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Trace metal concentrations in coastal marshes of the Lower Paraná River and the Río de la Plata Estuary

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Abstract

Cu, Cr, Pb, Zn and Fe in water, sediment and tissue of the emergent macrophyte *Schoenoplectus californicus* were studied in three coastal environments differing in aquatic chemistry and tide amplitude: a deltaic floodplain marsh, a coastal vegetated strip of the river and a tidal marsh at the south margin of the Río de la Plata Estuary. Metal content in water was not significantly different between the river and the floodplain marsh. Metal content in sediments showed higher values in the marshes than in the river, suggesting a retention in the marsh. Except for Cu, the highest metal content in sediments and water was observed in the tidal marsh. Pb in plants was undetectable. Metal content was higher in rhizomes, except Cr, which was mainly stored in stems. Rhizome metal content was higher in the river, probably related to the higher redox potential of its sediments. Inflorescence metal content was higher in the marshes: the highest Zn, Cr and Fe contents were measured in the tidal marsh; the highest Cu content was in the floodplain marsh, together with the highest organic matter content of the sediments. Zn, Cr and Fe increased in standing drying stems and in inflorescences in late fall. Inflorescences showed the highest metal content after seeds had been released.

Introduction

Wetlands serve as sinks for nutrients to the extent that constructed wetlands are currently being employed to improve water quality (D'Angelo & Reddy, 1994). While there is abundant literature on the behavior and chemistry of nutrients, there is less information on the behavior of metals entering wetlands (Masscheleyn et al., 1992). Because floodplains are subjected to complex sheet flow exchange with rivers, there is a need for a better understanding of the biogeochemical processes transforming and assimilating anthropogenic substances.

With an area of 3 10^6 km^2 and a mean discharge of 25 000 m^3 s^{-1}, the Río de la Plata basin is the second largest hydrographic system in América. The Río de la Plata basin is composed of the Paraná and the Uruguay Rivers, which together form the Río de la Plata Estuary. The Paraná River itself, and the Paraguay River, its main affluent, are fringed by a 10–50 km wide floodplain, occupied by a complex network of marshes and riparian forests. The deltaic region differs from the upper stretches in that marshes occupy most of the inundation plain and, because of tidal influence, a large but variable amount of water is daily exchanged between the river and the floodplain, its magnitude depending on river stage height, tidal amplitude and wind action. The Paraná basin is under strong human influence. Damming, deforestation followed by intense agriculture, erosion, large urbanizations and huge industrial settlements occur. Sao Paulo and Buenos Aires, the two largest urban settlements in South América, lie in the opposite extremes of the basin. In spite of metal loads, no significant downstream change in concentration in water was observed in the final 600 km stretch of the Lower Paraná (Villar et al., 1998) suggesting that floodpalin marshes represent a sink that counteracts inputs to the river.

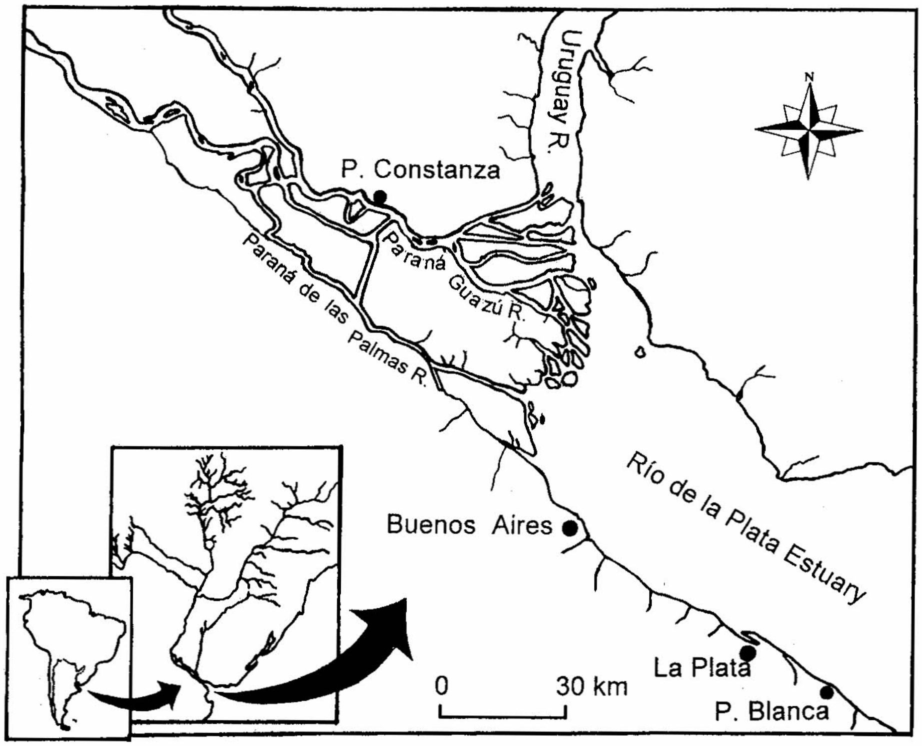

Figure 1. Location of the study sites at the Paraná River and at the Río de la Plata Estuary.

