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Assessment of Heavy Metal Accumulation in Two Aquatic Macrophytes: a Field Study

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ABSTRACT

In order to assess the potential of two autochthonous plant species of Argentina as bioindicator and/or fitoremediator of metals, the accumulation of zinc, copper, cadmium and mercury in *Schoenoplectus californicus* and *Ricciocarpus natans* was studied. Total and labile contents of surface (SS) and near root sediments (NRS) were analyzed. Labile contents in NRS were lower than in SS, which was associated to the presence of *S. californicus*. Copper and zinc were positively correlated with total organic matter (TOM) whereas cadmium was not, suggesting low affinity of Cd to TOM. *S. californicus* presented the same pattern of distribution of those found in sediments (Zn > Cu > Cd). Bioaccumulation factors were close to (cadmium) or higher (zinc) than 1, while it was not conclusive for copper, revealing the *S. californicus* behaviour as an accumulator for zinc and indicator for cadmium. *R. natans* presented the highest metal levels among all studied matrix, with the presence of mercury. These findings showed the capacity of both *S. californicus* and *R. natans* to accumulate and remove heavy metals from sediments and water, which might be useful for phytoremediation programs.

Keywords: aquatic macrophytes, *S. californicus, R. natans,* heavy metals, phytoremediation, bioindicator.

RESUMO

Avaliação da acumulação de metais pesados em duas macrófitas aquáticas: um estudo de campo

O acúmulo de zinco (Zn), cobre (Cu), cádmio (Cd) e mercúrio (Hg) foi estudado em duas macrófitas aquáticas autóctones da Argentina, *Schoenoplectus californicus* e *Ricciocarpus natans,* a fim de avaliar o seu potencial como bioindicadoras e/ou fitoremediadoras de metais pesados. Em paralelo, foram analisadas a concentração total e lábil dos sedimentos superficiais (SS) e dos sedimentos próximos à raiz (NRS). A concentração lábil nos NRS foi mais baixa que nos SS, o que esteve associado à *S. californicus*. Cobre e zinco estiveram correlacionados positivamente com a matéria orgânica total (TOM) em ambos os sedimentos, ao contrário do cádmio, que mostrou baixa afinidade pela TOM. A concentração dos metais em *S. californicus* apresentou o mesmo padrão de distribuição (Zn > Cu > Cd) encontrado nos sedimentos. O fator de bioacumulação (FB) variou de próximo (Cd) ou maior que 1 (Zn), a não uniforme (Cu), sugerindo *S. californicus* como acumulador de zinco e bioindicador de cádmio. *R. natans* apresentou os mais altos níveis de metais dentre todas as matrizes analisadas, além de apresentar concentrações de mercúrio, que não foi observado em nenhuma outra matriz. Conclui-se que ambas as espécies *S. californicus* e *R. natans* apresentam capacidades para remover metais pesados, podendo ser utilizadas em programas de fitoremediação.

Palavras-chave: macrófitas aquáticas, *S. californicus*, *R. natans*, metais pesados, fitoremediação, bioindicator.

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INTRODUCTION

During recent years pollution of aquatic systems by heavy metals has attracted attention of the scientific community. Unlike organic pollutants, natural processes of decomposition do not remove heavy metals. On the contrary, they may be accumulated in aquatic biota and can be converted to organic complexes, which may be even more toxic. Metals are introduced into aquatic systems as a result of weathering of soils and rocks, volcanic eruptions and a variety of human activities involving mining, processing and use of metals or substances containing metal contaminants (Jain, 2004). Once released in aquatic environments they are generally bound to particulate matter, which eventually settle down and become incorporated into sediments. Therefore, surface sediment is the most important reservoir or sink of metals and other pollutants in aquatic environments (Förstner & Wittmann, 1983). The metal mobility in sediments is controlled by numerous biotic and abiotic factors, such as microbial activity, pH, temperature, organic matter content, cation exchange capacity (CEC) and redox potential (Jain, 2004). These factors determine different chemical species with different bioavailability.

Macrophytes are aquatic plants growing in or near waters which can be emergent, submerged or free floating. They are an important component of aquatic communities due to their roles in oxygen production, nutrient cycling, water quality control, sediment stabilization, to provide habitat and shelter for aquatic life, and also for being considered efficient heavy metal accumulators (Vardanyan & Ingole, 2006). Due to these characteristics these plants have been successfully used as biological monitors and remediators of environments contaminated with heavy metals.

