



# Copper, zinc, and chromium accumulation in aquatic macrophytes from a highly polluted river of Argentina

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Received: 31 March 2022 / Accepted: 19 November 2022 / Published online: 29 November 2022  
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## Abstract

The aims of this study were to assess Cu, Zn, and Cr pollution in a highly polluted river in Argentina (Matanza-Riachuelo) and to evaluate tolerance strategies and toxic effects in aquatic macrophytes. Chemical techniques were used to assess the bioavailability of these metals and to evaluate their uptake and translocation by plants. The ultrastructure of the roots of a free-floating plant (*Eichhornia crassipes*) and the leaves of an emergent macrophyte (*Sagittaria montevidensis*) was examined using transmission electron microscopy. In the lower basin of the river, the highest concentrations of total heavy metals were detected in water (179 µgZn/g; 54 µgCu/g; 240 µgCr/g) and sediments (1499 µgZn/g; 393 µgCu/g; 4886 µgCr/g). In the upper basin of the river, low percentages of Zn and Cu (8 to 25%) were extracted with DTPA and EDTA, probably due to the lithogenic origin of these metals. Higher extraction percentages (24 to 66%) were obtained in the lower basin, in accordance with anthropogenic pollution. For Cr, extraction percentages were low in the upper basin of the river (<4.5%) and extremely low in the lower basin (<0.03%). In *S. montevidensis*, the BCF (bioconcentration factor) and TF (translocation factor) indexes were compatible with heavy metal exclusion mechanisms in sediments, whereas in the *E. crassipes*, root compartmentalization could be the main tolerance strategy. The leaves of *S. montevidensis* showed no evidence of damage, whereas ultrastructural alterations (plasmolyzed cells, disorganized membranes) were observed in *E. crassipes*.

**Keywords** Heavy metals · Wetland plants · Pollution · Chelating agents · Bioavailability · Ultrastructure

## Introduction

Heavy metals, such as Cu and Zn, are essential for plant growth, but Cr have no known biological function. However, high concentrations of essential and non-essential heavy metals are toxic to plants, especially when they are translocated to the aboveground biomass (Hall 2002; Weis and Weis 2004).

The discharge of toxic metals into aquatic ecosystems as a consequence of human activities generates significant pollution of soils, sediments, and water leading to an accelerated accumulation in the trophic network on which humans depend (Nriagu and Pacyna 1988; Meybeck 2013; Siddiqui and Pandey 2019).

As the high availability of binding sites make soils and sediments a natural sink for toxic compounds, the distribution of metals in the different geochemical phases reflects their mobility, bioavailability, and their potential risk to the biota (Ashraf et al. 2011; Fan et al. 2014; Arreghini et al. 2006, 2017).

The association of metals with a particular geochemical phase depends on several factors, such as their chemical affinity, the physical and chemical conditions (pH, redox potential, ionic strength), the relative proportion of the mineral and the organic fractions offering binding sites, competition with other metals, the kinetics of reactions in which they are involved, and the time of exposure (Fabrizio de Iorio 2010; Rendina and Fabrizio de Iorio 2012; Fan et al. 2014).

Responsible Editor: Elena Maestri

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Different industrial activities require intensive use of different heavy metals. Therefore, the lower basins of numerous contaminated rivers have received heavy discharges of residual water with high levels of Cu, Zn, and Cr among other pollutants, over time.

Copper toxicity is mainly related to the redox activity of the copper ions, which leads to the chemical synthesis of harmful reactive oxygen species (ROS) and damages critical structures and molecules (membranes, peptides, nucleic acids) at the molecular level. In natural environments, the organic matter acts as a chelating agent (a Lewis base) and forms stable coordination compounds with copper ions promoting its accumulation in sediments and diminishing its toxicity (McBride 1989; Kramer et al. 2004; De Schaepelaere and Janssen 2004).

Zinc is mainly associated with Fe and Mn oxides and carbonates in soils and sediments (McBride 1989). A high concentration of Zn in the photosynthetic tissues of plants has a detrimental effect on chlorophyll synthesis, also compromising key enzymes in ROS metabolism (Chaney 1993; Carrol et al. 2004; Mirshekali et al. 2012).

Chromium presents a wide range of oxidation states, the trivalent and the hexavalent oxidation states being the most common and stable in natural ecosystems (Fendorf 1995; Zayed et al. 1998). Cr (VI), as  $\text{CrO}_4^{2-}$  or  $\text{Cr}_2\text{O}_7^{2-}$ , is a soluble and strong oxidant able to generate high levels of ROS (Panda and Choudhury 2005; Shanker et al. 2005; Speranza et al. 2007). Cr (III) has a lower solubility and is stable in reducing and acidic environments mainly associated with soil and sediment organic matter (Whalley et al. 1999).

The Matanza-Riachuelo basin is one of the most polluted in Latin America (Blacksmith Institute 2013). The lower basin of this temperate lowland river belongs to a densely populated area (more than 3.5 million people) and drains into the binational estuary of Río de la Plata, which represents the main source of drinking water for the city of Buenos Aires and its surroundings. Many metallurgical, chemical, and petrochemical industries as well as meat processing plants and tanneries are located in this area, discharging metal-rich effluents to the river. In soils and sediments of the lower basin of the Matanza-Riachuelo river, several authors (Mendoza et al. 2015; do Carmo et al. 2021) reported concentrations above the guidelines for essential and non-essential metals.

The aims of this study were to assess the levels of contamination of Cu, Zn, and Cr in the water and sediment of the Matanza-Riachuelo river; to assess the bioavailability of these metals using different chemical extraction methods; to evaluate the uptake and translocation of metals in aquatic and wetland plants; and to determine ultrastructural alterations in the roots of a free-floating plant and the leaves of an emergent macrophyte.

## Materials and methods

### Study area and sampling design

The Matanza-Riachuelo basin is divided into three sub-basins of different land uses (Fig. 1). The upper sub-basin is mainly crops and livestock, while the highest population density and industrial activities are found in the lower sub-basin (Rendina and Fabrizio de Iorio 2012). This river presents a complex history of depositional processes, although, a dense vegetation cover has developed on its margins.

