH/mV meter. A sediment sample was analyzed in triplicate after digestion. For the determination of metals, samples were treated according to EPA method 200.2 (USEPA 1991a, b) and analyzed by atomic absorption spectrometry (Perkin-Elmer AAnalyst 800; APHA 1998). The analysis of Hg in sediment was carried out by cold-vapor atomic absorption spectroscopy (APHA 1998) after a separate digestion procedure using potassium permanganate as oxidizing agent.

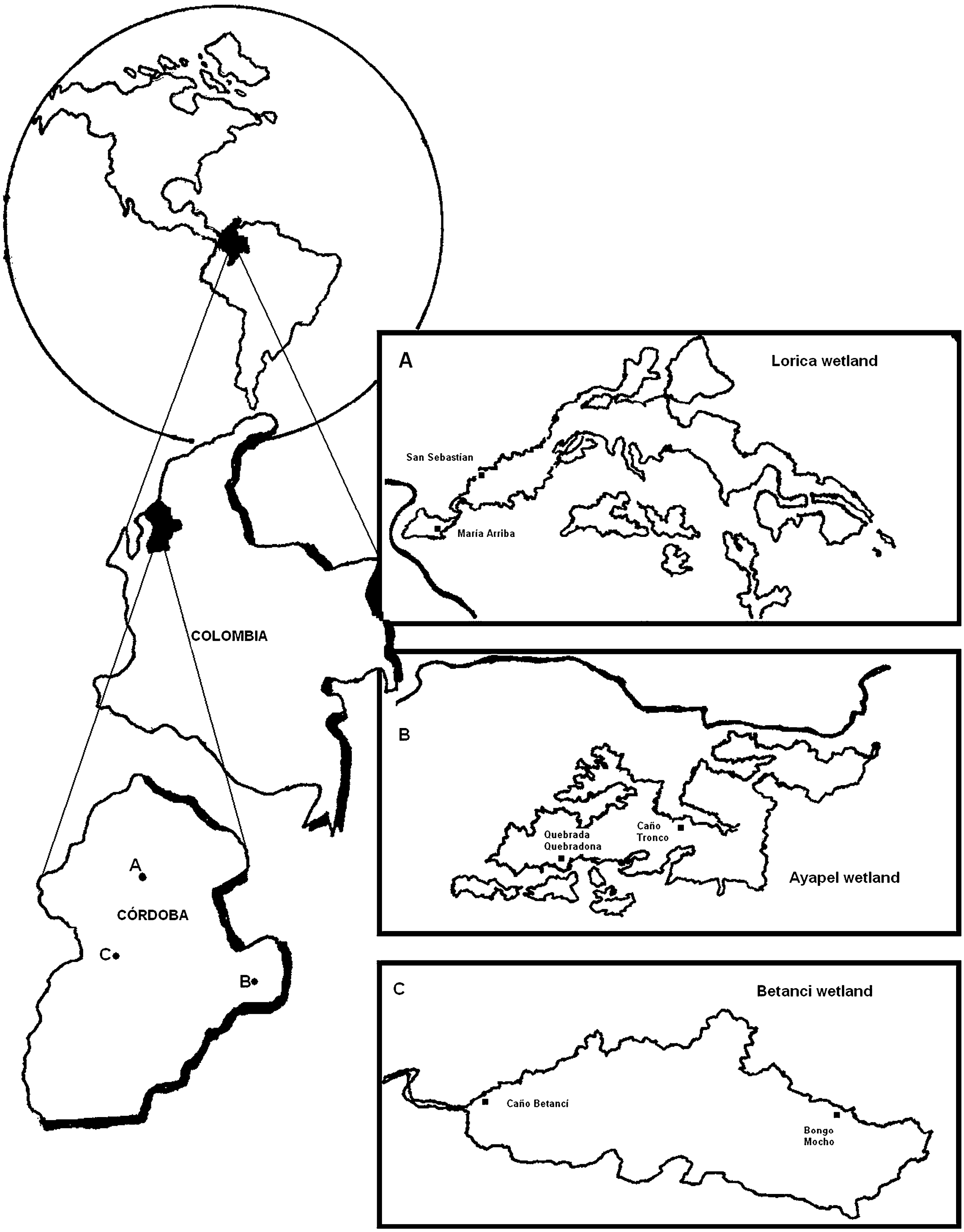


Fig. 1 Geographical location of the studied wetlands

Floating (*Pistia stratiotes* L. and *Eichhornia crassipes* (Mart.) Solms.) and rooted macrophytes (*Cyperus longus* L., *Marsilea quadrifolia* L., *Neptunia oleracea* Lour., *Ludwigia helminthorrhiza* (Mart.) H. Hara, *Polygonum punctatum* Elliott, and *Eichhornia azurea* (Sw.) Kunth.) were collected at the different sites. Macrophytes were sampled with a 0.50 × 0.50-m^2 sampler following Vesk and Allaway (1997). Four replicates were taken at each sampling. The macrophytes were then harvested and sorted by species in the laboratory, thoroughly washed with running tap water, and rinsed with deionized water to remove any sediment particles attached to the plant surfaces. The aboveground and underground tissues were then separated and oven-dried (70°C). The dried tissues were weighed and ground into powder for metal concentration analysis (Hg, Pb, Zn, Cu, and Cd). Tissue samples were digested according to EPA method 200.3 (USEPA 1991a, b) and analyzed by atomic absorption spectrometry (APHA 1998). Tissues were oven-dried (105°C) to constant weight to determine dry weight (APHA 1998). Not all species were sampled on all sites because some of them were not present during the low water level period.