Phytoremediation is considered an effective, low cost and preferred cleanup option for moderately contaminated areas. Although the capacity of aquatic macrophytes to accumulate metals is well documented (Szymanowska *et al.*, 1999; Demirezen & Aksoy, 2004; Deng *et al.*, 2004; Vardanyan & Ingole, 2006), their potential to accumulate heavy metals differ markedly among species.

The increase of environmental problems and scarceness of studies related to heavy metals, make the present study an important asset to find autochthonous species capable of cleaning up aquatic environments contaminated by metals. Thus, the aim of this work was to evaluate the capacity of two native macrophytes of Argentina, *Schoenoplectus californicus* and *Ricciocarpus natans*, to accumulate and remove heavy metals from their natural environment.

MATERIAL AND METHODS

Studied area and sample collection

The study was conducted at the end of the summer season in the Nahuel Rucá lagoon (37º 37’S – 57º 25’W) (Figure 1), a shallow water body located in a big wetland area in the Central East of Argentina. It belongs to Mar Chiquita coastal lagoon basin, an UNESCO MAB (Man and the Biosphere) Reserve since 1996. The studied lagoon have a total area of 245 ha, receives the inflow of Dulce creek at the Northwest coast (affluent), and its waters flow out by an artificial channel (effluent) at the South coast into Mar Chiquita lagoon, which is connected to the sea. The surrounding lands are used for agriculture and stockbreeding. Three sample sites were established for the study, where sediments, *S. californicus* and *R. natans* were collected in triplicate. Site 1 (S1) correspond to the affluent, Dulce creek; Site 2 (S2) is situated in an extensive area where a dense community of *S. californicus* is developed, forming a sedimentary island, and Site 3 (S3) correspond to the effluent, where waters flow out towards Mar Chiquita lagoon (Figure 1).

Sediments

Two kinds of sediment, surface sediments (SS) and near root sediments (NRS), were collected. Surface sediment samples were taken in areas without plants (2 m from reedbed) by clean plastic cores (9 cm long × 3 cm internal diameter); while NRS samples were taken manually from bulk sediments close to *S. californicus* roots. Samples were air-dried at room temperature to obtain a constant weight, grounded in a mortar, and sieved to 80 mesh (< 180 um) to clean off plant debris, keeping them at -20 ºC until metal determination. The amount of total organic matter (TOM) was determined as loss –of weight- on ignition (LOI); ashing the sample at 550 ºC for 1 hour. The grain size was obtained following the pipette method described by Galehouse (1971). Sediment pH was determined by potenciometry in water suspension (1:1, sediment:water ratio) after equilibration for 1 hr (Fields & Parrot, 1966).

Macrophytes

Schoenoplectus californicus (giant bulrush) and *Ricciocarpus natans* (purple-fringed riccia) were selected based on their wide geographical distribution, and the great representativeness in the studied lagoon. *S. californicus* is a perennial vascular plant that grows below water level along the American continent (Lahitte *et al.*, 1997) and takes up nutrients from sediments through their roots. Their presence in the littoral margins of streams and lakes, where metal concentrations are high, suggests a great tolerance to them (Arreghini *et al.*, 2001). *R. natans* is a cosmopolitan free floating liverwort that can uptake elements directly from water (Samecka-Cymerman *et al.*, 2002).

Aboveground (shoots) and underground (roots) tissues of *S. californicus* were sampled. Each sample was a pool of 10 plants. In the laboratory they were thoroughly rinsed with water to remove any sediment particles attached to the surface. *R. natans* was collected with a square sampler (30 × 30 cm). At the laboratory, remains and associated fauna were removed. Since *R. natans* is a liverwort (plants that lack vascular tissues, stems, flowers and roots), the whole body was analyzed. Both species were dried at room temperature to constant weight, ground into fine powder with a mortar to ensure sample homogenization and kept in plastic bags at – 20 °C prior to analyses.