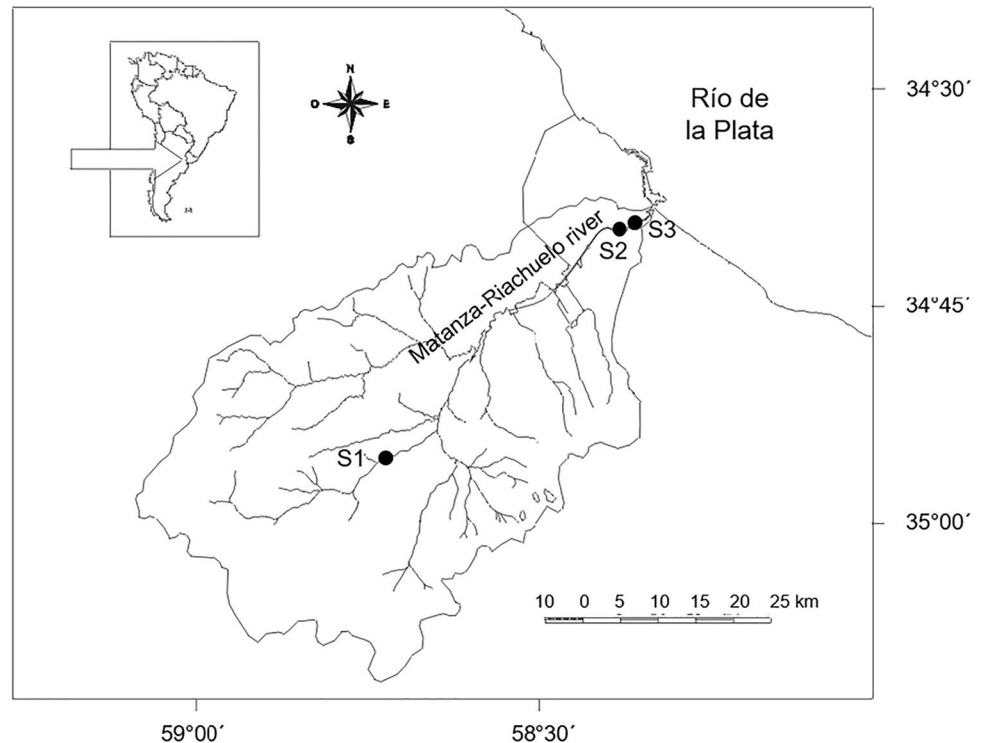
To reflect the contrast between the land use of the sub-basins, three sites were selected: S1 (upper sub-basin) and S2/S3 (lower sub-basin) (Table 1). S1 site is mainly surrounded by crop and livestock areas and several species of wetland and aquatic plants are found; this site shows the highest total coverage of the entire basin and the highest presence of native grass (Faggi and Breuste 2015). S2 site corresponds to a meander downstream in a rectified section of the channel where the decrease in speed favors the development of free-floating plants. This site also receives direct sewage discharge from a precarious population settlement. S3 site is located downstream of S2 in a newly rectified section of the river and near to its mouth in the Río de la Plata estuary. Samples of water, sediment, and plants were collected at these three sites (Table 1). Aquatic plants collected at this study were free-floating plants, *Lemna gibba* L. and *Eichhornia crassipes* (Mart.) Solms, rooted with leaves and stems floating plants, *Panicum elephantipes* Nees, *Alternanthera philoxeroides* (Mart.) Griseb., *Hydrocotyle ranunculoides* L. f., and emergent plants, *Schoenoplectus americanus* (Pers.) Volkart ex Schinz & R. Keller and *Sagittaria montevidensis* Cham. & Schldtl.

### Analytical procedures

#### Water

The water samples were taken in triplicate and immediately filtered through Whatman GF/C filters and transported to the laboratory at 4 °C for analysis. The pH (Orion EA 940 pHmeter) and electrical conductivity (EC) (LUFTMAN conductimeter) were measured. In filtered samples, concentrations of different solutes were determined using the following analytical methods: nitrate ( $\text{N-NO}_3^-$ ) by reduction with hydrazine sulfate and nitrite ( $\text{N-NO}_2^-$ ) by diazotization with sulfanilamide and N-(1-naphthyl) ethylenediamine and measured at 540 nm (Perkin Elmer Lambda 25 UV/visible spectrophotometer) (APHA 1992),

**Fig. 1** The Matanza-Riachuelo basin and the study sites



**Table 1** Location of sampling sites, species collected in each site, life form (FF, free floating; F, rooted with leaves and stems floating; E, emergent) and plant organs (R, root; Rhi, rhizome; St, stem; Sh, shoot; L, leaf)

	Location	Species	Commonname	Life form	Parts of the plant
S1	34°55'22" S	<i>Lemna gibba</i>	Swollen duckweed	FF	
	58°43'19" W	<i>Hydrocotyle ranunculoides</i>	Water pennywort	F	R, St, L
		<i>Alternanthera philoxeroides</i>	Alligatorweed	F	R, St, L
		<i>Schoenoplectus americanus</i>	Chairmaker's bulrush	E	R, Rhi, Sh
S2	34°39'32" S	<i>Eichhornia crassipes</i>	Water hyacinth	FF	R, St, L
	58°23'47" W	<i>Sagittaria montevidensis</i>	Giant arrowhead	E	R, Rhi, St, L
		<i>Panicum elephantipes</i>	Elephant panicgrass	F	R, St, L
S3	34°39'28" S	<i>Eichhornia crassipes</i>	Water hyacinth	FF	R, St, L
	58°22'27" W	<i>Sagittaria montevidensis</i>	Giant arrowhead	E	R, Rhi, St, L

ammonium ( $\text{N-NH}_4^+$ ) by spectrophotometric indophenol blue method measured at 640 nm (Perkin Elmer Lambda 25 UV/visible spectrophotometer) according to Mackereth et al. (1989). Suspended solids (SSs) were determined by gravimetry (filtering a water sample through a pre-weighed Whatman GF/C filters) (Golterman et al. 1978). In addition, water samples were filtered using a 0.45  $\mu\text{m}$  pore size filter to determine soluble reactive phosphorus (SRP) according to APHA (1992). Unfiltered water samples were taken in triplicate, acidified with concentrated nitric acid, and transported to the laboratory for heavy metals analysis. At the laboratory, 300 ml of each sample was concentrated by evaporation (1:12) and then mineralized with  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{HCl}$  (7:1:3).

### Sediment

Three composite sediment samples (each obtained from the mixture of five subsamples) were taken from the top 10 cm of the surface at each site and collected in plastic bags. Then, they were air-dried, and sieved with a 2-mm mesh. The pH and electrical conductivity were measured at laboratory. Carbon easily oxidable ( $C_{\text{eas ox}}$ ) was determined by the Walkley–Black method (Walkley and Black 1946). Total metal concentrations were determined in the sediment samples digested with  $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{HF}$ , aqua regia, and  $\text{HCl}$  (3:1:7:2:3). The DTPA (diethylene triamine pentaacetic acid) extracting solution was prepared to contain 0.005 M DTPA, 0.01 M  $\text{CaCl}_2$ , and 0.1 M triethanolamine and was

adjusted to  $\text{pH } 7.30 \pm 0.05$  using 0.5 M HCl (Page et al. 1982). Ten grams of air-dried sediment in 20 ml of DTPA extracting solution was shaken for 120 min in a horizontal shaker (BIOMINT BM021 orbital shaker) with a stroke of 2.5 cm and a speed of  $180 \text{ cycles min}^{-1}$  at room temperature. The suspensions were filtered by gravity through a Whatman 42 paper filter. Another ten grams of air-dried sediment in 0.05 M EDTA (ethylene diamine tetraacetic acid) solution was shaken and filtered as DTPA extraction. Two grams of air-dried sediment in 16 ml of  $\text{MgCl}_2$  was shaken as DTPA extraction for 1 h and then was centrifuged at 10,000 rpm (Tessier et al. 1979). All the used chemicals were of analytical grades, including nitric acid (65%), perchloric acid (70%), hydrofluoric acid (40%), and hydrochloric acid (37%). A standard reference material CRM 320 (river sediment) was used to verify the accuracy of metal determination. The recovery rates for heavy metals in the standard reference material ranged from 88 to 107%.