Bioaccumulation factor (BF) was calculated as the ratio of roots/sediment metal concentration. In addition, metal translocation factor (TF) within a plant was expressed as the ratio of leaves/roots metal concentration to show metal translocation properties from roots to shoots (Stoltz and Greger 2002).

2.2 Quality Assurance/Quality Control

All glassware were pre-cleaned and washed with 2 N HNO_3 prior to each use. All reagents were of analytical grade. Certified standard solutions were used. The blanks were run all the time. Replicate analyses (at least ten times) of the samples showed a precision of typically <4% (coefficient of variation). The sample preparation methods used were also checked against the spiked sample which is the certified solution standards; mean recoveries were in the range 95.89–98.13%. The detection limits for water were: Zn=10.0 μg l^{-1}, Hg=0.5 μg l^{-1}, Cu=50.0 μg l^{-1}, Pb=4 μg l^{-1}, and Cd=2 μg l^{-1} The detection limits for macrophyte and sediment analysis were 0.05, 0.01, 1, 1.1, and 0.2 μg g^{-1} for Cd, Hg, Cu, Pb, and Zn, respectively.

2.3 Statistical Analysis

Two-factor analysis of variance was used to determine whether significant differences existed in metal tissue concentrations (leaves and roots) and BFs and TFs among different sites and species. The normality of residuals was tested graphically, and the homoscedasticity of variances was checked by applying Bartlett's test. Duncan's test was used to differentiate means where appropriate. A level of $p<0.05$ was used in all comparisons. Also, regression analysis was carried out with metal concentrations in roots and leaves versus metal concentrations in sediment. Levels of $p<0.05$ and $p<0.01$ were used in the regression analysis.

3 Results

Table 1 shows the measured parameters in water and sediment. In water, pH was slightly acid, except in Betanci wetland where pH was neutral. The lowest conductivity was registered in Ayapel wetland, while the highest was registered in Betanci wetland. Ayapel wetland presented the lowest DO concentrations. However, all sites were oxygenated. Hg, Cu, Pb, and Cd concentrations were under the detection limits of the analytical method. Zn presented the highest concentrations in water.

Sediment presented slightly acid pH in all studied sites. The highest organic matter in sediment was registered in Caño Betanci (Betanci wetland). In spite of the fact that some metals were not detected in water, they were accumulated in the bottom sediment. Cu and Zn showed the highest concentrations in sediment (Table 1). Ayapel wetland presented the lowest concentration of Cu and Zn in sediment. The concentration of Pb and Hg did not present significant differences among the sediments of the studied wetlands.

Heavy metal concentrations in tissues of plants collected at the three wetlands are shown in Figs. 2 and 3. Cu and Zn presented the highest concentrations in tissues. Metal concentrations in roots were significantly higher than those obtained in leaves. However, several species presented a significantly higher Hg concentration in leaves than in roots (Fig. 2).

The highest root concentrations of Cu were observed in *E. crassipes* (María Arriba), *P. punctatum* (San Sebastián and María Arriba), and *L. helminthorrhiza* (San Sebastián; Fig. 2). The highest

Table 1 Sites sampled (area) of the three wetlands of the Córdoba State, Colombia, and parameters measured in water and sediments of the three wetlands studied

Parameters	Ayapel wetland (2,500 km^2)		Betanci wetland (1,200 km^2)		Lorica wetland (3,045 km^2)	
	Quebrada la Quebradona	Caño Tronco	Caño Betanci	Bongo Mocho	María Arriba	San Sebastián
Water						
pH	6.0	6.5	7.0	7.0	6.0	6.8
Conductivity ($\mu S\ cm^{-1}$)	80	110	191	204	165	170
Water temperature (°C)	31.8	29.9	27.9	27.9	31.2	31.0
Environment temperature (°C)	37	37	35	36	37	36
DO ($mg\ l^{-1}$)	4.9	4.7	5.4	5.7	5.6	5.5
Zn ($\mu g\ l^{-1}$)	50	40	30	40	30	50
Hg, Cu, Pb, Cd ($\mu g\ l^{-1}$)	ND	ND	ND	ND	ND	ND
Sediment						
pH	5.76	6.27	6.61	6.48	6.72	6.59
Redox potential (mV)	101	112	133	145	118	140
Organic matter (%)	8.3	8.5	12.6	8.4	10.9	8.4
Hg ($\mu g\ g^{-1}$)	0.146	0.118	0.191	0.161	0.182	0.189
Cu ($mg\ g^{-1}$)	0.631	0.386	1.13	1.29	1.19	1.17
Zn ($mg\ g^{-1}$)	0.451	0.473	1.74	1.17	1.76	1.59
Pb ($\mu g\ g^{-1}$)	0.190	0.180	0.200	0.150	0.070	0.110
Cd ($\mu g\ g^{-1}$)	0.016	0.015	0.027	0.013	0.014	0.014