Sample analysis

Plant tissues were digested in duplicate with concentrated perchloric and nitric acids (Merck, analytical grade, 1:3) for the

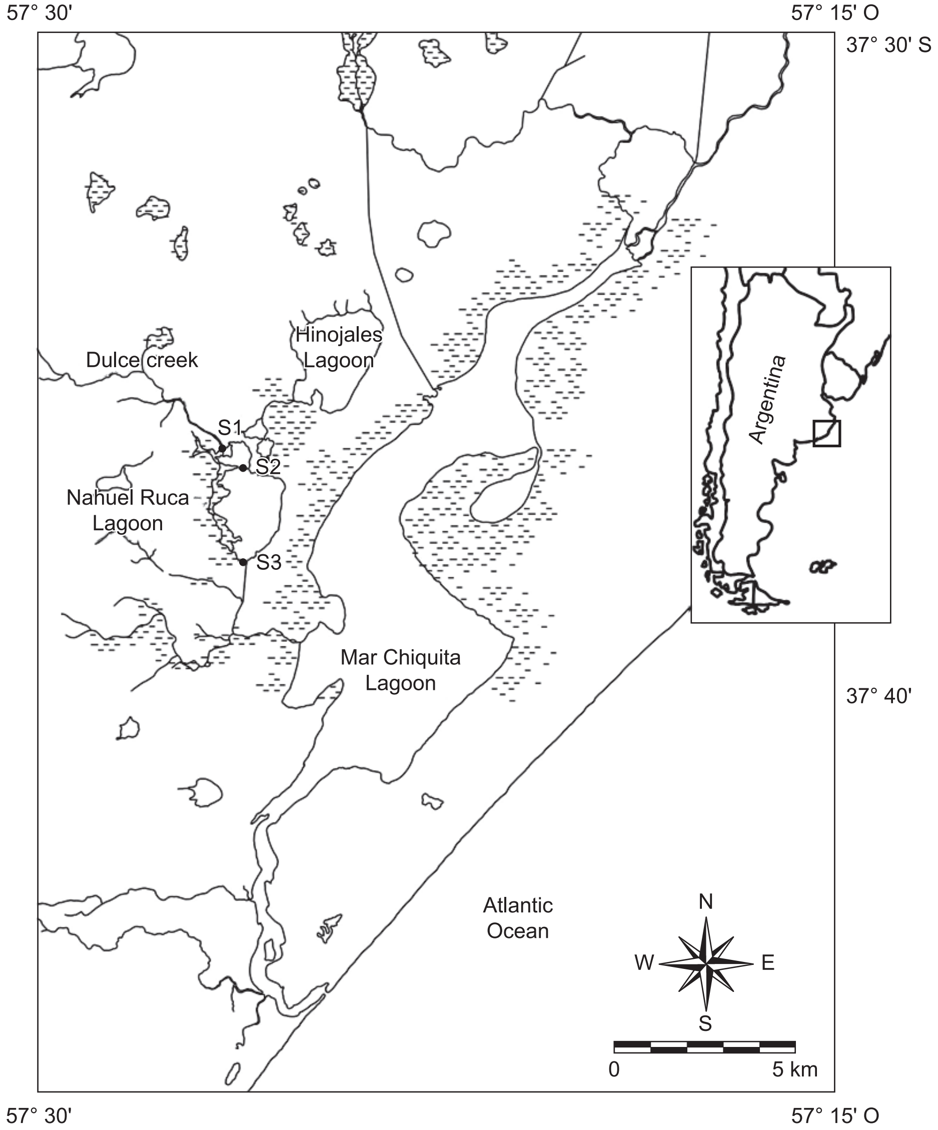

Figure 1 – Sampling sites (S1, S2 and S3) at Nahuel Ruca Lagoon, Central east of Argentina.

analyses of Cu and Zn (FAO & SIDA, 1983); with concentrated nitric acid (Merck, suprapur grade) for Cd (PAAR method 001H, 1998); and with a mix of concentrated nitric, sulphuric and hydrochloric acids (Merck analytical grade: 4:2:1) for Hg (BOE, 1991).

Total and labile fractions of sediments were determined. Total Cu, Zn and Cd were digested under same procedures applied for plants. Total Hg was performed by EPA method 245.5, using distilled water and aqua-regia (1:1). Luoma (1990) method was used to analyze the Cu, Zn and Cd labile fraction of sediments, being mineralized with hydrochloric acid (1N, Merck analytical grade) by shaking during 24 hs. Labile fraction corresponds to less stable chemical species constituting the fraction more likely to be bioavailable (Adami *et al*., 2007). Mercury labile fraction was not analyzed due to the lack of a validated technique.