## Plant

Plant samples of each species were taken in triplicate at different sites and transported to the laboratory in plastic bags. Plant samples were initially washed with the river water and then rinsed with tap and deionized water and scrubbed thoroughly to remove any particulate matter adhering to the plant material. Plants were separated into root, rhizome, leaf, and stem/shoot and were dried to a constant weight at  $70^\circ\text{C}$  and then ground into a powder using a blender. One gram of powder was placed into Teflon beaker (100 ml-PTFE Nalgene) and digested with  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and HCl (7:1:3).

All metal concentrations in all the extracts were measured by atomic absorption spectrometry with an air/acetylene flame (Perkin Elmer AAnalyst 200), using external standards prepared from stock solution of the metals (1000 mg/

kg, Merck). The results of the analysis are reported as dry weight. The detection limits (ppm) were calculated as the mean value of the reagent blank plus 3 times the standard deviation for 10 measurements of the blank (Tables 2, 3, and 4).

## Metal accumulation indexes for sediments

The enrichment factor (EF) is calculated using the following expression (Rendina and Fabrizio de Iorio 2012):

$$\text{EF} = C_i / C_{\text{res}}$$

where  $C_i$  represents the total concentration of a given metal at a study site and  $C_{\text{res}}$  represents the concentration of the same metal in the residual fraction, established by the sequential extraction technique (Tessier et al. 1979), from a reference site of the basin.

The geoaccumulation index ( $I_{\text{geo}}$ ) is calculated using the following expression (Müller 1981):

$$I_{\text{geo}} = \log_2(C_i / (1.5C_b))$$

where  $C_i$  represents the concentration of a given metal at the study site and  $C_b$  represents the concentration of the same metal at a reference site for the basin, following the same criteria established for the EF.

## Bioconcentration factor and translocation factor

The bioconcentration factor is obtained as the ratio:

$$\text{BCF} = C_r / C_s$$

where  $C_r$  indicates the heavy metal concentration in roots and  $C_s$  represents the heavy metal concentration in the

**Table 2** Mean  $\pm$  standard deviation of physical and chemical variables measured in water samples on each sampling site ( $n=3$ ). Different letters denote significant differences. CCME (Canadian Council of Ministers of the Environment). LNRP 24,051 (National Law of Hazardous Wastes of the Argentine Republic, Ley Nacional de Resid-

uos Peligrosos de la Argentina 24,051/1992). \*Chromium as Cr(III). EC, electrical conductivity; SS, suspended solids; SRP, soluble reactive phosphorus. Detection limits (ppm): Zn=0.08; Cu=0.07; Cr=0.26

		S1	S2	S3	CCME	LNRP 24,051
pH		$7.9 \pm 0.3$ a	$7.8 \pm 0.04$ a	$7.8 \pm 0.2$ a		
EC	(mS/cm)	$1.4 \pm 0.8$ a	$1.59 \pm 0.01$ a	$1.83 \pm 0.01$ a		
SS	(mg/L)	$2.9 \pm 0.5$ c	$50 \pm 2$ a	$27 \pm 3$ b		
N- $\text{NO}_3^-$	(mg/L)	$1.17 \pm 0.13$ a	$0.36 \pm 0.05$ b	$0.28 \pm 0.05$ b	2.94	-
N- $\text{NO}_2^-$	(mg/L)	$0.26 \pm 0.00$ a	$0.03 \pm 0.01$ b	$0.03 \pm 0.01$ b	0.06	0.06
N- $\text{NH}_4^+$	(mg/L)	$13.2 \pm 0.5$ a	$7.5 \pm 0.1$ b	$8.3 \pm 0.3$ b	0.39	1.37
SRP	(mg/L)	$2.02 \pm 0.04$ a	$1.53 \pm 0.12$ b	$2.23 \pm 0.27$ a	-	-
Zn total concentration	( $\mu\text{g/L}$ )	$37 \pm 1$ c	$179 \pm 13$ a	$104 \pm 10$ b	30	30
Cu total concentration	( $\mu\text{g/L}$ )	$11 \pm 4$ c	$54 \pm 3$ a	$33 \pm 3$ b	2–4	2
Cr total concentration	( $\mu\text{g/L}$ )	$12 \pm 4$ c	$240 \pm 19$ a	$173 \pm 4$ b	8.9*	2

**Table 3** Sediment physical and chemical variables (mean ± standard deviations,  $n=3$ ) (electrical conductivity, EC; carbon easily oxidizable,  $C_{\text{eas ox}}$ ; metal concentration on dry weight basis,  $\mu\text{g/g D.W.}$ ), geoaccumulation index ( $I_{\text{geo}}$ ) (Muller 1981) and enrichment factor (EF) (Rendina and Fabrizio de Iorio, 2012) for different sites of the Matanza-Riachuelo river (mean ± SD) ( $n=3$ ). Different letters show significant differences ( $p < 0.05$ ) between sites. <sup>a</sup>Total metal concentration in sediment of baseline site. <sup>b</sup>Residual metal concentration in sediment of baseline site. Interim sediment quality guideline (ISQG) and probable effect level (PEL) from the Canadian Council of Ministers of the Environment (CCME) (2002), and sediment

	pH	EC (mS/cm)	$C_{\text{eas ox}}$ (%)	$\mu\text{g/g D.W.}$	Zn		$\mu\text{g/g D.W.}$	Cu		$\mu\text{g/g D.W.}$	Cr	
					EF	$I_{\text{geo}}$		EF	$I_{\text{geo}}$		EF	$I_{\text{geo}}$
S1	6,8±0,1	1,3±0,7	1,4±0,1	104.3±4.5 c	1.5	-0.5	45.0±2.2 c	2.3	0.1	36.9±3.0 c	1.9	-0.2
S2	5,6±0,1	2,5±0,2	5,70±0,04	1499±8 a	21	3.3	393±9 a	20	3.2	4886±422 a	251	6.8
S3	5,4±0,1	1,1±0,3	5,6±0,5	1216±110 b	17	3.0	320±32 b	17	2.9	3029±478 b	155	6.1
Baseline Tc <sup>a</sup>	-	-	-	86.7±3.5	-	-	22.8±0.6	-	-	26.3±0.5	-	-
Baseline Rc <sup>b</sup>	-	-	-	71.1±1.2	-	-	19.2±0.8	-	-	19.5±0.2	-	-
CCME – ISQG	-	-	-	123	-	-	35.7	-	-	37.3	-	-
CCME – PEL	-	-	-	315	-	-	197	-	-	90	-	-
LNRP 24,051	-	-	-	500	-	-	100	-	-	250	-	-

guideline from residual use from National Law of Hazardous Wastes of the Argentine Republic (Ley Nacional de Residuos Peligrosos de la Argentina 24,051/1992, LNRP 24,051).  $I_{\text{geo}}$  classification: class 0 — practically uncontaminated ( $I_{\text{geo}} \leq 0$ ), class 1 — from uncontaminated to moderately polluted ( $0 \leq I_{\text{geo}} \leq 1$ ), class 2 — moderately polluted ( $1 \leq I_{\text{geo}} \leq 2$ ), class 3 — from moderately to heavily polluted ( $2 \leq I_{\text{geo}} \leq 3$ ), class 4 — heavily polluted ( $3 \leq I_{\text{geo}} \leq 4$ ), class 5 — from heavily contaminated to extremely polluted ( $4 \leq I_{\text{geo}} \leq 5$ ), class 6 — extremely polluted ( $5 \leq I_{\text{geo}}$ ). Detection limits (ppm): Zn=0.19; Cu=0.06; Cr=0.23