Sediment concentrations are expressed on the basis of dry weight (the water detection limits were: Hg=0.5 $\mu g\ l^{-1}$, Cu=50.0 $\mu g\ l^{-1}$, Pb=4 $\mu g\ l^{-1}$, Cd=2 $\mu g\ l^{-1}$)

ND not detected

Hg concentrations were observed in the plant tissues belonging to Ayapel wetland (Caño tronco and Quebrada la Quebradona sites). In all species and sites, Pb root concentrations were significantly higher than that of leaves (Fig. 3). The highest Pb root concentration was observed at *M. quadrifolia* on the site of Caño Tronco (0.245 $\mu g\ g^{-1}$), while the lowest was also registered in *M. quadrifolia* at Quebrada la Quebradona site (0.059 $\mu g\ g^{-1}$). For *C. longus*, the highest Zn root concentrations were registered in Bongo Mocho, San Sebastián, and María Arriba (Fig. 3). *E. azurea* and *P. punctatum* presented the highest Zn concentrations in roots at San Sebastián and María Arriba sites. *E. crassipes* presented the highest root concentration of Zn in María Arriba (270 $\mu g\ g^{-1}$), while *L. helminthorrhiza* showed the highest Zn root concentration at San Sebastián site (363 $\mu g\ g^{-1}$). The highest Cd concentrations in roots were registered in *L. helminthorriza* (San Sebastián site) and in *N. oleracea* (Quebrada la Quebradona site).

The lowest BFs were registered for Cu and Zn, indicating that these metals are mainly retained by sediment (Table 2). The metals that presented BF higher than 1 were Hg, Pb, and Cd, indicating a higher macrophyte uptake capacity of these metals. Cd presented this pattern on all sites, but Pb only at San Sebastián and María Arriba sites and Hg in Caño Tronco and Quebrada la Quebradona sites. According to the TFs, metals were accumulated fundamentally in roots (Table 3). Exceptions occurred for Hg in all sites and several species, with the exception of María Arriba.

Some significant correlations were found (Table 4), varying according to species, metal, and plant tissue. The concentrations of Zn, Pb, and Hg in *L. helminthorrhiza* roots significantly correlated with sediment metal concentrations, but only its Hg leaf concentration was correlated with Hg sediment concentration. Cu, Zn, and Pb concentrations in the leaves of *P. punctatum* correlated with metal concentration in sediment. These metal concentrations in roots did not correlate with sediment concentration.