The contaminant loads to the right margin of the Río de la Plata Estuary are mainly derived from small rivers draining the industrial belt around Buenos Aires (Figure 1).

Our study was aimed to provide a insight into the role of coastal marshes in determining metal cycling: to what extent do coastal marshes retain contaminants, and how much metal is taken up and stored by the vegetation?

Description of sites studied

Representative sites were selected in the deltaic region of the Paraná River and on the right margin of the Río de la Plata Estuary. Samplings were performed on four occasions during 1995–96 (Sep. & Dec. 95 and Mar.–Apr. & Jun. 96). The Paraná River was sampled at Puerto Constanza, on the north side of the Paraná Guazú distributary branch, about 60 km upstream of the mouth (Figure 1). The river is fringed by a dense strip of *Schoenoplectus californicus*, separated by a small ridge from a vast inundation plain covered by *S. californicus* and *Cyperus giganteus*. The river was sampled at the coastal strip of vegetation and at the marsh 50 m inside from the ridge. Average tidal amplitude at Puerto Constanza is 20 cm. Variation through the year of river height is typically 1 m.

The samplings at the right margin of the Río de la Plata Estuary were performed in a tidal marsh, at Punta Blanca, about 70 km downstream Buenos Aires city (Figure 1). The marsh, roughly 1 km long and 200 m wide, is separated from the Río de la Plata Estuary by a sand bar. A channel connects the marsh with the estuary allowing tidal exchange of water. Mean tidal amplitude at Punta Blanca is 0.60 m (SHN, 1996).

Materials and methods

Analytical procedures

Dissolved oxygen concentrations and pH were determined *in situ* with an YSI 51B recorder and with an ORION 250A pH meter, respectively. Conductivity was determined with a Luftman conductance meter. Subsurface water samples were taken in triplicate, filtered through pre weighed Whatman GF/C filters and brought to the laboratory in dark and cold boxes. Suspended matter was determined as the dry weight difference of the filters and dissolved nutrients were determined in the filtrate. Soluble reactive phosphorus (SRP, molybdate-ascorbic acid) and nitrates plus nitrites (cadmium reduction, followed by diazotation) were determined following Strickland & Parsons (1972). Ammonium (indophenol blue) was measured according to Mackereth et al. (1978). Calcium and magnesium (EDTA titration), sodium and potassium (flame photometry), bicarbonate (Gran titration), sulfate (turbidimetry) and chloride (silver nitrate titration) were determined following APHA (1985). Total phosphorus (TP) and total organic carbon (TOC) were determined in unfiltered samples after Strickland & Parsons (1972).

Subsurface water samples for trace metal analysis were taken in triplicate with plastic bottles previously washed with acid and rinsed in double deionized water (DDW). Samples were acidified *in situ* with *pro analysi* nitric acid. Bottom sediments were taken with a 4.5 cm diameter Plexiglass core. The 2 cm upper layer was dried at 60 °C and ground. Subsamples were taken for texture determination following the Boyoucus method. Organic matter was assessed through C determination in sediments with a CARLO ERBA 1108 Elemental Analyzer. Rhizomes, stems and inflorescences (when present) of *S. californicus*, were sampled, dried at 60 °C, weighed and ground. Three replicates were taken, each replicate consisting of a composite sample of 10 plants pooled together. In subsamples of inflorescences, seeds were separated from other tissues and weighed separately. Samples were prepared for metal analysis as follows: water samples were added with concentrated HNO_3 and refluxed in 250 ml flasks. Sediments and plant tissue samples were digested in a CEM Microwave Sample Preparation System MDS-2000 with advanced composite vessels. Calibration curves were obtained using commercially available certified stock solutions. Total Cu, Zn, Pb, Cr and Fe determinations in water, sediments and plant tissue were performed by atomic absorption spectrometry (Shimadzu AA6501) with a graphite furnace atomizer (Shimadzu GFA6000), following Bettinelli et al. (1989). The detection limits for Zn, Cu, Pb, Cr, Cd and Fe were 0.2, 1, 5, 1, 0.2 and 1 $\mu g\ l^{-1}$, respectively. Traceability of heavy metals results was assessed by the use of certified reference materials. Measured concentrations were within the certified range for *Ulva lactuca* (BCR-279) while Zn and Cu were 5% lower than the certified value in an apple leave sample (SRM 1515, NIST). Measured concentrations did not differ more than 5% from certified concentrations of the interlaboratory round robin (Environmental Specimen Bank, Zurich, Germany and IAEA).

Data analysis

Metal speciation was assessed with the MINEQL equilibrium computer program (Schecher & McAvoy, 1991).