**Table 4** Metal concentrations (mean ± standard deviations,  $n=3$ ,  $\mu\text{g/g D.W.}$ ) in different organs of aquatic macrophytes collected in sampling sites. (FF, free floating; F, rooted with leaves and stems floating; E, emergent). Detection limits (ppm): Zn=0.08; Cu=0.07; Cr=0.26

	Species	Life form	Plant organs	Zn	Cu	Cr
S1	<i>Alternanthera philoxeroides</i>	F	Stem	34.4±2.9	4.4±0.4	16±23
			Leaf	49.7±3.8	4.6±0.2	26±20
			Root	95±14	26.5±2.2	90±68
	<i>Lemna gibba</i>	FF	Stem	50±11	9.4±2.2	7.4±1.0
			Shoot	20.4±4.2	3.7±0.5	2.6±0.3
	<i>Schoenolpectus americanus</i>	E	Rhizome	38±12	5.5±1.1	4.7±1.6
			Root	79±12	23.9±5.3	16±8
			Stem	60.7±4.0	10.3±1.1	40±33
	<i>Hydrocotyle ranunculoides</i>	F	Leaf	27.3±3.6	11.3±1.3	30±22
Root			136±31	35±10	213±60	
Stem			62±17	16±6	25±10	
S2	<i>Sagittaria montevidensis</i>	E	Leaf	96±10	22±7	38±12
			Rhizome	290±142	26±11	11±11
			Root	361±91	44±14	45±19
	<i>Eichhornia crassipes</i>	FF	Stem	47.3±4.3	4.2±0.7	6.7±2.2
			Leaf	43.0±2.2	6.1±0.3	6.0±1.5
			Root	251±51	64±13	682±54
	<i>Panicum elephantipes</i>	F	Stem	21.2±5.2	2.5±0.5	7.3±5.3
			Leaf	29±12	7.8±1.8	38±22
			Root	112±88	22±9	94±42
S3	<i>Sagittaria montevidensis</i>	E	Stem	57±18	22.0±4.0	6.4±4.3
			Leaf	76±25	22.5±2.5	12.9±3.4
			Rhizome	309±102	44±34	4.3±0.4
	<i>Eichhornia crassipes</i>	FF	Root	320±40	34±13	51.7±6.8
			Stem	58.4±3.6	7.6±1.3	25±10
			Leaf	56±8	6.9±0.1	12.5±2.0
Root	116±37	36±15	261±95			

substrate (sediment for emergent plants and water for *P. elephantipes* and *E. crassipes*), both on dry weight basis.

The translocation factor is obtained as the ratio:

$$TF = C_l / C_r$$

where  $C_l$  indicates the heavy metal concentration in leaves (shoots in *S. americanus*) and  $C_r$  represents the heavy metal concentration in roots, both on dry weight basis.

### Transmission electron microscopy

For ultrastructural observations, roots of *E. crassipes* and leaves of *S. montevidensis* were collected and fixed in 2.5% glutaraldehyde for 8 h and followed by post-fixation with 2% osmium tetroxide, dehydrated in an alcohol series of increasing degree and embedded in epoxy resin. Ultrathin sections were cut using an ultramicrotome, stained with 1% uranyl acetate for 1 h and lead citrate for 15 min, and then placed on copper grids (Sigma-Aldrich, 300 mesh, 3.05 mm of diameter). The observations were performed in a Philips CM 200 transmission electron microscope (TEM) equipped with a LaB6 emission gun and an ultratwin objective lens operating at 120 kV.

### Statistical analysis

Data were examined for normal distribution using the Lilliefors test. Data that did not follow a normal distribution were log10 transformed and their distributions were re-examined. All variables were tested for homogeneity of variances using Levene's test. Variables were examined by one-way ANOVA. Differences are reported as significant at  $p < 0.05$ . Tukey test was used to reveal significant differences between sites. All statistical analyses were performed using GENSTAT Release 7.1 (2003).

## Results and discussion

### Water

The pH and the EC values did not differ significantly between the three study sites and they were similar to those of previous studies in the basin (Fabrizio de Iorio et al. 2006; Magdaleno et al. 2014). Suspended solid (SS) concentrations in water samples followed a decreasing order:  $S2 > S3 > S1$  ( $p < 0.01$ ) (Table 2).

The dissolved inorganic nitrogen (DIN) concentration was significantly higher in S1 (Table 2), the site in the upper basin of the river where agriculture activities are more relevant and where surface and subsurface runoff transport nitrogen fertilizers not assimilated by plants from the

river basin to the fluvial course. The DIN concentration in water followed a decreasing order in the three study sites:  $N-NH_4^+ > N-NO_3^- > N-NO_2^-$  (Table 2). In the natural environment, organic nitrogen and urea from inorganic fertilizers react chemically to form ammonium by ammonification and hydrolysis reactions. When molecular oxygen is available to microorganisms, ammonium is oxidized into nitrite and later into nitrate in a complex process mediated by aerobic nitrifying bacteria.  $N-NO_3^-$  and  $N-NO_2^-$  represent about 10% of DIN in S1, but less than 5% of DIN in S2 and S3 (Table 2), even though the pH values were appropriate for nitrifying microorganisms (Vymazal and Kröpfelová 2008). At all sites, the high concentration of ammonium and a relatively higher concentration of an unstable chemical form of DIN, such as nitrite, suggest that molecular oxygen could be a limiting factor for nitrification. Furthermore, in S2 and S3, water pollution could have an additional negative effect on nitrifying bacteria.

The lowest concentration of soluble reactive phosphorous (SRP) was recorded in S2 and there were no significant differences between S1 and S3 (Table 2). In the natural environment, phosphorous is found mainly in chemical compounds of low availability, such as organic phosphorous, and in inorganic salts of very low solubility. In those aquatic ecosystems where sedimentation processes are promoted, phosphorous associated with coarse particulate matter is removed from the water column and accumulated in bottom and shoreline sediments whereas phosphorous associated with suspended solids (SSs) is not necessarily available to primary producers. For this reason, there is a particular interest in measuring the potentially available forms of phosphorous (SRP) rather than the total phosphorous concentrations (TP). In S1, high SRP concentration is probably related to the use of chemical fertilizers in the cropping activities in the basin and with the associated runoff processes. On the other hand, in S3, the SRP could be a consequence of the chemical dissolution of salts of chromium and zinc used for anticorrosive treatment and passivation of metallic surfaces, major industrial activities in the lower basin (Nápoli 2009). In S2, the concentration of SS was higher and that of SRP was lower, probably due to surface precipitation of phosphorous in SS and because immobilized phosphorous is not detectable under conventional chemical techniques (Table 2).