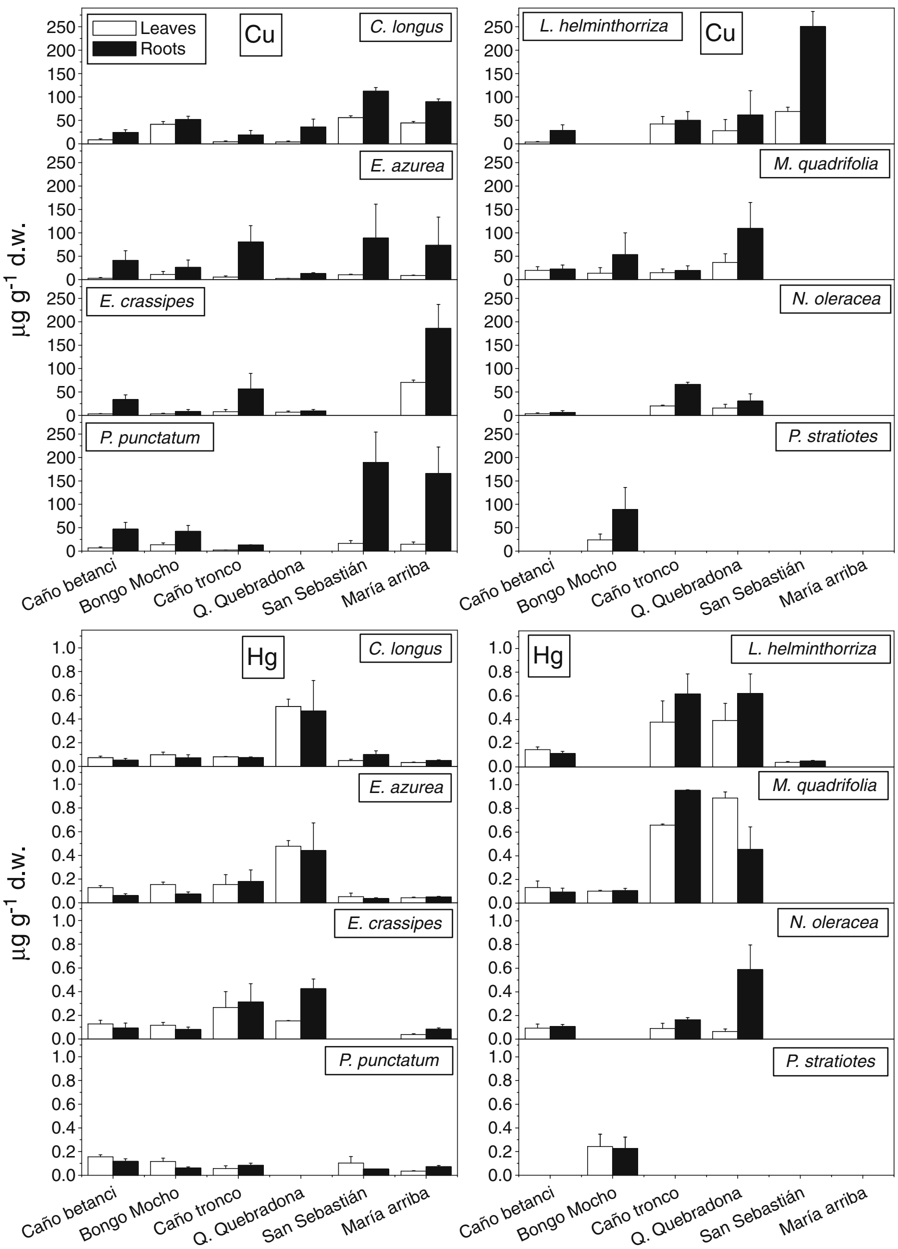


Fig. 2 Cu and Hg concentrations (µg g^{-1} dry weight) in the roots and leaves of the macrophytes sampled at each site

4 Discussion

Macrophyte species and populations differ widely in their ability to accumulate heavy metals. Our results show that metal concentrations in sediment and roots could be arranged in the decreasing order Zn > Cu > Hg > Pb > Cd. Even though metal concentrations in water were near the detection limits, metal concentration in sediment and in plant tissues presented significant values. Zn presented the highest concentration in water; this is probably the reason of the highest concentration in plants and sediment. Accordingly, the different compartments studied could be arranged as follows: sediment > roots > leaves > water, indicating that metal contamination could be easily detected in sediment or plant tissues. The general trend was that root tissues accumulated significantly higher concentrations of metals than leaves (with the exception of Hg), indicating high plant availability of metals as well as their limited

