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## Heavy metal accumulation in leaves of aquatic plant *Stuckenia filiformis* and its relationship with sediment and water in the Suquia river (Argentina)



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### ABSTRACT

In order to evaluate the *Stuckenia filiformis* plant species as an indicator organism of heavy metal pollution in biomonitoring studies of the aquatic ecosystem, the aim of this study was to determine the levels of heavy metal accumulation (Co, Cu, Fe, Mn, Ni, Pb and Zn) in leaves of the submerged macrophyte *S. filiformis* and the possible relationship of the concentrations of these metals with those found in surface water and sediment samples of the Suquia river. Sampling was carried out in July 2006 and February 2009, during the dry and wet seasons, respectively, at 7 sampling sites where three replicates of surface water, sediment and *S. filiformis* plants were collected. Cobalt, Ni and Zn in surface water were significantly higher in the samples collected in 2006 than those in 2009. In sediment, the concentrations of Co, Cu, Ni, Pb and Zn, along with organic matter, were significantly higher in 2006, while those of Fe were significantly greater in 2009. Copper and Pb exceeded the limits established for the protection of aquatic life by national (Cu: 2.0  $\mu\text{g L}^{-1}$ , Pb: 2.0  $\mu\text{g L}^{-1}$ ) and international organizations (Cu: 1.6  $\mu\text{g L}^{-1}$ , Pb: 2.5  $\mu\text{g L}^{-1}$ ) in surface water, while in sediment, Zn exceeded the limit for ecological screening levels (Zn: 121.0  $\text{mg kg}^{-1}$ ) in 2006. In the surface water and sediment samples, heavy metal concentrations were found to be higher downstream of Córdoba city (Sites 6 and 7) in both sampling campaigns, probably related to the contribution of pollutants from the effluent discharge of a wastewater treatment plant and industrial activities of the city. The aquatic plant *S. filiformis* showed a high capacity to accumulate heavy metals in its tissues, in areas of the river where higher values of heavy metals in the abiotic compartments surface water and sediments were observed. Copper, Pb and Zn incorporated as contaminants in surface water and sediments were able to be removed by *S. filiformis* by self-purification processes. Therefore, this species could be proposed as a suitable heavy metal bioindicator for the early stages of pollution in rivers.

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### 1. Introduction

An important role in population development is played by rivers because they provide water for human consumption, agriculture and industry. However, aquatic ecosystems suffer the consequences of human activities, as these environments have stormwater sinks, surface runoff, leaching and/or effluent discharges. Activities such as mining, agriculture and industrial plants with large urban settlements systematically produce pollutants that are discharged in a dissolved form or suspended in material in rivers, thus significantly decreasing water quality and increasing the ecological risk to human health [1]. In this sense, heavy metal pollution is of great concern worldwide as a result of the continuing increase in these emissions. Consequently, the river fluids become contaminated with these pollutants, which can have a

severe impact on human health, as well as on terrestrial and aquatic ecosystems, due to their toxicity, bioaccumulation, non-degradation and indefinite persistence [2,3]. The contribution of heavy metals can be discontinuous or in pulses [4,5]. In general, these pollutants when released into water systems bind to particulate matter, in which after eventually becoming decanted, are incorporated into the sediments. Thus, surface sediment is an important reservoir of heavy metals and other contaminants in the aquatic environment.

Macrophytes contribute significantly to the primary production of water bodies in the littoral zone, forming a fundamental part of the trophic structure of aquatic ecosystems. During the recirculation of nutrients, aquatic plants can uptake large amounts of metals from the environment [6], with this absorption capacity of metals through roots and leaves [7,8], combined with their sedentary nature, making these plants suitable for detecting changes or alterations in the aquatic environment [9,10]. High concentrations of metals in aquatic plants can be accumulated from the water column and/or from sediments [8,11],

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demonstrating the usefulness of macrophytes as biomonitors for aquatic systems. Moreover, measuring the accumulation of persistent pollutants in aquatic plants can provide time-integrated information about the presence of toxic compounds in the aquatic ecosystems.

In recent years, water pollution in the Suquia river basin, associated with population growth and economic and industrial development, has attracted increasing attention. This basin is represented by a drainage area of approximately 1700 km<sup>2</sup>, of which about 900 km<sup>2</sup> correspond to Cordoba city, where there has been significant population growth in the last 20 years (1.5 million inhabitants [12]) with many new industries having increased the risk of toxic effluent discharge to the river [13]. In turn, this basin supplies drinking water to Córdoba city and nearby towns (Carlos Paz, La Calera, Saldán, among others), which is also used in the production of electricity and as a source for agricultural irrigation and industrial or recreational activities [14]. Various studies have evaluated the negative impact of these activities on the water quality of the Suquia river, both spatially and temporally [13–16]. In addition, in the central region of Argentina, heavy metal pollution became evident through monitoring studies and using epiphytic lichens and vascular plants in the biomonitoring measurement of these contaminants in samples of total deposition of atmospheric particulate matter and in organic tissues [17–19]. These results showed that human activities, including industry, mining and agriculture, are an important source of metals that are incorporated into the environment [20–22]. Although the analysis of heavy metals from surface water and the sediments of rivers of the Suquia river basin has been previously used for the purpose of monitoring contamination [13,16,23], little research has focused on the presence of heavy metals in these abiotic and biotic compartments, such as in macrophytes and aquatic ecosystems [24].