Cu and Zn were determined by Atomic Absorption Spectrometer with flame mode (FAAS), total Hg was determined by cold vapor technique (CVAAS), and Cd by graphite furnace (GFAAS) in order to obtain more sensibility. Detection limits of Cu, Zn, Hg, and Cd were: 0.05, 0.05, 0.02, and 0.005 $\mu g.g^{-1}$ (dry weight), respectively.

The accuracy of chemical analyses was checked by using a standard reference material for sediments (NIST 1944) produced by the National Institute of Standards and Technology, (USA). The recovery rates were 91 ± 6% for all the metals analyzed in the sediment reference material. Blanks were also analyzed for potential contamination.

Statistical analyses

Values were reported as mean ± standard deviation (SD). Pearson's correlations were performed between total organic matter and metal levels in sediments, and between metal concentrations in roots of *S. californicus* and those of NRS in labile fraction. Significant differences among sites, tissues and kind of sediments were assessed by parametric tests: t-test and ANOVA (1 and 2 ways), and non parametric tests: U-Mann Wittney and Kruskall-Wallis, being previously checked the variance homogeneity by Levene´s test (Zar, 1984). Statistica software (1999) was used for the statistical analyses, and significance was assessed at 0.05 level.

RESULTS

Chemical parameters of sediments

The main chemical parameters of sediments are given in Table 1. Organic matter percentages in NRS were significantly higher ($p < 0.05$) than SS in S1 and S2, and similar in S3. S2 showed the highest percentages of organic matter ($p < 0.01$) in both SS and NRS. S1 and S3 showed the highest percentage of sand, while in S2 were highest for silt and clay. On contrary, no differences in pH were found between SS and NRS and among sites.

Total and labile metals in sediments

Concentrations of total metal and labile fraction at the three study sites are presented in Table 2. Total and labile fractions showed the same distribution pattern, Zn > Cu > Cd, for the SS and NRS; while Hg levels were below detection limits (< 0.02 µg.g^{-1}) in all analyzed samples.

Total Cu and Zn concentration in SS ranged from 8.4 to 23.0 µg.g^{-1} and from 26.0 to 56.0 µg.g^{-1}, respectively, and for NRS were from 6.4 to 22.4 µg.g^{-1} and from 19.5 to 58.7 µg.g^{-1}, respectively. Comparing Cu and Zn concentrations between sediments (SS and NRS) in each site, only S1 (NRS > SS) and S3 (SS > NRS) showed significant differences ($p < 0.05$). Maximum levels of Cu and Zn were found at S2, both in SS and NRS for total and labile fractions, followed by S1 and S3, with highly significative differences among the three sites ($p < 0.01$).

The highest total Cd levels were found in SS of S1 (0.42 µg.g^{-1}, mean value), followed by S2 (0.31 µg.g^{-1}) and S3 (0.22 µg.g^{-1}). Levels were significantly different ($p < 0.01$) among sites. In contrast, Cd concentrations in NRS did not show differences among sites ($p > 0.05$), ranging from 0.16 to 0.20 µg.g^{-1}. In the labile fraction, Cd levels ranged from 0.14 to 0.17 µg.g^{-1} and 0.08 to 0.10 µg.g^{-1} for SS and NRS, respectively. No differences were found among sites ($p > 0.05$). Comparing Cd content between sediments, results showed that SS was significantly higher than NRS ($p < 0.01$) in most of the samples among all studied sites.

The highest mean values for relative labile metal was found for Cu (57.3-78.7%), followed by Cd (37.3-64.8%) and Zn (29.3-53.5%) for both SS and NRS (Table 2), indicating that Cu presented the highest mobility. The distribution pattern of Cu labile percentages was S2 > S1 = S3 ($p < 0.05$) in SS, while there were no differences in NRS among sites ($p < 0.01$). In the case of Zn, both SS and NRS showed the same distribution (S2 > S1 > S3) ($p < 0.05$), while for Cd was: S3 > S2 = S1 for SS ($p < 0.01$) and S1 = S2 > S3 for NRS ($p < 0.05$).