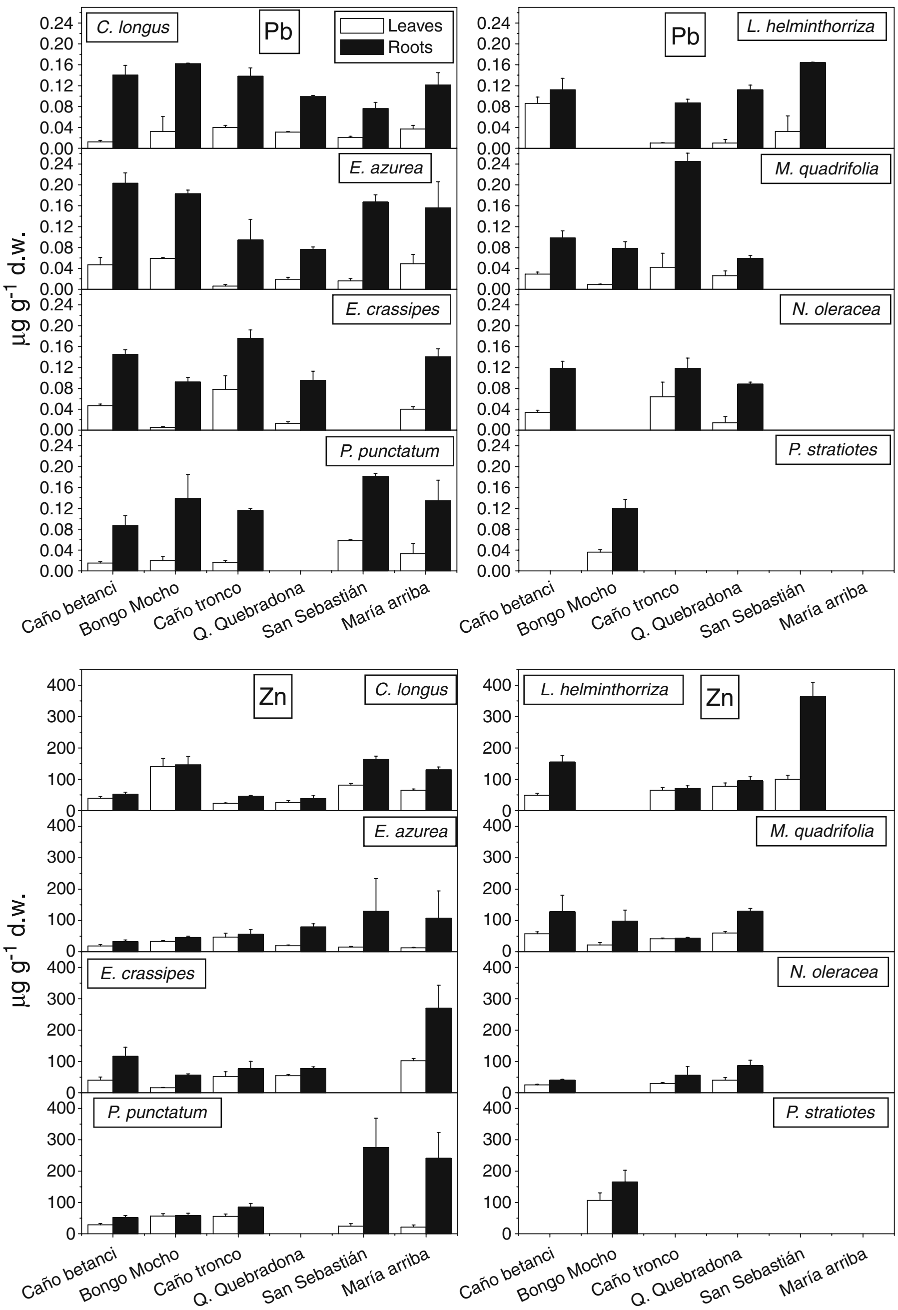
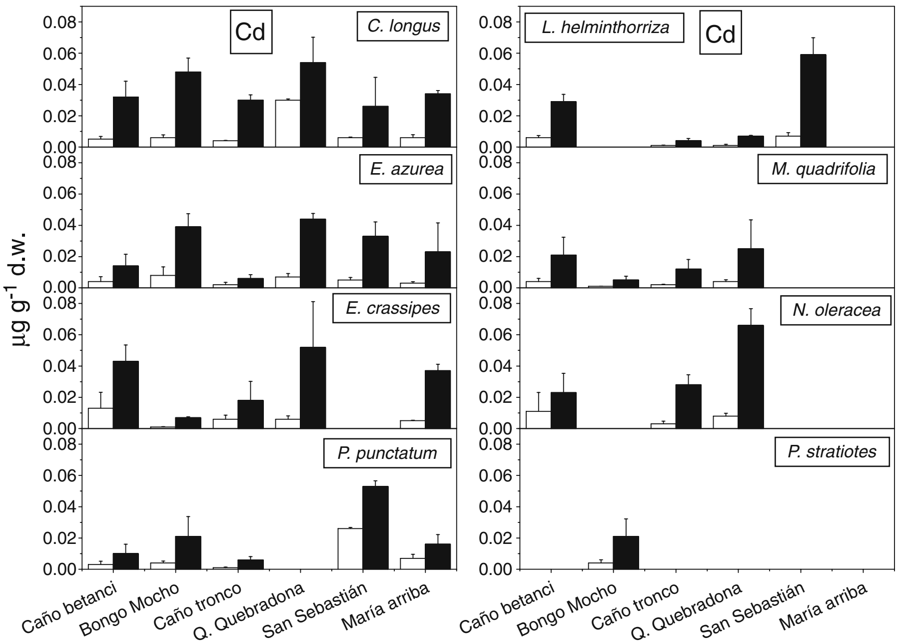


Fig. 3 Pb, Zn, and Cd concentrations (μg g^{-1} dry weight) in the roots and leaves of the macrophytes sampled at each site

mobility once inside the plant. Similar results were reported for rooted species (Deng et al. 2004; Keller et al. 1998; Taylor and Crowder 1983; Ye et al. 1997), in free-floating macrophytes (Banerjee and Sarker 1997; Hadad et al. 2007; Satyakala and Kaiser 1997), and in aquatic trees. Yu et al. (2008) studied the uptake and translocation of Cr(III) and Cr(VI) by two willow species. Roots and lower stems were the major sites for accumulation in weeping willows (*Salix babylonica* L.) exposed to Cr(VI) and Cr(III), respectively, while Cr was accumulated mostly in roots of hankow willows (*Salix matsudana* Koidz) amended with either of the chemical forms. Generally, only a small amount of metals taken up by roots is transported to the shoots. The exclusion of metals from aboveground tissues has been suggested as a

Fig. 3 (continued)



metal tolerance strategy (Taylor and Crowder 1983). A higher tolerance of roots than shoots together with a trend to decrease translocation with increasing metal concentration in the roots represents a common feature for the different metals and plants studied. Binding positively charged toxic metal ions to negative charges in the cell walls of the roots, metal phytate formation, and chelation to phytochelatins followed by accumulation in vacuoles have been invoked as mechanisms to reduce metal transport and increase metal tolerance (Chaney 1993; Loneragan and Webb 1993; Göthberg et al. 2004).

The present study shows that wetland plants can colonize sites with variable heavy metal concentrations in sediment. According to Kabata-Pendias and Pendias (2000), total metal in sediment in the ranges of 100–400 μg g^{-1} Pb, 70–400 μg g^{-1} Zn, 60–125 μg g^{-1} Cu, and 3–8 μg g^{-1} Cd would be considered toxic to plants. Zn and Cu sediment concentrations in the three wetlands studied greatly exceeded these limits. Therefore, the wetland plants grown on these contaminated sites have exhibited a high tolerance to these metals.