The submerged macrophyte *Stuckenia filiformis* (Family Potamogetonaceae) is a species native to South America and is widely represented in the rivers of the central region of Argentina. This plant is an aquatic grass, typically perennial, found in the sandy substrate of river beds with moderate currents, with floating rhizomes and roots sometimes present and with filiform leaves typically exceeding 1 m in length [25]. It forms clumps in places where fine sediment accumulates in small established banks that are home to complex communities of bacteria, unicellular algae and invertebrates, which constitute the diet of higher trophic levels such as fish [26]. In this way, this species has the optimum characteristics to be used as a bioindicator organism in biomonitoring studies of water pollution [27]. However, despite its wide distribution, the macrophyte *S. filiformis* has not been studied in relation to its use in biomonitoring of surface water quality or in obtaining experimental evidence of exposure to contaminants. In order to evaluate this aquatic plant species as an indicator organism for heavy metal pollution in biomonitoring studies of the aquatic ecosystem, the aim of this study was to determine the levels of heavy metal accumulations (Co, Cu, Fe, Mn, Ni, Pb and Zn) in leaves of the submerged macrophyte *S. filiformis* and the possible relationship of the concentrations of these metals with those found in surface water and sediment samples of the Suquia river.

## 2. Materials and methods

### 2.1. Study area and sampling

The present study was carried out in a section of the Suquia river middle basin, in Cordoba province, located in the central region of Argentina (Fig. 1). The rivers that form the drainage network of the Suquia river are formed by rain, with a marked seasonality of the flow due to the uneven distribution of rainfall throughout the year [28]. The Suquia river has a high flow period during the wet season from December to April, with an estimated flow of 15 m<sup>3</sup> s<sup>-1</sup>, whereas during the dry season from May to November, this figure is only 2.7 m<sup>3</sup> s<sup>-1</sup> [29]. The confluence of the Cosquín (N) and San Antonio (S) rivers and

the Los Chorrillos and Las Mojarras brooks (W) is the origin of San Roque lake, formed by the dam of the same name. From this site the Suquia river begins, which flows in the direction W-E and runs a length of 200 km. At 25 km, water of the Saldán brook enters, and the river flows through areas with agricultural, industrial and mining aggregate extraction activities and urban zones before emptying into Laguna Mar Chiquita (one of the largest salt water lakes in the world), which has been designated a Ramsar site no. 1176 [30], as it is considered to be one of the most important wetlands in Argentina and of the Chaco ecoregion in terms of richness and biodiversity [15]. The morphology of the area is variable, ranging from an average altitude of over 1500 m above sea level (m.a.s.l.) in the W at about 300 m.a.s.l. in the E. The geology of the area is characterized by Proterozoic metamorphic rocks with calc-alkaline granitoids and plains predominantly of loess scattered deposits that are mixed with Tertiary and Quaternary fluvial sediments [31]. The climate of the region is temperate, continental and subtropical, tending to semiarid. According to historical data of the Servicio Meteorológico Nacional [32] between 1961 and 1990, the average annual rainfall ranges from 700 to 800 mm. This rainfall is highly seasonal, with the most rainy summer season (December, January and February) having accumulated values greater than 400 mm, whereas the dry winter season (June, July and August) has a cumulative rainfall of up to 30 mm. The maximum water temperatures are produced during the rainy season (average temperature of 20 °C) and the minimum temperatures occur in winter (average temperature of 8 °C).

The sampling sites were selected based on previous studies on pollution sources and water quality of the rivers of Suquia river basin [14], which are in agreement that Córdoba city is primarily responsible for the pollution. The study sites of the present investigation were sampled during periods of low and high flow, in July 2006 and February 2009, respectively. To evaluate the spatial variation, we selected seven sampling sites, and for each sampling campaign three replicas of surface water, sediment and plants *S. filiformis* were collected at each site. Site 1 (31° 21' 60" S, 64° 30' 52" W, 766 m) was established as the reference, which was located on the Los Chorrillos brook prior to San Roque lake and Sites 2 to 7 were on the Suquia river. Site 2 (31° 20' 36" S, 64° 21' 18" W, 539 m) was located 18 km upstream from Córdoba city, before La Calera town; Site 3 (31° 17' 54" S, 64° 19' 53" W; 594 m) was located 15 km upstream from Córdoba city, before Saldán brook; Site 4 (31° 19' 16" S, 64° 18' 58" W, 516 m) was located on Saldán brook, before the mouth of the Suquia river; Site 5 (31° 20' 46" S, 64° 16' 58" W; 463 m) was located 12 km upstream from Córdoba city, after Villa Rivera Indarte town. At Sites 2 to 5, in terms of land use, are found mining of aggregate extraction and major roads; Site 6 (31° 24' 19" S, 64° 05' 29" W, 397 m) was located 1 km downstream of Córdoba city, after the discharge of effluent from the municipal wastewater treatment plant, and Site 7 (31° 25' 48" S, 64° 01' 22" W, 360 m) was located 9 km downstream from Córdoba city, after an industrial channel (of an automotive type, including auto-part, metallurgical and metal-mechanical activities) based in the southeast of Córdoba city. At Site 1, no samples of surface water, sediment or plant were taken in the 2006 sampling, and Site 6 had no aquatic plant samples for any of the sampling campaigns between 2006 and 2009.

The average monthly rainfall in the study area for the period of drought prior to the 2006 sampling was 2.5 mm (accumulated rainfall in May, June and July was 7.5 mm), while in the wet season of 2009 it reached 70.8 mm (accumulated rainfall in December, January and February was 219.7 mm) [32]. Environmental data for temperature, pH and electrical conductivity in water were analyzed "in situ" using a multiparameter probe.