At all sites, and like SS, the total concentration of heavy metals followed a decreasing order  $S2 > S3 > S1$  ( $p < 0.05$ ). These concentrations were always higher than the guideline level established by CCME (2002) and by the local regulation of the National Law of Hazardous Wastes of the Argentine Republic (Ley Nacional de Residuos Peligrosos de la República Argentina 24,051/1992, LNRP 24,051) (Table 2), although agriculture is the most important economic activity in S1. Since the high density of binding sites in suspended

solids and the chemical reactivity of heavy metals promote complexation and surface precipitation reactions, this could explain the correlation between SS and heavy metals in the water (Laidler and Meiser 1995; Brady and Weil 2008; Ji et al. 2016; Xia et al. 2018).

Zinc and copper are essential trace elements for plants and animals, being required for numerous critical molecular processes. However, at high concentrations, they are dangerous and can be toxic to the biota. Chromium is a very special transition metal that is not essential for plant growth and development and has different oxidation states of different chemical reactivity and toxicity. Cr (III) is considered the most stable and least toxic form of chromium, whereas Cr (VI) is more mobile and extremely toxic (Gardea-Torresdey et al. 2005; Sharma et al. 2020). Although it is difficult to establish a positive correlation between a specific heavy metal and a toxic response in highly polluted rivers, like the Matanza-Riachuelo, the higher concentration of heavy metals in the water at S2 and S3 is a risk for free-floating (*E. crassipes*) and rooted macrophytes (*P. elephantipes*) with leaves and stems floating (Tables 1 and 2).

A positive correlation between SS and heavy metal concentrations in the water suggests that suspended solids could be considered natural sinks for metals (Table 2). By limiting the dissolution of metals in the water, this retention represents an advantage since the soluble forms of metals are the most mobile and are usually the most toxic. However, SS can also be considered a vector of pollutants between the source and the sedimentation and accumulation sites. When sediments are removed by natural or anthropogenic processes, heavy metals like Cr are remobilized, and interactions between trivalent chromium and strong oxidants can regenerate the highly toxic form of hexavalent chromium (Fendorf 1995; Oze et al. 2007; Sharma et al. 2020).

## Sediments

In S1, the EC in the sediment was similar to that in water, the pH was close to neutrality, and percentages of easily oxidable carbon were similar to those recorded in soils of the drainage basin (De Siervi 2016). In S2 and S3, the pH values were more acidic and very high percentages of easily oxidable carbon were recorded. At these sites, the depositional environment promotes sedimentation while the high pollution restricts oxidation of organic matter (Table 3).

Total concentrations of heavy metals in sediment followed a decreasing order: S2 > S3 > S1 ( $p < 0.05$ ). Zn and Cr concentrations in S1 were lower than the ISQG (Interim Freshwater Sediment Quality Guidelines) of the CCME (Canadian Council of Ministers of the Environment), whereas the Cu concentration was higher than the ISQG but lower than the PEL (probable effect level) value of the CCME (Table 3). Moreover, heavy metal concentrations in

S1, where agricultural activities predominate, were lower than the guide levels established by the LNRP 24,051 for soils with residential use. In S2 and S3, heavy metal concentrations were much higher than the PEL levels of CCME and those established by the LNRP 24,051 (Table 3), as the lower basin of the Matanza-Riachuelo river is an area historically subject to significant pollution by organic matter since the mid-eighteenth century and by hydrocarbons and heavy metals when industrial activities intensified in the early years of the nineteenth century (Rock 1989). Since heavy metals have very high solid/liquid partition coefficients (Arreghini et al. 2021), they can be removed from river water associated with SS. The highest heavy metal concentrations in the S2 sediments could be related to the morphometry of the river, since this section of the channel constitutes a meander, and the sediment samples were collected from the river margin where sedimentation is promoted. At site S3, on the other hand, channel rectification increases the speed of the water current and limits the sedimentation of SS and associated heavy metals. This could explain the lower concentration of heavy metals recorded in S3 in relation to S2 (Table 3).

Total heavy metal concentrations in soil and sediments do not provide enough information on the degree of pollution, nor does it allow us to distinguish between natural (lithogenic) and anthropogenic contributions (Barbieri 2016). Therefore, different indexes have been proposed to establish both the origin and significance of metal enrichment.

The enrichment factor (EF) relates the total concentration of a given metal at a study site and its concentration in the residual fraction of a reference site in the basin. Whereas EF values close to unity are characteristic of uncontaminated sites, substantially higher values indicate anthropogenic metal enrichment. Due to the high level of pollution of the entire Matanza-Riachuelo river, it was not possible to identify a reference zone and the EF was calculated using reference levels of the Reconquista, a river nearby with a similar basin (surface area, lithology, and morphometry) to the Matanza-Riachuelo (Arreghini et al. 2007) (Table 3).

In S1, the EF values ranged between 1.5 and 2.3 suggesting moderate contamination by metals. In S2 and S3, the EF values ranged between 17 and 21 for Zn and Cu, respectively, reaching values of 155 for Cr in S3, and 251 for the same metal in S2 (Table 3). These data show the magnitude of metal enrichment in the lower basin (S2 and S3) of the Matanza-Riachuelo and the higher metal contamination in S2, where SS concentration in the water is higher and sedimentation processes are promoted. The higher EF value for Cr could be further explained considering the special properties of this metal since it has a reduced form with a very low chemical reactivity and a high affinity for the solid phase.

The geoaccumulation index ( $I_{geo}$ ) relates the concentration of a given metal at the study site and its concentration at a reference site for the basin. In relation to the EF index, the

$I_{\text{geo}}$  does not require the residual fraction to be established by the complex sequential extraction methodology of Tessier et al. (1979). According to the Muller scale for the  $I_{\text{geo}}$  (Müller 1981), S1 is uncontaminated by Zn and Cr, and between uncontaminated to moderately contaminated by Cu. On the other hand, S2 and S3 are heavily contaminated by Zn and Cu and extremely contaminated by Cr (Table 3).

The total concentration of heavy metals in the water and sediments provides useful information about the degree of pollution of a study site. Although these data are a key element in monitoring and remediation tasks, total metal concentration does not necessarily reflect the heavy metal availability and their potential biotoxicity. Different chemical extractants, like acid solutions, soluble salts, and chelating agents, have been proposed to estimate labile and potentially assimilable metals by plants. While  $\text{MgCl}_2$  promotes desorption of electrostatically attracted metals to the solid phase, DTPA and EDTA are synthetic chelating agents that can also mobilize complexed metals (Zhang et al. 2010).