The mean Zn concentration in plants (aboveground tissues) is 66 μg g^{-1} (Outridge and Noller 1991), and its toxic level is up to 230 μg g^{-1} (Borkert et al. 1998). The ranges of Zn in most wetland plants presented here were generally lower than the levels reported for other emergent vegetation (Cardwell et al. 2002). Only some of them were within the range of contaminated plants (100–400 μg g^{-1}) reported by Outridge and Noller (1991). The highest Zn concentration (363 μg g^{-1}) in roots was found in *L. helminthorrhiza* on San Sebastián site (Fig. 3). However, this species did not show symptoms of phytotoxicity.

Cu is also essential to plant growth, but it has toxic effects when shoots or leaves accumulate Cu in concentrations exceeding 20 μg g^{-1} (Borkert et al. 1998). Cardwell et al. (2002) investigated 15 aquatic species in southeast Queensland, Australia, and found that the highest Cu concentration in leaves of emergent plants was 34 μg g^{-1} and in roots was 1,571 μg g^{-1}. As to uncontaminated sites, an average Cu concentration of 37 μg g^{-1} in the aboveground tissues of *T. latifolia* was reported by Outridge and Noller (1991). In this study, several Cu values in leaves were higher than the concentrations already mentioned. As in the case of Zn, the higher than toxic level of metal concentration in some species indicates that internal metal detoxification tolerance mechanisms might exist in these wetland plants, in addition to their exclusion strategies (Taylor and Crowder 1983).

The range of Cd concentrations found in contaminated plants was 5–30 μg g^{-1} (Kabata-Pendias and

Table 2 BFs (roots/sediment) for the studied metals

Species	Hg	Cu	Zn	Pb	Cd
Caño Betanci					
C. longus	0.273	0.021	0.030	0.699	1.193
E. crassipes	0.558	0.031	0.058	0.707	1.752
M. quadrifolia	0.482	0.020	0.073	0.488	0.785
N. oleracea	0.551	0.006	0.023	0.591	0.859
P. punctatum	0.612	0.042	0.030	0.434	0.359
E. azurea	0.318	0.037	0.018	1.015	0.511
L. helminthorrhiza	0.589	0.025	0.089	0.558	1.056
Bongo Mocho					
C. longus	0.449	0.040	0.124	1.082	3.724
E. crassipes	0.504	0.007	0.048	0.613	0.532
M. quadrifolia	0.651	0.041	0.083	0.519	0.385
P. punctatum	0.383	0.033	0.049	0.930	1.585
E. azurea	0.504	0.020	0.039	1.219	2.993
P. stratiotes	1.404	0.069	0.141	0.801	1.642
Caño Tronco					
C. longus	0.625	0.049	0.098	0.768	2.010
E. crasssipes	2.644	0.146	0.163	0.975	1.209
M. quadrifolia	8.093	0.050	0.091	1.361	0.812
N. oleracea	1.394	0.172	0.117	0.655	1.865
P. punctatum	0.714	0.033	0.180	0.644	0.405
E. azurea	1.528	0.208	0.118	0.522	0.369
L. helminthorrhiza	5.241	0.129	0.148	0.484	0.249
Quebrada la Quebradona					
C. longus	3.204	0.057	0.086	0.521	3.346
E. crassipes	2.916	0.015	0.172	0.501	3.247
M. quadrifolia	3.122	0.174	0.287	0.312	1.539
N. oleracea	4.039	0.049	0.192	0.465	4.101
E. azurea	3.025	0.021	0.176	0.399	2.738
L. helminthorrhiza	4.260	0.098	0.210	0.587	0.445
San Sebastián					
C. longus	0.528	0.096	0.102	0.692	1.880
P. punctatum	0.272	0.162	0.172	1.647	3.818
E. azurea	0.185	0.076	0.080	1.518	2.389
L. helminthorrhiza	0.261	0.214	0.227	1.489	4.241
María Arriba					
C. longus	0.272	0.075	0.074	1.733	2.431
E. crassipes	0.451	0.156	0.153	1.993	2.641
P. punctatum	0.395	0.139	0.136	1.909	1.124
E. azurea	0.272	0.062	0.060	2.234	1.649