Data on limnological variates, metal content in water, sediments and plant tissue were tested for normality and homogeneity of variance using the Lilliefors and Bartlett tests, respectively (Sokal & Rohlf, 1981). Data which did not conform to the assumptions were transformed to logarithms. Two way ANOVA were performed to compare the limnological variates and metal content in water and sediments, with sampling site and date the main factors. Pairwise comparisons of sites and dates were performed by Tukey contrasts. One way ANOVA were performed to compare metal content in plant tissue between sampling sites in each sampling date. Sites were compared by Tukey contrasts. Software used was Statistica (1993).

Results

Water composition

Table 1 shows metal concentration in water at the three sampling sites. No significant differences were observed between the river and the floodplain marsh. Cr and Cu were higher in the tidal than in the floodplain marsh ($p < 0.05$). Zn in the tidal marsh was higher than in the floodplain marsh and than in the river, with a significance of $p = 0.06$. Pb was below the detection limit in most samplings at all sites.

Table 2 summarizes the limnological variates measured at the sampling sites. The river water was oxygenated and circumneutral. Conductivity was relatively low (102–166 $\mu S\ cm^{-1}$) and suspended matter high (59–95 $mg\ l^{-1}$). Water depth in the floodplain marsh was 15–30 cm during most of the study period, although occasionally water level dropped below the sediment surface. However, the marsh was never dry, and the sediment surface was always saturated with water. Suspended matter, oxygen, pH and nitrates were significantly lower in the marsh than in the river ($p < 0.01$). Temperature ranged 7–27 °C at surface. In spite of the marsh shallowness, vertical variations were observed. Oxygen concentration at the surface

Table 1. Heavy metal concentration in water at the Paraná River, its floodplain marsh and at the Río de la Plata tidal marsh. Mean ± standard deviation. Number of replicates: 3

	Date	Cu	Zn	Pb	Cr	Fe
			μg l^{-1}			mg l^{-1}
River	12 Sep. 95	8 ± 1.0	18 ± 6	<5	5 ± 1	2.0 ± 0.1
	8 Dec. 95	5 ± 3.2	30 ± 2	<5	11 ± 8	2.2 ± 0.5
	3 Apr. 96	5 ± 0.6	25 ± 6	7	11 ± 2	4.8 ± 0.2
	4 Jun. 96	3 ± 0.0	26 ± 0	<5	8 ± 6	3.3 ± 0.0
Floodplain marsh	12 Sep. 95	4 ± 1.5	24 ± 14	<5	3 ± 0	1.3 ±0.1
	8 Dec. 95	4 ± 2.9	25 ± 7	<5	9 ± 6	1.4 ± 0.1
	3 Apr. 96	5 ± 0.7	20 ± 9	<5	7 ± 1	6.9 ± 1.5
	4 Jun. 96	3 ± 0.6	25 ± 2	<5	4 ± 1	3.1 ± 1.1
Tidal marsh	5 Sep. 95	12 ± 5.4	20 ± 7	<5	9 ± 3	2.1 ± 0.8
	12 Dec. 95	7 ± 3.3	53 ± 16	<5	9 ± 5	11.0 ± 6.7
	26 Mar. 96	7 ± 1.2	31 ± 5	8 ± 2	22 ± 2	5.9 ± 0.8
	12 Jun. 96	4 ± 1.2	34 ± 7	<5	13 ± 6	3.4 ± 0.7

was 1–5.9 mg l^{-1}. Vertical variations were recorded, with oxygen depletion towards the sediment surface. Nitrate decreased from the river (mean: 212 μg N l^{-1}) to the floodplain (mean: 27 μg N l^{-1}), while ammonium did not show significant differences between sites. Bicarbonate, SRP and calcium were higher in the floodplain marsh ($p < 0.01$ for the former and $p < 0.05$ for the latter). Conductivity, as well as other major ions (sodium, potassium, magnesium and sulfate) did not show significant differences between the river and the floodplain marsh. The tidal marsh showed higher pH, oxygen, nitrates and sulfates than the floodplain marsh ($p < 0.05$). Suspended matter, conductivity, alkalinity, hardness, as well as most measured ions were also significantly higher than in the floodplain marsh ($p < 0.05$), except SRP. Large daily variation was observed. During the high water phase of each tidal cycle water composition resembled that of the coastal estuary water, while it progressively differed along the receding stage. Oxygen, pH and nitrate decreased along the receding phase, with depletion in summer (data not shown).