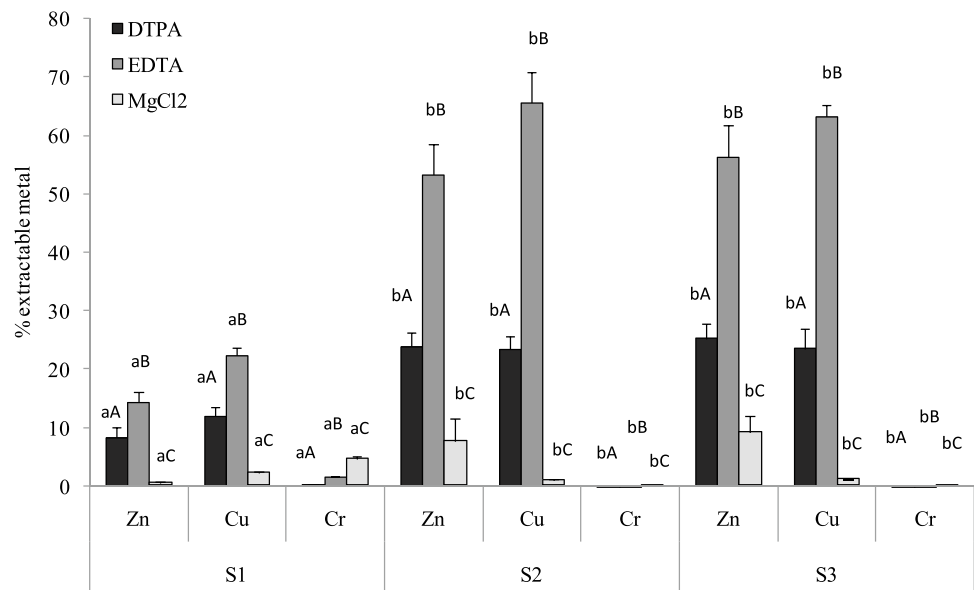
At all study sites, the extraction percentage of Zn and Cu from sediments followed a decreasing order:  $\text{EDTA} > \text{DTPA} > \text{MgCl}_2$  ( $p < 0.05$ ) (Fig. 2). Using EDTA, more than 50% of Zn and more than 60% of Cu were extracted from the S2 and S3 sediments, while the extraction diagrams were similar between these sites (Fig. 2). Since these percentages depend on the ability of the extracting agents to mobilize metal ions, similar extraction diagrams suggest similar sediments, at least in relation to the characteristics of the binding sites. The higher concentrations of Zn and Cu in S2, in relation to S3, could be explained by hydrodynamic conditions that promote sedimentation and increase the number of similar binding sites for metals. In S1, EDTA extraction percentages of Zn and Cu were below 15% and

25% respectively (Fig. 2) suggesting not only lower environmental mobility but also a qualitative difference between S1 in relation to the S2 and S3 sediments. At all study sites, chromium was the metal with the lowest mobility estimated by the aforementioned extraction methods (Fig. 2). The high concentration of total chromium in the sediments reported in S2 and S3 (Table 2) could be explained not only by anthropogenic pollution but also especially by the chemical characteristics of the sediments to retain this metal. In S1, the extraction percentage of Cr with  $\text{MgCl}_2$  was less than 5%, whereas in S2 and S3, these percentages were less than 0.2% for the three extractant agents used (Fig. 2). Unlike Zn and Cu, the S2 and S3 sediments were comparatively more efficient in immobilizing Cr in relation to S1 sediment. Since different sediments had different extraction diagrams for different metals, this analysis could be useful in establishing the environmental availability of pollutants and therefore in the implementation of remediation strategies.

## Plants

In S1, the Zn and Cu concentrations in roots were higher than those found in the aboveground biomass of *A. philoxeroides* and for the three metals analyzed in *H. ranunculoides* and *S. americanus*. In S2 and S3, the concentration of Zn in the belowground structures (roots and rhizomes) in *S. montevidensis* was higher than that of the aerial structures (stems and leaves), whereas *E. crassipes* and *P. elephantipes* showed the highest concentration in roots for the three metals analyzed (Table 4). Heavy metal concentrations were higher for the plants harvested in S2 and S3, except for *P. elephantipes*, which presented values similar to those recorded in the S1 species. The highest concentration of Zn

**Fig. 2** Percentage of DTPA — extractable (diethylene triamine pentaacetic acid), EDTA — extractable (ethylene diamine tetraacetic acid — extractable) and exchangeable metal concentrations in sediments (mean  $\pm$  SD) ( $n = 3$ ). Different letters indicate significant differences ( $p < 0.05$ ) between sites (lowercase letters) and between extraction methods (capital letters)





was recorded in roots of *S. montevidensis* from S2 and S3, followed by roots of *E. crassipes*. For chromium, roots of *E. crassipes* presented higher concentrations than those of *S. montevidensis* and no differences were observed in the case of Cu (Table 4).

Remarkable progress has been made in understanding the mechanisms that control metal uptake by plants (Hall 2002; Clemens 2006; Cheng et al. 2014a; Thakur et al. 2022), and there are also chemical techniques, such as those used in this study, aimed at establishing their environmental mobility (Du Laing et al. 2009; Rendina and Fabrizio de Iorio 2012). However, the high variability that characterizes the uptake and translocation of trace elements and non-essential heavy metals requires the use of specific indexes to better estimate their bioavailability and potential toxicity (Ernst 1996).

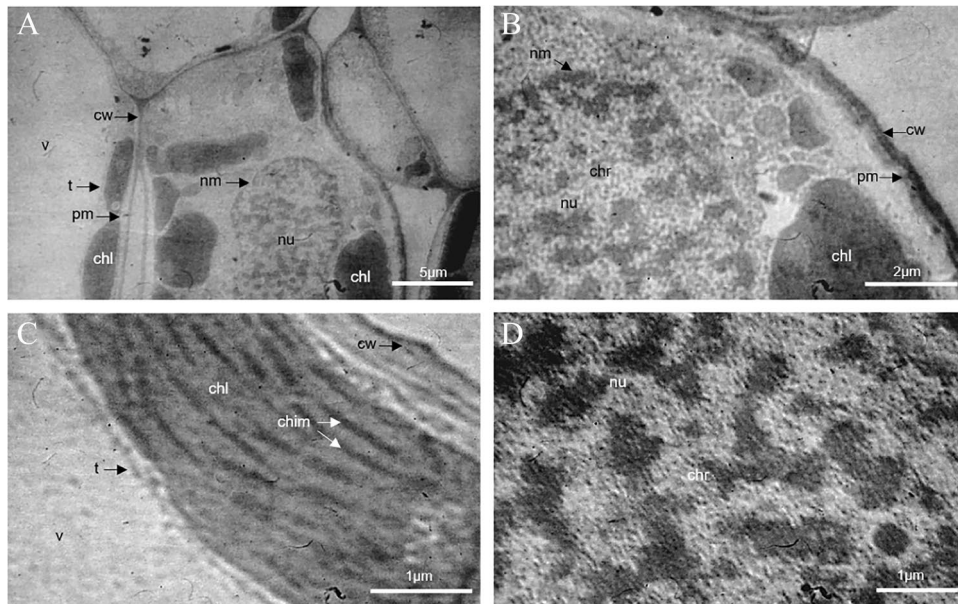
The BCF (bioconcentration factor) index relates the concentration of a metal in roots to the total concentration of the same metal in the substrate (soil, sediment, or water according to the life form of the plant). Values greater than unity indicate bioconcentration while very low values of the index suggest the existence of mechanisms that prevent the uptake and accumulation of heavy metals in the biomass. In S1, where metal concentrations in the sediment were significantly lower, even lower than ISQG values (Table 3), and where the lowest extraction percentages of metals were also recorded (Fig. 2), the highest BCF values were obtained, especially for a non-essential metal like Cr in *A. philoxeroides* and *H. ranunculoides* (Table 5). At the same site, *L. gibba* showed relatively high values of this index, especially for Zn. Thus, in an environment with low levels of bioavailable metals, wetland plants may over-accumulate essential and non-essential metals in their biomass. This process may respond to the absence of mechanisms to prevent the uptake, and it is not necessarily an evidence of their remediation ability in polluted sites. In sediments of S2 and S3, the highest concentrations of heavy metals and organic carbon were found (Table 3). For Zn and Cu, the extraction percentages were comparatively high