Values are means of three replicates

Table 3 TFs (leaves/root) for the studied metals

Species	Hg	Cu	Zn	Pb	Cd
Caño Betanci					
C. longus	1.439	0.357	0.75	0.083	0.166
E. crassipes	1.4	0.091	0.348	0.323	0.354
M. quadrifolia	1.396	0.886	0.511	0.302	0.211
N. oleracea	0.902	0.566	0.628	0.288	0.988
P. punctatum	1.368	0.147	0.559	0.176	0.367
E. azurea	2.142	0.074	0.594	0.414	0.379
L. helminthorrhiza	1.3	0.125	0.317	0.796	0.21
Bongo Mocho					
C. longus	1.394	0.808	0.962	0.197	0.12
E. crassipes	1.522	0.368	0.285	0.057	0.074
M. quadrifolia	0.982	0.258	0.22	0.114	0.198
P. punctatum	1.95	0.322	0.974	0.172	0.327
E. azurea	2.142	0.416	0.72	0.323	0.202
P. stratiotes	1.075	0.268	0.644	0.302	0.207
Caño Tronco					
C. longus	1.1	0.22	0.499	0.288	0.134
E. crasssipes	0.852	0.138	0.671	0.615	0.418
M. quadrifolia	0.69	0.764	0.959	0.174	0.228
N. oleracea	0.57	0.307	0.863	0.569	0.126
P. punctatum	0.668	0.172	0.651	0.137	0.215
E. azurea	0.852	0.07	0.84	0.06	0.497
L. helminthorrhiza	0.595	0.847	0.929	0.114	0.24
Quebrada la Quebradona					
C. longus	1.323	0.111	0.67	0.31	0.594
E. crassipes	0.368	0.73	0.704	0.131	0.126
M. quadrifolia	1.884	0.335	0.465	0.431	0.237
N. oleracea	0.113	0.513	0.468	0.15	0.117
E. azurea	1.228	0.208	0.244	0.253	0.168
L. helminthorrhiza	0.625	0.455	0.82	0.091	0.126
San Sebastián					
C. longus	0.5	0.487	0.399	0.234	0.283
P. punctatum	1.993	0.109	0.110	0.323	0.492
E. azurea	1.41	0.159	0.178	0.096	0.168
L. helminthorrhiza	0.771	0.178	0.289	0.196	0.12
María Arriba					
C. longus	0.661	0.458	0.394	0.302	0.187
E. crassipes	0.474	0.435	0.531	0.288	0.134
P. punctatum	0.491	0.098	0.049	0.232	0.517
E. azurea	0.858	0.276	0.166	0.312	0.184

Values are means of three replicates

Table 4 Correlation coefficients between metal concentrations in tissues and sediment

Species	Hg	Cu	Zn	Pb	Cd
Roots					
C. longus	ns	ns	ns	ns	ns
E. crassipes	0.6933**	ns	ns	ns	ns
M. quadrifolia	0.8816**	ns	ns	ns	ns
N. oleracea	ns	0.8967**	ns	ns	ns
P. punctatum	ns	ns	ns	ns	ns
E. azurea	ns	ns	ns	ns	ns
L. helminthorrhiza	0.8856**	ns	0.6566*	0.7749**	ns
Leaves					
C. longus	ns	0.6974**	ns	ns	ns
E. crassipes	0.6601*	ns	ns	ns	ns
M. quadrifolia	ns	ns	ns	ns	0.6525*
N. oleracea	ns	0.8595**	ns	ns	ns
P. punctatum	ns	0.6920*	0.8000**	0.6304*	ns
E. azurea	ns	ns	ns	ns	ns
L. helminthorrhiza	0.7684*	ns	ns	ns	ns

ns no significant correlation

*$p<0.05$; **$p<0.01$

Pendias 2000). The data for Cd in plants obtained in the present study were lower than these values and even than the value of uncontaminated plants (1.9 µg g^{-1}; Outridge and Noller 1991). An internationally accepted criteria to ascertain the risks of Cd is the Zn/Cd ratio based on the antagonist effect that Zn in the soil or sediment exerts on the Cd assimilation by plants. The consensus is that the Zn/Cd ratios near 1,000 (Jones and Jarvis 1981) can efficiently exert an antagonism in plants faced with Cd. In our study, the Zn/Cd ratio was between 28,125 and 126,042, which indicates that Cd could not exert a phytotoxic effect on plants.

The highest Pb concentration in roots of 0.24 mg kg^{-1} was observed for *M. quadrifolia*. These results indicated that the studied species presented lower Pb concentrations in roots than the range proposed by Outridge and Noller (1991) for uncontaminated freshwater plants (6.3–9.9 mg kg^{-1}), 27 mg kg^{-1} being the Pb concentration toxic to plants (Beckett and Davis 1977). Consequently, the macrophytes studied were not contaminated by this metal.

Hg concentrations in leaves were higher than in roots in several species and sites (Table 3). Evidence exists showing different ways of Hg accumulation in plant tissues. Aksoy et al. (2005) proposed that a fraction of heavy metals contained in leaves may likely be due to atmospheric deposition. Coelho et al. (2009) reported that sea grasses accumulated considerable amounts of Hg in the aboveground biomass, with belowground/aboveground ratios reaching as high as 1.4, while rooted macrophytes accumulated less Hg in their aboveground biomass than macroalgae. In the work of Coquery and Welbourn (1994), there was no evidence for the transport of Hg from roots to shoots of the submerged isoetid macrophyte *Eriocaulon septangulare* With.