The relationship between each metal contents and organic matter in sediments are listed in Table 3. Cu and Zn were

Table 1 – Percentage of total organic matter (TOM) (mean ± standard deviation), pH and grain size (%) in the surface sediments (SS) and near root sediments (NRS) sampled at Nahuel Rucá lagoon.

Site	SS					NRS	
	pH	TOM (%)	Sand (%)	Silt (%)	Clay (%)	pH	TOM(%)
S1	8.19	5.68 ± 0.61	59.2	28.0	12.8	7.8	10.41 ± 0.16
S2	7.53	21.17 ± 0.74	26.1	48.9	25.0	7.7	19.22 ± 0.60
S3	8.27	5.75 ± 0.67	69.6	14.5	15.8	8.2	4.85 ± 1.55

Table 2 – Total and labile metal concentrations (µg.g^{-1}, dry weight) in surface sediments (SS) and near root sediments (NRS) from Nahuel Rucá lagoon.

Sediment	Fraction	S1				S2				S3			
		Cd	Hg	Cu	Zn	Cd	Hg	Cu	Zn	Cd	Hg	Cu	Zn
SS	Total	0.42 ± 0.03[a]	< LD[c]	13.49 ± 0.18	28.50 ± 1.10	0.31 ± 0.02	< LD	21.86 ± 1.14	54.45 ± 1.62	0.22 ± 0.03	< LD	9.20 ± 0.74	28.50 ± 2.20
	Labile	0.17 ± 0.02 (43.4 ± 5.8) [b]	< LD	7.70 ± 0.19 (57.3 ± 1.3)	10.40 ± 0.57 (36.5 ± 1.5)	0.17 ± 0.01 (53.1 ± 1.5)	< LD	16.30 ± 0.06 (74.9 ± 3.9)	26.53 ± 0.45 (48.7 ± 0.7)	0.14 ± 0.01 (64.8 ± 7.6)	< LD	5.30 ± 0.72 (57.4 ± 3.5)	8.33 ± 0.67 (29.3 ± 1.6)
NRS	Total	0.16 ± 0.02	< LD	17.19 ± 1.90	48.21 ± 3.89	0.17 ± 0.03	< LD	20.84 ± 1.91	52.37 ± 5.81	0.2 ± 0.03	< LD	7.13 ± 0.70	21.56 ± 1.80
	Labile	0.10 ± 0.02 (63.6 ± 10.9)	< LD	11.30 ± 1.07 (66.1 ± 4.3)	20.06 ± 0.35 (41.7 ± 2.6)	0.09 ± 0.02 (51.6 ± 8.8)	< LD	16.30 ± 0.24 (78.7 ± 8.0)	27.80 ± 0.59 (53.5 ± 5.1)	0.08 ± 0.01 (37.3 ± 5.5)	< LD	4.60 ± 1.30 (64.7 ± 17.9)	6.20 ± 0.87 (29.1 ± 6.8)

[a]: mean ± standard deviation. [b]: percentage of labile metal in relation to total metal concentration (mean % ± standard deviation). [c]: levels below the limit of detection.

positively correlated, with significant p values; while Cd had no significative correlation at most of the sites.

Metals in Schoenoplectus californicus

The concentrations of Zn, Cu and Cd in shoots and roots of *S. californicus* are given in Table 4. Results showed that both tissues presented the same distribution pattern seen in the sediments, where Zn > Cu > Cd and Hg were always below detection limit (< 0.02 µg.g^{-1}).

The Cu concentrations in shoots and roots ranged from 1.8 to 5.34 and 8.95 to 12.1 µg.g^{-1}, respectively, while Zn concentration ranged from 20.3 to 30.87 µg.g^{-1} in shoots and from 16.59 to 35.48 µg.g^{-1} in roots . Cd concentration ranged from 0.09 to 0.15 µg.g^{-1} in shoots and from 0.09 to 0.13 µg.g^{-1} in roots. Only Cu levels were significantly higher in roots than in shoots ($p < 0.05$).

The translocation factors (TF), the ratio of shoot to root metals, could be use as an indicator of the internal metal transport (Deng *et al.*, 2004). Data showed that Cu and Zn were generally retained in roots, indicated by TF values < 1, except for Zn in S3 (1.69 ± 0.85) (Table 5). In the case of Cd, TF values were close or slightly superior to 1 (0.96-1.34, mean values), indicating a transport from underground to aboveground tissues.