Table 2. Measured limnological variates at the Paraná River, its floodplain marsh and at the Río de la Plata tidal marsh. Mean of four samplings ± standard deviation. Number of replicates at each sampling: 3

	River	Floodplain marsh	Tidal marsh
T (°C)	21 ± 6	18 ± 8	22 ± 7
O_2 (mg l^{-1})	7.3 ± 1.2	3.4 ± 2.4	8.5 ± 1.9
Cond. (μS cm^{-1})	126 ± 28	167 ± 58	443 ± 150
pH	7.0 ± 0.4	6.0 ± 0.3	8.0 ± 0.9
Susp. mat. (mg l^{-1})	74 ± 15	13 ± 4	77 ± 52
N-NH_4^+ (μg l^{-1})	21 ± 6	36 ± 33	101 ± 87
N-NO_3^- (μg l^{-1})	212 ± 64	27 ± 19	426 ± 184
SRP (μg l^{-1})	41 ± 14	137 ± 80	102 ± 16
TP (μg l^{-1})	175 ± 58	133 ± 22	377 ± 89
TOC (mg l^{-1})	4.6 ± 1.9	7.8 ± 4.8	8.6 ± 3.4
HCO_3^- (mg l^{-1})	42 ± 5	55 ± 5	95 ± 35
$SO_4^{2=}$ (mg l^{-1})	7.1 ± 2.7	6.1 ± 1.6	10.0 ± 2.0
Cl^- (mg l^{-1})	12.4 ± 2.6	14.3 ± 2.8	59.2 ± 10.1
Ca^{2+} (mg l^{-1})	7.9 ± 1.2	10.0 ± 1.2	11.5 ± 5.6
Mg^{2+} (mg l^{-1})	3.9 ± 0.5	4.9 ± 1.4	11.2 ± 2.1
Na^+ (mg l^{-1})	15.2 ± 4.6	16.5 ± 4.8	48.0 ± 3.0
K^+ (mg l^{-1})	2.6 ± 0.5	2.3 ± 1.0	4.8 ± 0.4

Sediments characteristics

Table 3 shows metal content in bottom sediments at the three sampling sites. Metal content within the sediments did not show a temporal trend. The river showed the lowest metal content, the floodplain marsh was intermediate, the tidal marsh showed the largest metal content ($p < 0.01$), except for Cu which was similar at both marshes. Table 4 shows pH, carbon content and texture of sediments at the three sampling sites. The river sediments were sandy with low organic matter while marsh sediments were clayey with high organic matter, highest at the floodplain marsh. Both marsh sediments showed a black layer at varying depths. In

Table 3. Heavy metal concentration in sediments at the Paraná River, its floodplain marsh and at the Río de la Plata tidal marsh. Mean ± standard deviation. Number of replicates: 3

	Date	Cu	Zn	Pb	Cr	Fe
		(mg kg^{-1})				(%)
River	12 Sep. 95	29 ± 3	48 ± 8	<20	41 ± 7	2.0 ± 0.3
	8 Dec. 95	26 ± 6	35 ± 1	<20	45 ± 11	1.7 ± 0.1
	3 Apr. 96	12 ± 3	46 ± 4	29 ± 10	31 ± 9	2.2 ± 0.2
	4 Jun. 96	19 ± 2	66 ± 4	<20	46 ± 4	2.4 ± 0.1
Floodplain marsh	12 Sep. 95	58 ± 3	89 ± 5	28 ± 3	45 ± 7	2.8 ± 0.1
	8 Dec. 95	32 ± 7	64 ± 4	<20	55 ± 1	2.1 ± 0.2
	3 Apr. 96	29 ± 4	84 ± 14	31 ± 10	59 ± 19	2.5 ± 0.3
	4 Jun. 96	39 ± 6	92 ± 15	<20	58 ± 8	2.3 ± 0.3
Tidal marsh	5 Sep. 95	60 ± 0	107 ± 3	54 ± 2	60 ± 0	4.2 ± 0.1
	12 Dec. 95	37 ± 4	83 ± 6	42 ± 2	90 ± 1	3.9 ± 0.1
	26 Mar. 96	36 ± 6	113 ± 18	<20	90 ± 9	4.4 ± 0.8
	12 Jun. 96	45 ± 1	130 ± 1	23 ± 0	83 ± 1	4.5 ± 0.4

late summer most of the sediment profile was black except for a thin superficial layer. A year-round smell denoted sulfur release from the floodplain marsh. The river sediments did not show this black layer. Instead, a grey profile showed reddish sediments around active roots and rhizomes while black areas were observed around dead rhizomes.

Metals in plants

Table 5 shows metal content in plant tissue at the three sampling sites. Cr was higher in stems than in inflorescences and rhizomes. Within the stems, Cr increased in late fall (June), when standing stems became dry. In early fall (late March–early April), Cr in stems was higher in the tidal than in the floodplain marsh ($p < 0.05$). The rhizomes showed a higher content in the first sampling, decreased through the growing period and increased again in late fall. Significant higher contents were measured at the tidal marsh in the last two samplings ($p < 0.05$). The inflorescences developed earlier at the tidal marsh, where the first inflorescence sampling was performed in Sep. 95, while in the river and floodplain marsh this was not until Dec. 95. Within the inflorescences, Cr was higher at the earlier developmental stages and decreased in the Mar.–Apr. sampling, along with seed release. In Dec. 95, seeds contributed 30–50% to inflorescence dry weight, decreasing to 2–12% in Mar.–Apr. As in stems, Cr in inflorescences showed a final increase in late fall, after seeds had been released. In fall, Cr in the inflorescence was higher in the tidal marsh ($p < 0.05$).