When the Cu and Zn sediment concentrations increased, these metal concentrations in tissues also increased in *P. punctatum*, *L. helminthorriza*, and *E. crassipes*, probably because they have a higher tolerance and metal accumulation capacity than the other species. Therefore, *E. crassipes*, *L. helminthorriza*, and *P. punctatum* could be proposed as Cu and Zn biomonitors. The different propagation form and the morphology of the plants studied are also important characteristics in the acquisition and accumulation of contaminants. Free-floating species reproduce principally by extending stolons on the surface of the water. Some emergent species reproduce mainly by occupying submersed and aerial spaces, while other emergent species have a vegetative reproduction by extension and ramification of their rhizomes, thus occupying aerial and underground spaces (Bernard 1999). The species that present a high biomass, such as *E. crassipes* (Wolverton and Mcdonald 1979) and *Polygonum* spp. (Tang and Fang 2001) are efficient contaminant bioaccumulators. Maine et al. (2006) reported that in a pilot and in an industrial constructed wetland, *E. crassipes* carried out the highest metal removal in the studied period due to its high productivity and to its tolerance capacity to the effluent composition. *E. crassipes* was widely studied for many years, but *Ludwigia* spp. and *Polygonum* spp. have been scarcely studied (Elifantz and Tel-Or 2002; Rai 2008; Tang and Fang 2001; Wei et al. 2009) and represent promissory species to be studied in further works.

The BF values for Hg, Pb, and Cd showed higher metal concentrations in roots in comparison with sediment in some macrophyte species, while BF values for Cu and Zn indicated they were mainly accumulated in sediment. Cd is a mobile metal in soils and sediment (Singh and McLaughlin 1996), and it is easily transported into roots. Because it is not an essential element for plants, it does not translocate to leaves as it can be corroborated with TF values in Table 3. As can be seen in Table 1, Cu and Zn presented high concentrations in sediment. The BF values for these metals indicated that these metals were accumulated mainly in sediment in comparison with plant roots. Contrarily, Hg was mainly accumulated in roots at Caño Tronco and Quebrada la Quebradona sites. The gravel sediment observed at these sites was not an efficient compartment of Hg accumulation, being transported to root tissues. According to the TF, Hg was translocated to leaves in several species and sites.

It can be seen that some plants presented significantly higher metal concentration than the corresponding sediment, but due to the fact that the total mass of sediment is higher than the corresponding plant biomass in a given area, sediment is the main metal compartment in the aquatic system. Nevertheless, the advantage of macrophytes is the possibility of being harvested, which leads to the important removal rates of metals in short times. Furthermore, it is important to highlight that macrophytes in conjunction with microorganisms influence the biogeochemical cycles (Barko et al. 1991; Sorrell and Boon 1992; Ye et al. 2001), promoting metal retention in the sediment. Most macrophytes play a role in maintaining oxidizing conditions by shoot-to-root oxygen transport (Armstrong et al. 1978). Such conditions promote formation of iron oxides, hydroxides, and oxyhydroxides and consequently result in metal removal by adsorption and co-precipitation. Reducing conditions would promote ion release to the water by reduction of the oxides and oxyhydroxides trapped in the substrate (Goulet and Pick 2001). Most metals in the pore water precipitate as metal oxides or adsorb onto organic matter at redox potentials higher than 100 mV. Between 100 and −100 mV, metal oxides are reduced, resulting in a release of dissolved metals. These metals can still adsorb onto organic matter if adsorption sites are available. Below −100 mV, metals may be mainly associated with sulfides (Goulet and Pick 2001). According to sediment redox potential, co-precipitation with iron oxyhydroxides probably determined metal retention in sediment.

Our study showed poor correlations between root or leaf and sediment metal concentrations (Table 4). This is in agreement with previous works (Dunbabin and Bowmer 1992; Greger 1999; Jackson et al. 1993; Keller et al. 1998; Zhang et al. 2009). Plants grown in metal-enriched substrata take up metal ions in varying degrees. This uptake is largely influenced by the bioavailability of metals. Notwithstanding, metal concentration determined in sediment is expressed as total metal concentrations, without discriminating among different metal forms. It would be desirable to determine metal speciation in future works to estimate which fraction is bioavailable for plants.

5 Conclusions

The studied wetland plants demonstrated that they can grow in metal-polluted areas and have the potential to uptake the studied metals. Metal translocation into leaves appears to be very restricted in all wetland plants so that harvesting of the aerial parts of plants will not be an effective source of metal removal in wetland systems. However, in the view of toxicology, this could be a desirable property as metals would not pass into the food chain via herbivores, thus avoiding potential risks to the environment. Hg is an exception to the general metal behavior since it translocates to leaves, this observation being of significant importance in relation to toxicological effects and metal bioaccumulation capacity.

The poor correlations registered between root or leaves versus sediment concentrations indicate that metal concentrations in plants depend not only on total metal sediment concentration.

Besides their metal uptake capacity, some species can develop a high biomass, which enhances their phytoremediation capacity. *E. crassipes* and *P. punctatum* could be proposed as Cu and Zn biomonitors and phytoremediators, being useful species to be utilized in constructed wetlands for the treatment of industrial effluents. Even though macrophytes are important metal accumulators in wetlands, sediment is the main metal compartment due to the fact that its total mass is greater than the corresponding plant biomass in a given area.

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