### 2.2. Sample preparation for the analysis of surface water and sediment

All glassware used in the field and in the laboratory was left in a solution of HNO<sub>3</sub> 10% V/V (Merck Química Argentina) for 24 h and then washed with ultra-pure water, which was obtained using a

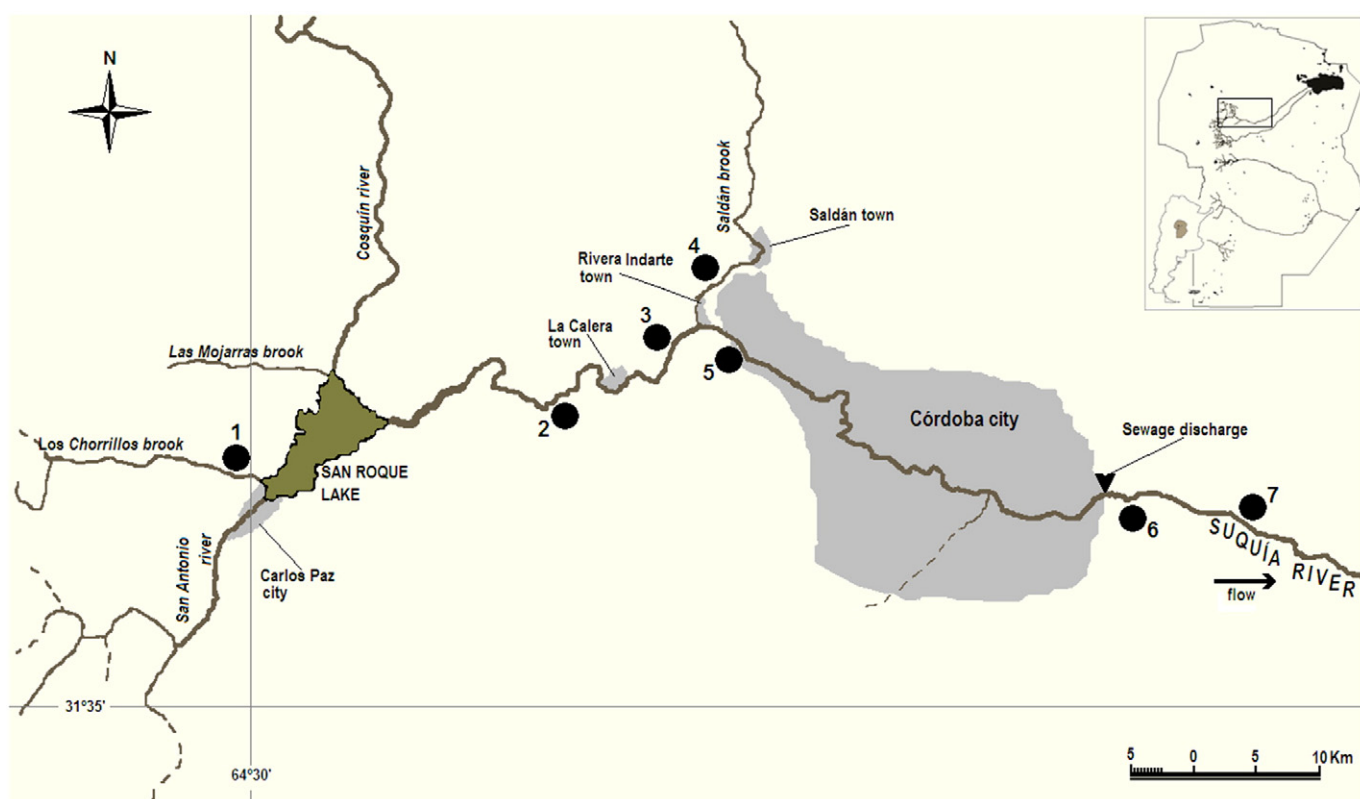


Fig. 1. Sampling sites (\*) in the Suquia river middle basin.

water purification system consisting of a tandem filtration through activated carbon, reverse osmosis and ion exchange, with a membrane filtration (0.45  $\mu\text{m}$ ) (Millipore Simplicity® con SimPak®1, EE.UU.).

Surface water samples for metal analysis were collected in the littoral zone, approximately 10 cm below the water surface of the river. Three replicates were collected of water samples at each sampling site using clean polyethylene bottles. These were acidified immediately using  $\text{HNO}_3$  63% W/W to  $\text{pH} \leq 2$  and then filtered with filter paper of 2.0  $\mu\text{m}$  (Scheicher & Schüll, Blauband 5893, no. 300210) [13]. The analysis of Co, Cu, Fe, Mn, Ni, Pb and Zn was performed by GFAAS (graphite furnace atomic absorption spectrometer, AAnalyst 600, equipped with the AS 800 autosampler, Perkin Elmer, USA). To evaluate the recovery rate of the various elements, 5 mL of the water sample was prepared by injecting an aliquot of an element of a standard solution for atomic absorption spectrometry (AccuStandard®, Fluka, 1000  $\text{mg L}^{-1}$  in 1% nitric acid).

Injected samples were analyzed by GFAAS, with the recovery percentages found being 90–110% (data not shown). Appropriate dilutions were carried out with the addition of matrix modifiers ( $\text{CsCl}$ ,  $\text{La}_2\text{O}_3$ ,  $\text{CaCl}_2$  y  $\text{H}_2\text{O}_2$ ) before measurement of an element. The repeatability of measurements (principally of atomic absorption) was  $\geq 97\%$ , calculated by comparing the values obtained in triplicate (three measurements in each sample or injected sample). The stability of the equipment was verified by measuring the calibration curve both before and after sample measurements. Blank solutions, containing only reagents without river water, were used to deduct the content of metals arising from reagents and laboratory tools.