(Fig. 2). However, the BCFs calculated for *S. montevidensis* were lower than those calculated in S1 for species with the same life form, such as *S. americanus* and *A. philoxeroides* (Table 5). For Cr, the lowest extraction percentages were obtained (Fig. 2), and the BCFs were markedly under than unity for *S. montevidensis* (Table 5). Thus, the low BCFs obtained in polluted environments could be explained not only by the active response of tolerant plant species (Taylor and Crowder 1983; Hansel et al. 2001; Cheng et al. 2014b; Dai et al. 2017; Pasricha et al. 2021) but also by the passive effect generated by the retention of metals associated to the bonding sites of the sediments (e.g., functional groups of the organic matter) (Boguta et al. 2022; da Silva et al. 2022). The roots of *E. crassipes* from S2 and S3 showed high concentrations of Zn, Cu, and especially Cr (Table 4), although heavy metal concentrations in water were markedly lower than those determined in sediments (Tables 2 and 3). For this reason, the BCF values were high for the three metals analyzed (Table 5). Besides, a considerable decrease in root biomass was observed in relation to plants collected from a non-polluted site (Photo 1). The higher uptake of metals could be attributed to their greater bioavailability in the water in relation to the sediment, while the decrease in root biomass could be due to their toxic action. However, this last statement is not conclusive since the lower basin of the Matanza-Riachuelo river has a complex mixture of pollutants (Biruk et al. 2017) which can produce similar deleterious effects on macrophytes. Considering that *E. crassipes* is a metal-accumulating macrophyte that can be easily harvested as a whole plant, several authors have proposed its use for remediation of polluted water bodies (Odjegba and Fasidi 2007; Saha et al. 2017; Zhang et al. 2019).

The TF (translocation factor) index relates the concentration of a given metal in aboveground structures (leaves or stems) with the concentration in belowground structures (roots or rhizomes). In terrestrial ecosystems, high values of the index are characteristic of plants from unpolluted sites and are also recorded in hyperaccumulating species from

**Table 5** Bioconcentration factor (BCF) and translocation factor (TF) for each species of sampling sites. (Mean  $\pm$  standard deviations,  $n=3$ )

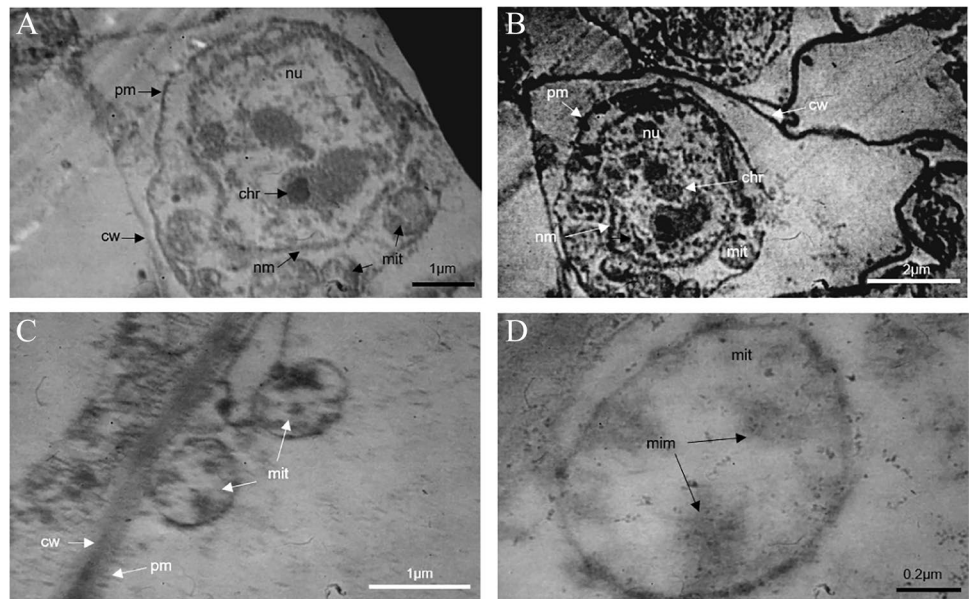
	Species	BCF			TF		
		Zn	Cu	Cr	Zn	Cu	Cr
S1	<i>Shoenoplectus americanus</i>	0.76 $\pm$ 0.13	0.53 $\pm$ 0.10	0.44 $\pm$ 0.19	0.26 $\pm$ 0.06	0.16 $\pm$ 0.06	0.18 $\pm$ 0.07
	<i>Alternanthera philoxeroides</i>	0.91 $\pm$ 0.17	0.59 $\pm$ 0.06	2.43 $\pm$ 1.88	0.53 $\pm$ 0.04	0.18 $\pm$ 0.02	1.12 $\pm$ 1.65
	<i>Hydrocotyle ranunculoides</i>	1.31 $\pm$ 0.35	0.77 $\pm$ 0.28	5.78 $\pm$ 1.30	0.21 $\pm$ 0.07	0.35 $\pm$ 0.12	0.13 $\pm$ 0.09
	<i>Lemna gibba</i>	1.35 $\pm$ 0.33	0.84 $\pm$ 0.10	0.62 $\pm$ 0.23	-	-	-
S2	<i>Sagittaria montevidensis</i>	0.24 $\pm$ 0.06	0.11 $\pm$ 0.03	0.01 $\pm$ 0.003	0.28 $\pm$ 0.10	0.54 $\pm$ 0.24	1.01 $\pm$ 0.67
	<i>Eichhornia crassipes</i>	1.40 $\pm$ 0.27	1.20 $\pm$ 0.19	2.84 $\pm$ 0.16	0.18 $\pm$ 0.04	0.10 $\pm$ 0.02	0.01 $\pm$ 0.002
	<i>Panicum elephantipes</i>	0.62 $\pm$ 0.51	0.41 $\pm$ 0.16	0.39 $\pm$ 0.17	0.41 $\pm$ 0.29	0.41 $\pm$ 0.20	0.48 $\pm$ 0.33
S3	<i>Sagittaria montevidensis</i>	0.26 $\pm$ 0.04	0.11 $\pm$ 0.04	0.02 $\pm$ 0.004	0.24 $\pm$ 0.05	0.70 $\pm$ 0.18	0.25 $\pm$ 0.04
	<i>Eichhornia crassipes</i>	1.12 $\pm$ 0.32	1.09 $\pm$ 0.42	1.51 $\pm$ 0.53	0.51 $\pm$ 0.17	0.22 $\pm$ 0.12	0.05 $\pm$ 0.03