Table 4. Texture, C content and pH in bottom sediments at the Paraná River, its floodplain marsh and at the Río de la Plata tidal marsh. Number of replicates: 3

	River	Floodplain marsh	Tidal marsh
C (%)	0.4	10	4
Clay (%)	8	40	39
Lime (%)	34	36	45
Sand (%)	58	24	16
pH	6.4–7	5.5–6.6	6.2–6.6

Pb in plant tissue was below the detection limit (<1 mg kg^{-1}) at the three sampling sites, irrespective of Pb content in sediments.

Cu was higher in rhizomes and inflorescences than in stems. The Cu content in rhizomes was higher at the river ($p < 0.05$), in spite of the higher Cu content of the tidal sediments. Cu in stems did not show significant differences between sampling sites. In the last two samplings, higher Cu contents were found in the inflorescences of the floodplain marsh than in the river and tidal marsh ($p < 0.05$).

Zn was higher in rhizomes, intermediate in inflorescences and lower in stems at the three sampling sites.

Table 5. Metal content in *S. californicus* stems, inflorescenses and rhizomes at the Paraná River, its floodplain marsh and at the Río de la Plata tidal marsh. Mean ± standard deviation. Number of replicates: 3

		Date	Cu	Zn	Pb	Cr	Fe
					(mg kg^{-1})		
River	Stem	8 Dec. 95	3.1 ± 0.7	4.8 ± 2.3	<1	2.0 ± 0.06	73 ± 6
		3 Apr. 96	2.1 ± 0.0	6.3 ± 0.0	<1	2.2 ± 0.6	147 ± 13
		4 Jun. 96	1.8 ± 0.2	12.0 ± 1.0	<1	7.1 ± 1.2	113 ± 16
	Infloresc.	8 Dec. 95	4.6 ± 0.5	6.1 ± 1.9	<1	1.3 ± 0.5	52 ± 12
		3 Apr. 96	3.6 ± 0.6	7.8 ± 3.2	<1	0.14 ± 0.03	76 ± 19
		4 Jun. 96	3.9 ± 0.3	14.5 ± 0.7	<1	0 .8 ± 0.14	248 ± 36
	Rhizome	4 Jun. 96	18.0 ± 1.4	74.0 ± 4.2	<1	1.5 ± 0.1	1205 ± 64
Floodplain marsh	Stem	12 Sep. 95	4.3 ± 2.3	12.1 ± 2.9	<1	1.8 ± 0.3	31 ± 20
		8 Dec. 95	2.9 ± 0.4	3.6 ± 1.2	<1	1.6 ± 0.6	31 ± 3
		3 Apr. 96	5.4 ± 1.1	3.0 ± 1.6	<1	1.7 ± 1.2	48 ± 9
		4 Jun. 96	1.5 ± 0.1	8.7 ± 0.3	<1	5.6 ± 1.1	174 ± 2
	Infloresc.	8 Dec. 95	3.9 ± 0.3	8.6 ± 0.6	<1	2.2 ± 1.0	43 ± 4
		3 Apr. 96	5.4 ± 1.1	6.5 ± 0.9	<1	0.2 ± 0.05	92 ± 11
		4 Jun. 96	7.1 ± 0.3	22.0 ± 0.6	<1	1.7 ± 0.96	260 ± 25
	Rhizome	12 Sep. 95	5.2 ± 0.4	20.0 ± 10.8	<1	4.3 ± 2.7	225 ± 85
		8 Dec. 95	6.5 ± 1.0	43.7 ± 17.0	<1	0.44 ± 0.2	615 ± 35
		3 Apr. 96	4.2 ± 1.9	2.8 ± 1.0	<1	0.32 ± 0.1	322 ± 123
		4 Jun. 96	6.1 ± 0.7	33.7 ± 11.6	<1	1.0 ± 0.2	415 ± 52
Tidal marsh	Stem	5 Sep. 95	1.5 ± 0.3	7.4 ± 1.2	<1	2.5 ± 1.5	78 ± 34
		12 Dec. 95	3.3 ± 0.1	2.4 ± 1.1	<1	4.3 ± 2.3	193 ± 23
		26 Mar. 96	2.2 ± 0.8	5.5 ± 2.2	<1	3.2 ± 0.6	113 ± 42
		12 Jun. 96	1.6 ± 0.3	10.8 ± 1.3	<1	5.8 ± 0.4	489 ± 128
	Infloresc.	5 Sep. 95	4.9 ± 2.4	24.5 ± 2.1	<1	3.0 ± 0.6	-
		12 Dec. 95	3.9 ± 0.2	8.9 ± 2.1	<1	1.5 ± 1.3	69 ± 10
		26 Mar. 96	3.1 ± 0.3	10.1 ± 4.4	<1	1.1 ± 0.3	145 ± 26
		12 Jun. 96	4.1 ± 0.5	27.0 ± 1.0	<1	2.4 ± 0.2	427 ± 41
	Rhizome	5 Sep. 95	4.4 ± 1.6	35.7 ± 8.4	<1	1.3 ± 1.3	155 ± 56
		12 Dec. 95	4.4 ± 1.4	56.0 ± 35.0	<1	0.76 ± 0.5	1933 ± 306
		26 Mar. 96	3.2 ± 2.0	28.9 ± 24.0	<1	0.63 ± 0.3	225 ± 65
		12 Jun. 96	2.9 ± 1.4	31.0 ± 12.0	<1	2.3 ± 1.0	504 ± 50