The bioaccumulation factors (BAF) were established as [level in root]/[labile metal level in NRS], and were used to assess the capacity of *S. californicus* to uptake metals from the surrounding sediments. The mean values varied from 1.28 to 2.88 for Zn, 0.79 to 1.63 for Cu and 1.04 to 1.33 for Cd (Table 5). Cu and Zn levels in roots seem to be correlated to those of labile fraction of NRS; but these relations were not statistically significatives. The lack of correlation was expected for Cd, due to similar levels presented in roots and labile NRS.

Metals in Ricciocarpus natans

Metal concentrations in *R. natans* are showed in Table 6. The distribution pattern in the three studied sites was Zn > Cu > Cd = Hg. The mean values of Cu and Zn ranged from 15.30 to 27.27 and 52.35 to 78.79 µg.g^{-1}, respectively; *R. natans* presented Cd levels ranging from 0.11 to 0.25 µg.g^{-1}. It is worth mentioning that Hg was detected only in this macrophytes, with values ranged from 0.14 to 0.15 µg.g^{-1}. Differences among sites were not analyzed due to the movement of this kind of plants in the lagoon surface.

Table 3 – Correlation coefficients between the metal concentration in sediment fraction and TOM content.

Site	Fraction	Sediment	Cd	Cu	Zn
S1	Total	SS	ns	0.9968***	0.8352*
		NRS	ns	ns	ns
	Labile	SS	-0.9966**	ns	0.9334**
		NRS	ns	0.9391**	0.8763*
S2	Total	SS	ns	0.8058*	0.9210**
		NRS	0.9914***	0.9533**	0.8464*
	Labile	SS	ns	ns	ns
		NRS	ns	0.8644*	0.9066**
S3	Total	SS	ns	0.9839***	0.9988***
		NRS	ns	0.8698*	ns
	Labile	SS	ns	0.9958***	ns
		NRS	ns	0.9989***	0.9998***

* $p < 0.1$, ** $p < 0.05$, *** $p < 0.01$, ns: not significant.

Table 4 – Metal Concentrations (µg.g^{-1}, dry weight) in shoots and roots of *Schoenoplectus californicus* sampled at Nahuel Rucá lagoon.

Site	Shoots				Roots			
	Cd	Hg	Cu	Zn	Cd	Hg	Cu	Zn
S1	0.10 ± 0.01^{a}	< LD^{b}	2.66 ± 0.78	22.71 ± 9.50	0.11 ± 0.02	< LD	11.90 ± 1.30	34.66 ± 3.52
S2	0.12 ± 0.03	< LD	1.80 ± 0.47	20.31 ± 8.84	0.09 ± 0.00	< LD	12.10 ± 2.96	35.48 ± 7.50
S3	0.13 ± 0.02	< LD	5.34 ± 2.40	30.87 ± 13.60	0.10 ± 0.01	< LD	8.95 ± 1.39	16.59 ± 2.61

^{a}: mean ± standard deviation. ^{b}: levels below limit of detection.

Table 5 – Bioaccumulation factors (BAF) and translocation factors (TF) of metals in *Schoenoplectus californicus* sampled at Nahuel Rucá lagoon.

Site	BAF			TF		
	Cd	Cu	Zn	Cd	Cu	Zn
S1	1.13 ± 0.26^{a}	1.08 ± 0.08	1.80 ± 0.08	0.96 ± 0.17	0.22 ± 0.06	0.66 ± 0.24
S2	1.04 ± 0.25	0.79 ± 0.20	1.28 ± 0.29	1.30 ± 0.29	0.14 ± 0.04	0.46 ± 0.15
S3	1.33 ± 0.39	1.63 ± 0.30	2.88 ± 0.23	1.34 ± 0.15	0.61 ± 0.18	1.69 ± 0.85

^{a}: mean ± standard deviation.

Table 6 – Metal Concentrations (μg.g^{-1}, dry weight) in *Ricciocarpus natans* sampled at Nahuel Rucá lagoon.

Site	Cd	Hg	Cu	Zn
S1	0.25 ± 0.14[a]	0.14 ± 0.08	22.27± 4.27	58.32 ± 10.96
S2	0.17 ± 0.04	0.15 ± 0.03	27.19 ± 7.72	78.79 ± 6.20
S3	0.11 ± 0.02	0.15 ± 0.04	15.30 ± 1.85	52.35 ± 5.51

[a]: mean ± standard deviation.