**Fig. 3** TEM micrographs of transverse sections of mesophyll cells of *S. montevidensis*. Cell wall (cw), plasmatic membrane (pm), nucleus (nu), tonoplast (t), vacuole (v), chloroplast (chl), chloroplast internal membrane system (chlm), nuclear membrane (nm), and chromatin (chr). **A** Undifferentiated cell (right) and differentiated cell with a large central vacuole and chloroplasts aligned towards the cell wall

(left). **B** Detail of an undifferentiated cell with a functional plasma membrane, a large and well-preserved nucleus, a chloroplast, smaller organelles and cell content. **C** A chloroplast of a well differentiated cell, with functional external and internal (thylakoids) membrane systems. **D** Preserved chromatin in a nucleus of a differentiated cell

**Fig. 4** TEM micrographs of transverse sections of parenchyma root cells of *E. crassipes*. Cell wall (cw), plasma membrane (pm), nuclear membrane (nm), chromatin (chr), mitochondria (mit), and mitochondria internal membrane system (mim). **A** and **B** Plasmolyzed cells with damage in the plasma membrane. **C** and **D** Mitochondria with a disorganized internal membrane system



locations with high (natural or anthropogenic) metal concentration. Very low values of the TF index suggest the existence of internal plant mechanisms to avoid the translocation of metals, preventing their toxic action (Rascio and Navari-Izzo 2011; Shuvaeva et al. 2013; Pasricha et al. 2021). However, in aquatic ecosystems, different patterns can be observed. In S1, the calculated TFs were less than unity with

the exception of Cr for *A. philoxeroides* (Table 5). The prone life form of this plant allows the uptake of nutrients and toxic compounds directly from the water and independently of the root uptake system, so the TF index was not useful in this case. In S2, *S. montevidensis* presented the highest TF for Cr, while *E. crassipes* presented low values of the index for Cu and especially for Cr (Table 5). Since *S. montevidensis* has

**Photo 1** Samples from *E. crassipes* collected from an unpolluted site (left) and a highly polluted site of the Matanza-Riachuelo river (right). Bars = 5 cm



a very low BCF for Cr (Table 5), it cannot be considered a hyperaccumulating species while the accumulation of potentially toxic metals in roots could be a tolerance strategy in *E. crassipes* to prevent damage to photosynthetic structures by Cu and Cr, both metals with high redox activity.

In summary, the uptake of metals and their distribution among the different plant organs may depend not only on the total or available concentration of the metal in the environment but also on the metabolic role of the element in the plant, and also on the associated mechanisms of toxicity, on the life form and the species studied (Jackson 1998; Serrano and Rodríguez-Navarro 2001; Bonanno et al. 2017). In *S. montevidensis*, the results obtained are compatible with exclusion mechanisms, while in *E. crassipes* root compartmentalization would be the dominant detoxification process for metals.

### Ultrastructural analysis in cells of leaves and roots of aquatic plants

Due to the high concentration of metals in water and sediment of S2 and S3 (Tables 2 and 3), and the complex mixture of pollutants reported in previous studies, evidence of toxicity would be expected to be found in aquatic plants collected in the lower basin of the Matanza-Riachuelo river. However, no macro or mesoscopic evidence of damage to leaves and/or roots of *S. montevidensis* and *E. crassipes* from S2 was detected, except the scarce root development of roots of *E. crassipes* compared to roots from unpolluted sites, as reported above. The samples were observed under the transmission electron microscope (TEM) for evidence

of ultrastructural alterations (organelles, vacuole, nucleus, membranes) compatible with the toxic effect reported for heavy metals with redox activity (Dalla Vecchia et al. 2005; Mangabeira et al. 2011; Basile et al. 2015).

*Sagittaria montevidensis* translocated a relatively high percentage of Cr to its photosynthetic tissues, while in *E. crassipes*, most of the uptake of metals was accumulated in the root, especially for Cr (Table 5). Therefore, TEM observations were focused on the leaves of *S. montevidensis* and the roots of *E. crassipes*.

Under the light microscope, the leaves of *S. montevidensis* presented a normal design, with the photosynthetic parenchymal tissues clearly visible, in which abundant chloroplasts were distinguished. Mesophyll cells with numerous lenticular-shaped chloroplasts were observed under the TEM (Fig. 3). No plasmolysis was observed, nor evidence of damage in the internal membrane system of the cells (chloroplast, nucleus), nor condensation of nuclear chromatin, and there was no presence of electron-dense corpuscles that usually constitute local accumulations of metals (Fig. 3) (Sresty and Madhava Rao 1999). These observations, associated with the high TF values for metals and especially for Cr (Table 5), would indicate the absence of toxic effects, and so *S. montevidensis* can be considered a species tolerant to the environmental conditions of the lower basin of the Matanza-Riachuelo river.

When observing the cells of the root cortex of *E. crassipes* under the TEM, numerous evidences of toxicity were found. A large number of plasmolyzed cells were observed: mitochondria with disorganized internal membranes, nuclear membranes in process of disintegration as well as condensed

chromatin (Fig. 4). These effects cannot be attributed exclusively to pollution by heavy metals, especially in a highly polluted river like the Matanza-Riachuelo, but cellular damage is compatible with the deleterious effects produced by heavy metals (Mangabeira et al. 2011). Due to its free-floating life form, *E. crassipes* is exposed to concentrations of pollutants that are much lower than those recorded in sediments (Tables 2 and 3). Immobilization in roots could be evidence of the potential toxicity of metals to photosynthetic tissues, and *E. crassipes* could be considered a sensitive species.

## Conclusions

The lower basin of the Matanza-Riachuelo river is severely polluted by anthropogenic activities. However, the high concentrations of metals in the water and sediments have not prevented the settlement of wetland plants of different life forms, from free-floating to marshy species. The differences observed in the extraction percentages of heavy metals by the extracting agents evaluated, and between different study sites, suggest that the extraction diagrams could be considered an additional tool in sediment characterization. Low levels of available metals, estimated using extracting agents, indicate that the sediments have a high retention capacity for metallic pollutants. In *S. montevidensis*, BCF and TF data are compatible with exclusion mechanisms of heavy metals, whereas in *E. crassipes*, root compartmentalization could constitute the dominant strategy. TEM observations did not detect any damage to the leaves of *S. montevidensis*, but alterations were found in the root cells of *E. crassipes*. Even considering these damages could not be unequivocally attributed to the heavy metals evaluated in this study, they are consistent with toxic effects reported in the literature.

**Author contribution** All the authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Roberto Jose Maria Serafini, Silvana Arreghini, Horacio Esteban Troiani, and Alicia Rosa Fabrizio de Iorio. The first draft of the manuscript was written collectively by all the authors. All authors read and approved the final manuscript.

**Funding** This study was funded by the National Science and Technology Agency (ANPCyT) through the PICT-2012–2837 and the University of Buenos Aires through UBACyTAG548.

**Data availability** All data generated or analyzed during this study are included in this published article.

## Declarations

**Ethical approval** Not applicable.

**Consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Competing interests** The authors declare no competing interests.

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