In the littoral zone of the river, approximately the first 10 cm of the fine sediment surface of the river was collected for metal analysis of the sediments, with three replicates being collected of sediment samples from each sampling site. These samples were collected using a clean plastic core tube and sealed in polyethylene bags, before being taken in coolers to the laboratory where they were oven dried for 48 h at  $60 \pm 2$  °C. Prior to analysis, the samples were dry-sieved using a 63  $\mu\text{m}$  acrylic mesh. Then, 5 g of the <63  $\mu\text{m}$  dried material was

carbonized in an oven at 450 °C for 4 h, and the ashes were digested using a mixture of HCl (20%) and concentrated  $\text{HNO}_3$  (3: 1) (V/V) [33]. The solid residue was separated by centrifugation, and the sample was diluted with ultrapure water to a final volume of 25 mL. Finally, the Co, Cu, Fe, Mn, Ni, Pb and Zn contents were analyzed using FAAS (air-acetylene flame atomic absorption spectrometer, Perkin Elmer 3110, USA), with blanks being prepared using the same protocol without sediment (only reagents). Recovery studies were also carried out by adding individual atomic absorption spectrometry standard solutions (AccuStandard®, 1000  $\text{mg L}^{-1}$  in 1% nitric acid) of three randomly selected suspended sediment samples (1 mg Fe or 10 mg of other metal  $\text{kg}^{-1}$  sediment), which were mixed before drying. The injected samples were treated and analyzed as normal sediment in order to evaluate the recovery rate, which yielded an 80–95% recovery rate, after correcting with the dry weight (data not shown). The organic matter percentage (OM %) was determined according to Peltola and Åström [34] by the combustion of samples at 500 °C for 4 h.

### 2.3. Sample preparation for macrophyte analysis

At each sampling site, the aquatic plant samples of *S. filiformis* were collected in triplicate, at a constant depth of 40 cm. Each sample consisted of a pool of 2–3 plants, which were washed in the river before being placed in polyethylene bags and taken to the laboratory in coolers. Once there, the plants were rinsed again with distilled water to remove any material adhering to their surfaces, dissected using a lyophilizer chamber of acrylic and trays (Rifcor® Model L-A-B4) and preserved in plastic bags until being analyzed. Samples of the dried plant material (5 g) were carbonized in an oven at 450 °C for 4 h, and the ashes were digested using a mixture of HCl (20%) and concentrated  $\text{HNO}_3$  (3:1) (V/V) [35]. For metal determinations, solid residues were removed by centrifugation and the samples were diluted with ultrapure water to a final volume of 25 mL. Finally, the contents of Co, Cu, Fe, Mn, Ni, Pb and Zn were analyzed using FAAS (air-acetylene flame atomic absorption spectrometer, Perkin Elmer 3110, USA). Digestion blanks



were prepared and analyzed in the same manner, with results being expressed in  $\text{mg kg}^{-1}$  DW (dry weight). The quality control was evaluated with certified material ( $\pm$  uncertainty for certified value, with 95% confidence) of Oriental Tobacco Leaves (ICHTJ-CTA-OTL-1), using the same protocol to check the validity of the analytical method. Certificate material samples revealed that the concentrations of Cu, Mn, Ni, Pb and Zn were  $13.9 \pm 0.485$ ,  $394 \pm 10.6$ ,  $5.94 \pm 0.75$ ,  $5.08 \pm 1.03$  and  $51.2 \pm 4.09 \text{ mg kg}^{-1}$  DW, respectively. This method, therefore, gave concentrations that were within the range for certification for Cu, Mn and Zn, but 12.6% higher for Ni and 20.3% greater for Pb.

#### 2.4. Statistical analysis

Statistical analyses were based on the mean values of determinations made for three replicates obtained at each sampling site in the campaigns of 2006 and 2009. Assumptions of normality and homoscedasticity were tested using the Shapiro–Wilk test and Levene test, respectively. Since not all the variables satisfied these assumptions, non-parametric tests were also used (Kruskal–Wallis). This procedure was in agreement with Reimann and Filzmoser [36], who showed that geochemical data are strongly bimodal and non-normal. When the Kruskal–Wallis null hypothesis was rejected (significance level  $< 0.05$ ), post hoc pairwise comparisons were performed to investigate differences between pairs of means. The Spearman correlation coefficients were calculated in order to study the relationships among the chemical elements of the three systems and among the metals in each system.

### 3. Results and discussion

#### 3.1. Heavy metals in surface water and sediment

Higher mean values of temperature ( $p < 0.001$ ) and pH ( $p < 0.01$ ) were measured in the water of the Suquía river in 2009, while greater electrical conductivity ( $p < 0.01$ ) was observed in 2006 ( $25.3 \pm 0.7$  °C,  $7.6 \pm 0.3$ ,  $0.301 \pm 0.228 \text{ mg L}^{-1}$  in 2009,  $14.9 \pm 1.2$  °C,  $8.1 \pm 0.5$ ,  $0.694 \pm 0.585 \text{ mg L}^{-1}$  in 2006).

The heavy metals Co ( $p < 0.001$ ), Ni ( $p < 0.05$ ) and Zn ( $p < 0.05$ ) measured in surface waters were significantly higher in samples collected in 2006 (Table 1). In sediment, Co ( $p < 0.01$ ), Cu ( $p < 0.05$ ), Ni ( $p < 0.001$ ), Pb ( $p < 0.05$ ) and Zn ( $p < 0.05$ ), along with organic matter ( $p < 0.05$ ), were significantly higher in 2006, while those of Fe ( $p < 0.05$ ) were significantly greater in 2009 (Table 1). No significant differences in the levels of Mn were found between sampling campaigns.