DISCUSSION

Total and labile metals in sediments

The present field study shows the same distribution pattern (Zn > Cu > Cd) that those reported for lakes from different geographical location and impact levels (Szymanowska *et al.*, 1999; Samecka-Cymerman & Kempers, 2001; Mathew *et al.*, 2003). Furthermore, heavy metal levels found in Nahuel Rucá lagoon were below guideline values established by Australian and Dutch regulation as contamination indexes for freshwater total sediments (Zn – 140 μg.g^{-1} d.w.; Cd – 0.8 μg.g^{-1} d.w.; Hg – 0.3 μg.g^{-1} d.w. and; Cu – 30 μg.g^{-1} d.w.; Moss & Costanzo, 1998; Szymanowska *et al.*, 1999), suggesting a low anthropogenic contribution of those metals.

Maximum Cu and Zn levels found at S2 could be associated with the highest TOM content and finest grain size (mainly silt and clay). S2 corresponds to the sedimentary island that functions as a retention zone of suspended particulate matter with high capacity to trap metals. It is well known that organic matter and fine sediments (Förstner & Wittmann, 1983), such as clay and silt, play an important role in the binding of metals. In fact, the differences found for Cu and Zn contents among sediments (SS-NRS) were associated with differences in their TOM contents (Table 3). These results were in agreement with those found by Cousins *et al.* (2002) for lagoon sediments of Australia, who attributed the strong relationship to the high Cation Exchange Capacity (CEC) of organic matter, mainly responsible for the binding of trace metals.

Although S2 showed the highest TOM values for Cd, maximum levels were not found at that site. The lack of correlation between Cd and TOM for all sites, suggests a low affinity between them, previously reported by Pardo *et al.* (1990). Maximum Cd levels were registered at S1 decreasing to S2 and S3, following the water movement within the lagoon suggesting that the input of this metal to the lagoon is through the Dulce creek.

The higher Cd concentrations found in SS regarding NRS can be related to the presence of *S. californicus*.

Based on the pattern found in the percentages of relative labile metal, Cu and Cd presented the highest mobility during the sampling period. Although Zn presented the highest concentration, its lability values were lower than Cu, indicating a smaller mobility to water column. Tsai *et al.* (1998) reported that Zn bound to carbonates is commonly found as a major fraction, being removed with low pH (~ 5) (Mathew *et al.*, 2003). By other way, Maskall and Thornton (1998) reported that percentages of Zn in residual fraction increase when sediment pH is > 7. Thereby, the low rate of Zn mobility is a consequence of the pH in the sediments (7,52 to 8,20).

Metals in Schoenoplectus californicus

Copper and Zn are essential micronutrients to plants. Thus, aboveground tissues of plants from uncontaminated sites normally present levels around 66 and 37 μg.g^{-1} d.w. for Zn and Cu, respectively (Deng *et al.*, 2004). Levels for Cd in plants are usually around 0.1 μg.g^{-1} d.w.; Brooks, 1998). The levels found in *S. californicus* were below of the mentioned values for Zn and Cu and slightly higher for Cd, but inside the range established as background concentrations in plants by Kabata-Pendias & Pendias (1993) and Markert (1992) for Cd (0.03-0.5 μg.g^{-1} d.w.), Cu (2-20 μg.g^{-1} d.w.) and Zn (15-80 μg.g^{-1} d.w.).

Most studies indicated that roots accumulate more metals than the aboveground tissues for emergent macrophytes such as *Typha spp.*, *Juncus effusus, Phragmites australis*, *Schoenoplectus validus* (Dunbabin & Bowmer, 1992; Deng *et al.*, 2004). This exclusion of metals from aboveground tissues has been suggested as a metal tolerant strategy (Deng *et al.*, 2004) and plants that use this strategy are designated as non-accumulator species. Copper and Zn levels in *S. californicus* were higher in roots; therefore the studied species presented an exclusion strategy for these metals.