Within the rhizomes, no seasonal trend was evident. In fall, Zn content was higher in the river. Zn was higher in initial inflorescence developmental stage, decreasing in the two following samplings (Dec. 95 and Mar.–Apr. 96), to increase again in late fall (Jun. 96). The river and floodplain marsh also showed the late fall increase, with Zn content at the later sampling higher in the tidal marsh, intermediate in the floodplain marsh, and lower in the river ($p < 0.05$). Zn in stems was higher at the beginning of the growing period (Sep. 95), when young stems were about 50 cm tall, decreased along the growth period, when stems grew up to two meters, and showed a maximum in late fall, when stems became dry. At the beginning of the growing period, Zn in stems was higher in the floodplain than in the tidal marsh ($p < 0.05$), while at the end of the growing season, no significant differences existed between them, being lower at the floodplain marsh than at the river ($p < 0.05$).

Fe was often higher in rhizomes, without seasonal trend. Fe in inflorescences showed large increments in late fall, at all sites, and was higher in the tidal marsh ($p < 0.05$), while in stems, it showed a large increment in late fall in the marshes, but not in the river, and was higher in the tidal than in the floodplain marsh ($p < 0.05$).

Discussion

Since the floodplain marsh is fed by the river, incoming floodplain and river waters have the same chemical composition. Within the marsh, changes in water composition were noticeable in suspended matter, oxygen, pH and nitrate depletion, while bicarbonate, calcium and SRP increased. Although not statistically significant, the lower metal concentration in floodplain water was consistent with a significantly higher sediment metal content at this site, suggesting enhanced metal retention by the marsh. Higher metal concentrations in water in the tidal marsh suggests a higher load at this site leading to higher Fe, Cr and Zn sediment content. Metal retention was attained together with a high organic matter content of marsh sediments, consistent with results from Otte et al. (1993). Macrophyte primary production was high at the three sampled sites (Villar et al., 1996, and unpublished data). Organic matter accumulated in the marsh, but not in the river sediments, where flushing caused sediments to be dominated by sand. The observed oxygen and nitrate depletion in the floodplain water was indicative of a large demand of electron acceptors, caused by organic matter decomposition in the marsh sediments. The black sediments of the marshes suggest FeS_2 formation. In the oxygenated, circumneutral river water, metals were predicted to be present mainly as Zn^{2+}, Pb^{2+}, $Cu(OH)_2$ and Fe_2O_3 by the MINEQL program. Villar et al. (1998) showed that the particulate metal fractions were significant in the river. Partial dissolution of carbonate-rich riverine suspended matter, upon settling to the acid floodplain sediments, caused increased calcium, bicarbonate and SRP concentrations in the floodplain waters (Bonetto et al., 1994). Acidification may also cause desorption of sorbed metals. Diffusion of dissolved metals into the reductive sediments would cause their fixation as sulfide precipitates (MINEQL; Comish & Ong,1988). Higher metal retention by marsh sediments suggests that metal fixation prevailed over metal dissolution here. As the tidal marsh waters were harder and more alkaline than the floodplain waters, metals would mostly be associated to carbonates (MINEQL program). Since the sedimentary environment of the tidal marsh was also acid and reductive, metal speciation in the sediments was expected to be as in the floodplain marsh. Both Cr(VI) and Cr(III) may be expected to be transported by river water, the former dissolved and the latter particulate (Masscheleyn et al., 1992). Within the marshes, waterlogging causes settling of the particulate Cr(III) fraction. Masscheleyn et al. (1992) showed that dissoved Cr(VI) spiked to wetland soil and the overlying water was reduced to Cr(III) and removed from solution before nitrate was exhausted. Since in our study incoming nitrate from the river is fastly depleted within the floodplain environment, it may be expected that Cr(VI) would be reduced to Cr(III) at the water-sediment boundary. Sedimentary fixed Cr(III) would not be converted to Cr(VI), even if the sediments were reoxydized (Masscheleyn et al., 1992).