The mean concentrations of all heavy metals in surface water, except for Cu and Pb (Table 1), were recorded within the limits for the protection of aquatic life by national (Cu:  $2.0 \text{ } \mu\text{g L}^{-1}$ , Ni:  $25 \text{ } \mu\text{g L}^{-1}$ , Pb:  $2.0 \text{ } \mu\text{g L}^{-1}$ , Mn:  $100 \text{ } \mu\text{g L}^{-1}$ , Zn:  $30 \text{ } \mu\text{g L}^{-1}$  [37]) and international organizations (Cu:  $1.6 \text{ } \mu\text{g L}^{-1}$ , Co:  $24.0 \text{ } \mu\text{g L}^{-1}$  [38]; Mn:  $80.0 \text{ } \mu\text{g L}^{-1}$  [39];

Ni:  $52.0 \text{ } \mu\text{g L}^{-1}$ , Pb  $2.5 \text{ } \mu\text{g L}^{-1}$ , Zn  $120.0 \text{ } \mu\text{g L}^{-1}$  [40]). Although copper is an essential micronutrient for all organisms, it is known to be toxic at high concentrations in surface waters [41,42]. In contrast, Pb is not essential, whose toxicity is manifested even at low concentrations [43]. Both these metals, therefore, may be toxic to the aquatic organisms found in the Suquía river.

The average concentrations of all the heavy metals in the sediment analyzed, except for Zn in 2006 (Table 1), were within the limits established for ecological screening levels [38] (Cu:  $31.6 \text{ mg kg}^{-1}$ , Ni:  $22.7 \text{ mg kg}^{-1}$ , Pb:  $35.8 \text{ mg kg}^{-1}$ , Co:  $50 \text{ mg kg}^{-1}$ , Zn:  $121.0 \text{ mg kg}^{-1}$ ). High concentrations of Zn in sediments may have a negative impact on aquatic plant communities, as demonstrated by Carling et al. [44] in wetlands adjacent to the Great Salt Lake (Utah).

Heavy metal concentrations, in surface waters in 2006 and 2009, revealed significant differences between the sampling sites (Table 2). In general, heavy metal concentrations were found higher downstream of Córdoba city (Sites 6 and 7) in both sampling campaigns, which was probably related to the contribution of pollutants from effluent discharges from anthropogenic sources on both sides of the river, to infiltration or stormwater discharges flowing into the river, or to the discharge of effluents from the wastewater treatment plant and industrial activities of the city. These results demonstrate that the heavy metal concentrations in surface waters of the Suquía river were higher than concentrations observed in previous studies conducted in the same river [23] or in other rivers of Córdoba province [5].

The spatial variation of the heavy metal concentrations in sediments (Table 3) of both sampling campaigns showed significant differences for each metal studied, except for Fe in 2006. As mentioned earlier, the sediment results revealed that the Fe levels were higher in 2009 than in 2006 (Table 1), with the maximum concentrations of this metal being registered in 2009 in areas where large amounts of organic matter were deposited (Table 3). In this regard, Charzeddine et al. [45] noted that the external supply of Fe in the rainy season was able to form colloidal dispersions of amorphous iron hydroxide,  $\text{Fe}(\text{OH})_3$  and goethite,  $\alpha\text{-FeO}(\text{OH})$ , which were retained by the organic matter. Similarly, Wedepohl [46] indicated that this element is found in large proportions in the upper crust, and consequently its concentrations in aquatic environments tend to increase considerably due to the drag action exerted by rainfall, surface runoff and/or leaching.

The Spearman correlation analysis did not reveal any association between the heavy metal concentrations in surface water and those in sediments, except for Pb ( $r = 0.66$ ,  $p < 0.0019$ ) and Zn ( $r = 0.92$ ,  $p < 0.001$ ), which were also the metals that showed the highest concentrations in 2006 downstream from Córdoba city (Site 7) (Table 4). Therefore, the presence of heavy metals measured in the water matrix was not related to another matrix, such as sediment. Furthermore, the sediment samples revealed a strong association between Cu (Spearman correlation,  $r = 0.58$ ,  $p < 0.001$ ), Pb ( $r = 0.32$ ,  $p < 0.05$ ) and Zn ( $r = 0.46$ ,  $p < 0.001$ ) with organic content. In the Suquía river, the

**Table 1**  
Mean values and standard deviation ( $\pm$  SD) of the concentrations of Co, Cu, Fe, Mn, Ni, Pb and Zn in surface water, sediments and *S. filiformis* collected at different sites in 2006 and 2009 on the Suquía river, Córdoba, Argentina. Results of the variance analysis (Kruskal–Wallis) between years are shown for each metal along with the OM % in sediments.

	Surface water ( $\mu\text{g L}^{-1}$ )			Sediment ( $\text{mg kg}^{-1}$ DW)			<i>S. filiformis</i> ( $\text{mg kg}^{-1}$ DW)		
	2006	2009	Kruskal–Wallis	2006	2009	Kruskal–Wallis	2006	2009	Kruskal–Wallis
Co	$8.89 \pm 3.24$	$4.66 \pm 2.00$	***	$5.78 \pm 1.39$	$4.27 \pm 1.08$	**	$1.80 \pm 1.00$	$3.35 \pm 0.42$	***
Cu	$3.52 \pm 3.28$	$6.19 \pm 10.00$	ns	$17.90 \pm 17.55$	$8.34 \pm 2.50$	*	$10.09 \pm 5.79$	$10.09 \pm 4.96$	ns
Fe	$308 \pm 225$	$297 \pm 409$	ns	$5842 \pm 1171$	$7892 \pm 3190$	*	$4495 \pm 2658$	$4702 \pm 2754$	ns
Mn	$61.3 \pm 47.1$	$45.1 \pm 21.1$	ns	$402 \pm 310$	$340 \pm 120$	ns	$1669 \pm 1016$	$769 \pm 497$	**
Ni	$14.39 \pm 8.40$	$7.93 \pm 8.33$	*	$14.53 \pm 4.23$	$9.03 \pm 2.25$	***	$5.68 \pm 5.26$	$9.30 \pm 4.82$	*
Pb	$11.61 \pm 4.49$	$12.51 \pm 10.16$	ns	$22.35 \pm 10.08$	$15.96 \pm 8.60$	*	$7.92 \pm 4.30$	$8.26 \pm 4.48$	ns
Zn	$12.7 \pm 12.5$	$6.1 \pm 5.4$	*	$171.6 \pm 183.1$	$82.5 \pm 86.8$	*	$52.5 \pm 47.8$	$60.0 \pm 42.6$	ns
OM %				$11.2 \pm 4.1$	$7.8 \pm 3.5$	*			