The similar cadmium concentrations found in shoots and roots and their translocation factors are indicating a transport of this metal from underground to aboveground tissues. Although not essential for plant growth, Cd^{+2} ions are readily taken up by roots and translocated into the leaves in many plant species (Demirezen & Aksoy, 2004), depressing growth by affecting photosynthesis and nutrient uptake. The mechanism of Cd accumulation has not been elucidated yet, but its uptake by roots is probably via a system involved in the transport of another essential divalent micronutrient, possibly Zn^{2+}. Cadmium is a chemical analogue of the latter and plants may not be able to differentiate between the two ions (Kirkham, 2006). Although *S. californicus* is perennial, during fall-winter period it loses shoots. The Cd accumulated in the aboveground tissues is incorporated to sediments and could be a detoxification mechanism of plant.

The BAF, index of sediment-plant transference, > 1 indicates that plants are enriched by these elements (accumulator), while around 1 indicates a rather indifferent behaviour of the plant towards these elements (indicator) and a ratio clearly < 1 shows that the plant exclude these elements from uptake (excluders) (Chamberlain, 1983). The BAF values near to 1 found for *S. californicus* indicate the presence of Cd, while BAF values > 1 showed a tendency to accumulate Zn. This tendency is related to the high physiological requirement of Zn (Klaassen, 2001). Cu presented variable BAF values (smaller, equal or greater than 1), indicating a non-clear behaviour.

Metals in Ricciocarpus natans

R. natans presented the highest levels of Cu, Cd, Zn and Hg of all studied matrices (sediments included), exceeding the range established as background concentrations in plants (Kabata-Pendias & Pendias, 1993 and Markert, 1992) for Cu (34.91 µg.g^{-1} d.w.). This indicates not only the metal availability but the great capacity of *R. natans* to concentrate them from water. This ability could be related to the thinner cuticle and the abundance of thin sheets of tissue in intimate contact with the aqueous phase, which favour the assimilation (Samecka-Cymerman *et al.*, 2002). Furthermore, Gerdol *et al.* (2000) reported the abundance of cation exchange sites on bryophytes cell walls, which also increase the metal absorption. Moreover, it is recognized that bryophytes contains more proteins and less fibre than emergent plants (Olguin & Hernandez, 1998), suggesting a more binding sites to accumulate metals. These particular morphology and physiology allow aquatic bryophytes to be hyperaccumulators of heavy metals from water (López & Carballeira, 1993).

It must be highlighted that Hg was only found in *R. natans* and its values exceed the range established as background concentration in plants (< 0.03 µg.g^{-1} d.w.; Kabata-Pendias & Pendias, 1993). However, high Hg levels (0.45 – 1.7 µg.g^{-1}, d.w.) were also reported for aquatic bryophytes from streams of Swiss Alps, although water levels were below the detection limit (Hg < 0.001 µg.L^{-1}) (Samecka-Cymerman & Kempers, 1998). Nelson (1996) have already reported that aquatic bryophytes usually concentrate this metal up to several orders of magnitude higher than water, and Hg was, in some cases, only detected in tissues. A possible explanation could be the presence of sites with active mercury methylation in roots of floating macrophytes, such as the water hyacinth (*Eichhornia crassipes*) (Mauro *et al.*, 1999). Guimaraes *et al.* (2000) found that methylation levels in roots of *Eichhornia azurea*, *E. crassipes*, *Paspalum sp.* and *Salvinia sp.* were one order of magnitud higher than in the underlying sediments. As reported by Baldantoni *et al.* (2004), the concentration of trace elements in sediments is an integration of long-term exposure, whereas in water is mainly related to recent contamination. In the same way, bryophytes may respond quickly to environmental change than vascular plants, which are structurally more complex and have well-developed cuticles (Stephenson *et al.*, 1995). Thus, it could be concluded that the distribution of Hg at the lagoon (absence in *S. californicus* and sediments; detected in *R. natans*) indicates recent inputs. In addition, *R. natans* demonstrated to be a sensitive bioindicator of this metal and it can be used as an early warning tool.

Finally, *R. natans* and *S. californicus* are commonly found in freshwater bodies of a large relevant region of Argentina and America. Both species have shown capacity to accumulate metals, and can be used as phytoindicator of some metals. Since *R. natans* is highly productive (in optimal environmental conditions; i.e. temperature, pH, nutrients, light) (Olguin & Hernandez, 1998) and easy to harvest, this bryophyte might be considered for bioremediation programs to remove some heavy metals from the water of polluted environments. However, the potential use of *S. californicus* for bioremediation must be further studied.

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