Zn and Pb in sediments in this study lie amongst the lowest values quoted by Bryan & Langston (1992) in a review on metal accumulation in sediments of United Kingdom Estuaries (Zn: 100–3000; Pb: 20–2753 $\mu g\ g^{-1}$), and Zn is lower than most values reported by Otte et al. (1991) in a survey along the Dutch coastal marshes (60–600 $\mu g\ g^{-1}$). Cr was higher than most reported levels in the English estuaries (27–207 $\mu g\ g^{-1}$) and was lower than those reported in the area influenced by industrial loads of Lake Mezzola basin, in Northern Italy (148–264 $\mu g\ g^{-1}$, Baudo et al., 1985). Cu lie in the middle of the quoted range (7–2398 $\mu g\ g^{-1}$) for English Estuaries, was higher than most reported figures (6–60 $\mu g\ g^{-}1$) for Dutch marshes, and similar to reported values in Lake Mezzola basin (15–51 $\mu g\ g^{-1}$, Baudo et al., 1985).

Metal concentration in plant tissue was generally higher in the rhizomes, except Cr which was higher in the stems, a fact often interpreted as inactivation and storage of excess toxic elements in the cell walls (Baudo et al., 1985). Otte et al. (1991) found two to three times higher metal content in the roots that in shoots of monocotyledons (like *S. californicus*) whereas dicotyledons showed similar metal concentration in shoots and roots. In our study, the higher Fe, Zn and Cu, but similar Cr content measured in rhizomes in the river in spite of having the lowest metal content in the sediments suggests an influence of sediment redox condition on metal availability. Both strongly reduced and oxidized conditions produce metal immobilization as sulfide precipitates and insoluble hydrous oxides, respectively, with greatest mobility associated with intermediate redox potential (Jackson et al., 1993). Gambrell et al. (1991) showed that high levels of soluble Zn occurred at acid pH and oxidized conditions. Gambrell (1994) reported that Cu and Zn plant uptake increased with soil redox conditions. On the contrary, soluble Cr is less affected by soil pH and redox values (Gambrell et al., 1991; Masscheleyn et al., 1992).

At the river, larger metal content (except Cr) in rhizomes was accompanied by generally lower metal contents in stems and inflorescences. It seems likely that metal translocation may vary in response to site-specific conditions. Otte et al. (1991) did not find a correlation between metal content in shoots and roots of different species in a survey of Dutch coastal marshes.

Within the marshes, higher Fe, Cr and Zn in the inflorescences occurred where Fe, Cr and Zn in the sediments were higher, suggesting a causal relationship. Otte et al. (1993) found a correlation between Zn in roots and inflorescences of *Spartina anglica*, and sediment Zn. In our study, Cu in sediments was not significantly different in both marshes, while inflorescences showed higher Cu in the floodplain marsh. The organic matter pool is larger in the floodplain than in the tidal marsh, hence it may be expected that a larger concentration of natural organic ligands and therefore a larger Cu availability will occur in the floodplain marsh. Jackson et al. (1993) found that Cu in plant tissue was correlated to sediment organic matter and pH, but not to metal concentration of the sediments.

Seasonal variation of heavy metal concentrations in plant parts have often been quoted (Otte et al., 1991). Reallocation of nutrients and reserve substances from drying stems to rhizomes, as suggested by decreased N and P content in stems (Villar et al., 1996 and unpublished data), contributed to increased Zn, Fe and Cr stem concentration in late fall. However, a similar increase in metal content in fall was observed in inflorescences, without a parallel decrease in N or P content. Concentrating Fe, Zn and Cr in decaying plant parts, such as standing dry stems and inflorescence structures after seeds had been released, represents a selective allocation and provides *S. californicus* with a detoxification mechanism. Baudo et al. (1985) observed increasing Cr, Cu and Zn concentrations in the inflorescences of *Phragmites australis* along the growing period. Metals were selectively accumulated in the lemna of spikelets.

Metal concentration in plant tissue was lower than in sediments. Similarly, Baudo et al. (1985) reported that values measured in *Typha* and *Phragmites* never exceeded those in the substrate. Although the mouth of urban streams draining the industrial belt arround Buenos Aires show severe contamination (Villar et al., 1998), metal concentrations in plant tissue found in this study lie within reported ranges and were lower than surveys of heavily contaminated areas (Baudo et al., 1985; Otte et al., 1991).

Conclusion

This study has shown that *S. californicus* coastal marshes represent large metal sinks, and therefore counteract cultural imputs to the river. Metals are mainly stored in the sediments. However, the role of macrophytes is important because they provide the organic matter pool of the marsh soil and enhance the retention of the small sized fractions of the river suspended matter. High organic matter and clay content and, consequently, low redox potentials, confers the marsh soil its capacity to retain metals. *S. californicus* attained good growth in highly contaminated sites (Villar et al., 1998). High tolerance seems related to the formation of insoluble sulfur compounds of most metals in these sediments. Marsh plants are known to oxidize the rhizosphere (Reddy et al., 1989) and thus create a microenvironment in which uptake of nutrients and metals occur. Yet, *S. californicus* may reduce excess metal uptake by translocating it to decaying plant structures.