ns, not significant; \*, significant at the 0.05 probability level; \*\*, significant at the 0.01 probability level; \*\*\*, significant at the 0.001 probability level. OM, organic matter; DW, dry weight.

**Table 2**

Mean values and standard deviation ( $\pm$ SD) of the concentrations of Co, Cu, Fe, Mn, Ni, Pb and Zn in surface water in 2006 and 2009 from the Suquía river, Córdoba, Argentina. Results of the variance analysis (Kruskal–Wallis) between sampling sites for each year are shown, with values in each vertical column followed by the same letter not differing significantly at  $p < 0.05$  (pairwise comparisons of means).

Site	Surface water ( $\mu\text{g L}^{-1}$ )							
	Co [2006]	Co [2009]	Cu [2006]	Cu [2009]	Fe [2006]	Fe [2009]	Mn [2006]	Mn [2009]
1	–	3.77 $\pm$ 0.19 c	–	1.77 $\pm$ 0.35 b	–	85 $\pm$ 6 b	–	16.4 $\pm$ 0.9 c
2	5.95 $\pm$ 1.45 b	3.99 $\pm$ 0.90 c	0.59 $\pm$ 0.15 e	1.37 $\pm$ 0.16 b	175 $\pm$ 10 b	163 $\pm$ 43 b	19.9 $\pm$ 0.7 cd	44.5 $\pm$ 5.8 b
3	6.16 $\pm$ 0.20 b	4.17 $\pm$ 0.50 c	0.99 $\pm$ 0.16 de	1.84 $\pm$ 0.33 b	171 $\pm$ 14 b	157 $\pm$ 16 b	34.7 $\pm$ 2.2 c	41.3 $\pm$ 4.4 b
4	6.43 $\pm$ 0.17 b	6.24 $\pm$ 0.84 b	1.53 $\pm$ 0.19 cd	1.81 $\pm$ 0.15 b	163 $\pm$ 8 b	144 $\pm$ 0 b	59.9 $\pm$ 6.0 b	46.3 $\pm$ 1.2 b
5	8.46 $\pm$ 0.82 b	8.63 $\pm$ 0.46 a	1.99 $\pm$ 0.03 c	1.87 $\pm$ 0.11 b	98 $\pm$ 2 b	145 $\pm$ 5 b	7.5 $\pm$ 2.0 de	37.6 $\pm$ 1.8 b
6	12.80 $\pm$ 0.67 a	3.06 $\pm$ 0.12 c	6.93 $\pm$ 0.51 b	6.84 $\pm$ 0.65 b	621 $\pm$ 66 a	128 $\pm$ 19 b	117.2 $\pm$ 15.9 a	39.2 $\pm$ 5.0 b
7	13.53 $\pm$ 0.79 a	2.76 $\pm$ 0.29 c	9.10 $\pm$ 0.11 a	27.80 $\pm$ 11.49 a	619 $\pm$ 56 a	1259 $\pm$ 292 a	128.5 $\pm$ 5.9 a	90.6 $\pm$ 5.1 a
Kruskal–Wallis	***	**	***	***	***	***	***	***

Site	Surface water ( $\mu\text{g L}^{-1}$ )					
	Ni [2006]	Ni [2009]	Pb [2006]	Pb [2009]	Zn [2006]	Zn [2009]
1	–	4.48 $\pm$ 0.47 b	–	6.09 $\pm$ 1.75 b	–	3.4 $\pm$ 1.2 b
2	9.55 $\pm$ 0.23 b	3.28 $\pm$ 0.69 b	7.03 $\pm$ 0.56 b	5.74 $\pm$ 2.88 b	2.9 $\pm$ 0.5 b	5.4 $\pm$ 3.9 b
3	8.87 $\pm$ 0.30 b	3.87 $\pm$ 0.39 b	8.38 $\pm$ 0.40 b	7.83 $\pm$ 2.48 b	3.8 $\pm$ 0.4 b	3.5 $\pm$ 2.0 b
4	8.55 $\pm$ 1.02 b	4.69 $\pm$ 0.93 b	9.71 $\pm$ 0.65 b	13.49 $\pm$ 1.33 b	5.5 $\pm$ 2.2 b	2.3 $\pm$ 0.3 b
5	7.44 $\pm$ 4.16 b	3.17 $\pm$ 0.21 b	9.29 $\pm$ 1.69 b	4.99 $\pm$ 2.43 b	3.8 $\pm$ 0.6 b	4.2 $\pm$ 1.6 b
6	25.58 $\pm$ 0.40 a	9.11 $\pm$ 0.41 b	16.78 $\pm$ 1.42 a	15.98 $\pm$ 5.07 b	29.7 $\pm$ 1.8 a	6.0 $\pm$ 1.4 b
7	26.37 $\pm$ 0.11 a	26.93 $\pm$ 6.16 a	18.46 $\pm$ 1.04 a	33.47 $\pm$ 7.32 a	30.9 $\pm$ 1.2 a	18.2 $\pm$ 0.6 a
Kruskal–Wallis	***	***	***	***	***	***

\*\* , significant at the 0.01 probability level; \*\*\* , significant at the 0.001 probability level.

contribution of heavy metals (including Cu, Pb and Zn) from anthropogenic emission sources may be the same as that which led to the deposition of these metals in the sediments.

### 3.2. Heavy metal accumulation in leaves of *S. filiformis*

In general, aquatic plants collected in the Suquía river showed no significant differences in the heavy metal concentrations in their tissues between the two sampling campaigns, except for Co and Ni, which were higher in 2009 than in 2006, and for Mn, which was greater in 2006 than in 2009 (Table 1).

Although comparing concentrations in different species generates inaccuracies due to different exposure and uptake processes, at least this type of comparison gives an indication of contaminant levels in other areas. The heavy metal concentrations measured in the aquatic

plant *S. filiformis* were higher than those indicated by Harguinteguy et al. [5] in the submerged rooted macrophyte *Myriophyllum aquaticum* in the Xanaes river (Córdoba, Argentina), in an area with intensive agriculture. On the other hand, Nimptsch et al. [24] reported changes in water quality, using *Myriophyllum quitense* as a biomarker of heavy metal exposure and eutrophication in the Suquía river basin (Córdoba, Argentina).

The species *S. filiformis* can also be found in the literature identified by the name *Potamogeton filiformis*, which is synonymous [47]. Nedeau et al. [48] found that the cover percentage of *P. filiformis* in an urban stream was lower downstream of industrial effluent discharges. In this study, the average concentrations of heavy metals in *S. filiformis* varied significantly along the Suquía river in both sampling campaigns (Table 5), with higher accumulation levels of Co, Cu, Ni, Pb and Zn being observed downstream of industrial effluent discharges from

**Table 3**

Mean values and standard deviation ( $\pm$ SD) of the concentrations of Co, Cu, Fe, Mn, Ni, Pb and Zn in sediments in 2006 and 2009 from the Suquía river, Córdoba, Argentina. Results of the variance analysis (Kruskal–Wallis) between sampling sites for each year are shown with values in each vertical column followed by the same letter not differing significantly at  $p < 0.05$  (pairwise comparisons of means).

Site	Sediment ( $\text{mg kg}^{-1}$ DW)							
	Co [2006]	Co [2009]	Cu [2006]	Cu [2009]	Fe [2006]	Fe [2009]	Mn [2006]	Mn [2009]
1	–	2.34 $\pm$ 0.16 d	–	4.07 $\pm$ 0.24 c	–	5072 $\pm$ 133 b	–	158 $\pm$ 14 d
2	5.84 $\pm$ 0.46 ab	5.07 $\pm$ 0.33 ab	5.69 $\pm$ 0.51 c	7.73 $\pm$ 0.25 b	6319 $\pm$ 1149	10,666 $\pm$ 786 a	353 $\pm$ 84 ab	527 $\pm$ 39 a
3	6.25 $\pm$ 0.41 a	5.57 $\pm$ 0.30 a	5.46 $\pm$ 0.32 c	8.53 $\pm$ 0.57 b	6491 $\pm$ 526	12,526 $\pm$ 905 a	425 $\pm$ 22 ab	439 $\pm$ 10 b
4	7.07 $\pm$ 0.82 a	4.76 $\pm$ 0.33 abc	6.66 $\pm$ 0.94 c	9.22 $\pm$ 1.62 b	6496 $\pm$ 946	11,151 $\pm$ 906 a	904 $\pm$ 392 a	374 $\pm$ 16 bc
5	7.31 $\pm$ 0.27 a	4.72 $\pm$ 0.18 abc	6.32 $\pm$ 0.31 c	12.55 $\pm$ 1.62 a	4703 $\pm$ 864	5603 $\pm$ 671 b	479 $\pm$ 52 ab	210 $\pm$ 26 d
6	3.70 $\pm$ 0.33 c	3.62 $\pm$ 0.31 c	34.32 $\pm$ 3.77 b	8.51 $\pm$ 0.09 b	4624 $\pm$ 470	5141 $\pm$ 259 b	131 $\pm$ 11 b	327 $\pm$ 25 c
7	4.47 $\pm$ 0.30 bc	3.80 $\pm$ 0.69 bc	48.97 $\pm$ 5.65 a	7.77 $\pm$ 0.65 b	6419 $\pm$ 763	5089 $\pm$ 158 b	120 $\pm$ 17 b	347 $\pm$ 21 c
Kruskal–Wallis	***	**	***	***	ns	***	**	***