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References

APHA, 1985. Standard Methods for the Examination of Water. Amer. Publ. Health Assoc., Washington, 1268 pp.

Baudo, R., E. Canziani, G. Galanti, P. Guilizzoni & G. Rapetti, 1985. Relationships between heavy metals and aquatic organisms in lake Messola hydrographic system, (Northern Italy). 6. Metal concentrations in two species of emergent macrophytes. Mem. Ist. ital. Idrobiol. 43: 161–180.

Bettinelli, M., U. Baroni & N. Pastorelli, 1989. Determinazione diretta di elementi in traccia in matrici ambientali mediante impiego dellþ ETA-AAS Zeeman e midificazione di matrice. In Minoia, C. & S. Caroli (eds), Applicazioni dell'ETA-AAS Zeeman nel laboratorio chimico e tossicologico. Eddizioni Libreria Cortina, Padova (Vol. 1): 49–81.

Bonetto, C., L. de Cabo, N. Gabellone, A. Vinocur, J. Donadelli & F. Unrein, 1994. Nutrient dynamics in the deltaic floodplain of the Lower Paraná River. Arch. Hydrobiol. 131: 277–295.

Bryan, G. W. & W. J. Langston, 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Envir. Pollut. 76: 89–131.

Comish, M. F. & J. H. Ong, 1988. Trace metals. In Bodeck, I.; J. W. Lyman, W. F. Rechl & D. Rosemblat (eds), Environmental Inorganic Chemistry. Pergamon Press, New York: 7.0/1–7.15/11.

D'Angelo, E. M. & K. R. Reddy, 1994. Diagenesis of organic matter in a wetland receiving hypereutrophic Lake Water: II. Role of inorganic electron acceptors in nutrient release. J. envir. Qual. 23: 937–943.

Gambrell, R. P., 1994. Trace and toxic metals in Wetlands – A Review. J. envir. Qual., 23: 883–891.

Gambrell, R. P., J. B. Wiesepape, W. H. Patrick & M. D. Duff, 1991. The effects of pH, redox, and salinity on metal release from a contaminated sediment. Wat. Air Soil Pollut. 57–58: 359–367.

Jackson, L., J. Rasmussen, R. Peters & J. Kalff, 1991. Empirical relationships between the element composition of aquatic macrophytes and their underlying sediments. Biogeochemistry 12: 71–86.

Jackson, L., J. Kalff & R. Rasmussen, 1993. Sediment pH and redox potential affect the bioavailability of Al, Cu, Fe, Mn and Zn to rooted aquatic macrophytes. Can. J. Fish. aquat. Sci. 50: 143–148.

Mackereth, F., J. Heron & J.Talling, 1978. Water analysis: some revised methods for limnologists. Freshwater Biol. Assoc. Cd. Pub. No 36, 120 pp.

Masscheleyn, P., J. Pardue, R. DeLaune & W. H. Patrick, 1992. Chromium redox chemistry in a Lower Mississippi Valley Bottomland hardwood wetland. Envir. Sci. Technol. 26: 1217–1226.

Otte, M. L., S. J. Bestebroer, J. M. van der Linden, J. Rozema & R. A. Broekman, 1991. A survey of Zinc, Copper and Cadmium concentrations in salt marsh plants along the Dutch Coast. Envir. Pollut. 72: 175–189.

Otte, M. L., M. Haarsma, R. Broekman & J. Rozema, 1993. Relation between heavy metal concentrations in salt marsh plants and soil. Envir. Pollut. 82: 13–22.

Reddy, K. R., W. H. Patrick & C. Lindau, 1989. Nitrification-denitrification at the plant root-sediment interface in wetlands. Limnol. Oceanogr. 34: 1004–1013.

Schecher, W. & D. McAvoy, 1991. MINEQL: a chemical equilibrium program for personal computers. Environmental Research Software, Edgewater.

SHN, 1996. Tablas de marea. Separata zona Río de la Plata. Servicio de Hidrografía Naval. Buenos Aires, 86 pp.

Sokal, R. & F. J. Rohlf, 1981. Introducción a la bioestadística. Reverté, Barcelona, 362 pp.

Statistica, 1993. Statistica for windows. Release 4.3. Copyright Statsoft Inc.

Strickland, J. & T. Parsons, 1972. A practical Handbook for seawater analysis. Bull. 167. J. Fish. Res. Bd. Can. Ottawa, 311 pp.

Villar, C., L. de Cabo & C. Bonetto, 1996. Macrophytic primary production and nutrient concentrations in a deltaic floodplain marsh of the Lower Paraná River. Hydrobiologia 330: 59–66.

Villar, C., M. Tudino, C. Bonetto, L. de Cabo, J. Stripeikis, L. d'Huicque & O. Troccoli, 1998. Heavy metals concentration in the Lower Paraná River and right margin of the Río de la Plata Estuary. Verh. int. Ver. Limnol. 26: 963–966.

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