Site	Sediment ( $\text{mg kg}^{-1}$ DW)							
	Ni [2006]	Ni [2009]	Pb [2006]	Pb [2009]	Zn [2006]	Zn [2009]	OM % [2006]	OM % [2009]
1	–	6.26 $\pm$ 0.51 c	–	9.21 $\pm$ 0.79 d	–	34.9 $\pm$ 1.5 c	–	7.9 $\pm$ 0.2 b
2	9.26 $\pm$ 0.98 c	8.83 $\pm$ 0.25 bc	14.10 $\pm$ 0.60 c	13.42 $\pm$ 0.79 cd	46.8 $\pm$ 8.1 b	44.8 $\pm$ 1.3 c	8.5 $\pm$ 0.4 d	16.0 $\pm$ 0.4 a
3	11.75 $\pm$ 1.09 bc	9.05 $\pm$ 0.47 bc	15.95 $\pm$ 0.91 c	8.92 $\pm$ 0.21 d	49.3 $\pm$ 3.4 b	32.8 $\pm$ 4.3 c	8.8 $\pm$ 0.2 d	7.4 $\pm$ 0.5 bc
4	13.50 $\pm$ 2.51 abc	10.77 $\pm$ 1.20 ab	18.93 $\pm$ 2.87 bc	9.68 $\pm$ 1.19 cd	50.3 $\pm$ 9.5 b	32.2 $\pm$ 4.4 c	11.2 $\pm$ 0.4 c	5.1 $\pm$ 1.1 c
5	20.26 $\pm$ 2.56 a	12.91 $\pm$ 1.12 a	16.85 $\pm$ 0.79 c	20.87 $\pm$ 0.36 b	71.6 $\pm$ 2.6 b	58.4 $\pm$ 15.7 bc	6.3 $\pm$ 0.2 e	5.4 $\pm$ 1.2 c
6	17.27 $\pm$ 1.13 ab	7.59 $\pm$ 0.39 c	25.72 $\pm$ 2.91 b	15.47 $\pm$ 0.88 bc	313.9 $\pm$ 20.5 a	84.7 $\pm$ 5.4 b	18.6 $\pm$ 0.9 a	6.7 $\pm$ 0.3 bc
7	15.17 $\pm$ 3.71 ab	7.80 $\pm$ 1.61 bc	42.55 $\pm$ 4.61 a	34.17 $\pm$ 4.09 a	497.7 $\pm$ 136.8 a	289.9 $\pm$ 11.5 a	13.8 $\pm$ 1.0 b	6.4 $\pm$ 0.4 bc
Kruskal–Wallis	*	***	***	***	***	***	***	**

ns, not significant; \*, significant at the 0.05 probability level; \*\*, significant at the 0.01 probability level; \*\*\*, significant at the 0.001 probability level. OM, organic matter; DW, dry weight.

**Table 4**  
Spearman correlation coefficients between heavy metal concentrations in water and sediment collected at the same sites of the Suquia river.

		Surface water						
		Co	Cu	Fe	Mn	Ni	Pb	Zn
<i>Sediment</i>								
Co		0.10	-0.38*	-0.28	-0.27	-0.29	-0.33*	-0.31
Cu		0.81***	0.19	0.39**	0.83***	0.67***	0.30	0.87***
Fe		-0.27	-0.27	-0.27	-0.11	-0.41**	-0.24	-0.30
Mn		-0.31	-0.18	-0.23	-0.28	-0.33*	-0.19	-0.39**
Ni		0.73***	-0.17	0.02	0.24	0.24	-0.02	0.34*
Pb		0.54***	0.63***	0.71***	0.79***	0.85***	0.66***	0.82***
Zn		0.61***	0.54***	0.70***	0.86***	0.87***	0.62***	0.92***

\* Significant at the 0.05 probability level; \*\* Significant at the 0.01 probability level; \*\*\* Significant at the 0.001 probability level.

Córdoba city in both sampling campaigns (Site 7). At Site 6, no aquatic plants were found in the samples of 2006 and 2009 (Table 5), with the absence of this species possibly being related to the high levels of contaminants in these areas.

3.3. Analysis of correlation between the accumulation of heavy metals in surface water, sediment and *S. filiformis*

As *S. filiformis* is a submerged aquatic plant with roots in the sediment and floating roots in the water column, it might be able to capture heavy metals from the water and sediment phase. In this study, in order to evaluate whether surface water or sediment was the main source of heavy metals in *S. filiformis* leaves, a Spearman correlation analysis was carried out between the heavy metal concentrations in surface water and sediments and those in the macrophytes (Table 6). These results showed significant and positive correlations for Cu, Mn, Pb and Zn in the sediments and the aquatic plant (Table 6). Therefore, these elements may have been incorporated by *S. filiformis* through the root system from the sediment. This is in agreement with Jackson [6], who reported that the root uptake of elements with subsequent translocation to above-ground tissues has been shown for a variety of elements and thus may be an important vector for extracting elements from the sediment, which otherwise remain buried. In addition, this author also

**Table 6**  
Spearman correlation coefficients between heavy metal concentrations in water and sediment, with heavy metal concentrations in the aquatic plant *S. filiformis* collected at the same sites in the Suquia river.

		<i>S. filiformis</i>						
		Co	Cu	Fe	Mn	Ni	Pb	Zn
<i>Surface water</i>								
Co		-0.16	0.25	0.26	0.20	0.05	0.21	0.13
Cu		0.28	0.65***	0.74***	0.72***	0.78***	0.68***	0.75***
Fe		0.41*	-0.13	-0.07	0.25	0.02	-0.03	0.13
Mn		-0.14	-0.02	-0.04	-0.33	-0.02	-0.02	-0.28
Ni		-0.19	0.68***	0.59***	0.26	0.48**	0.60***	0.30
Pb		-0.01	0.67***	0.77***	0.62***	0.68***	0.68***	0.59***
Zn		0.28	0.72***	0.84***	0.80***	0.82***	0.75***	0.82***
<i>Sediment</i>								
Co		-0.60***	0.12	0.32	-0.46**	-0.43**	0.08	0.19
Cu		-0.35*	0.55***	-0.22	-0.42*	-0.01	0.81***	0.83***
Fe		-0.01	0.40*	0.29	-0.26	0.07	0.13	0.18
Mn		0.60***	-0.43**	-0.28	0.53***	0.20	-0.11	-0.25
Ni		-0.22	0.01	-0.18	-0.01	0.03	0.39*	0.30
Pb		-0.25	0.29	-0.18	-0.21	-0.17	0.62***	0.61***
Zn		-0.41*	0.64***	-0.26	-0.43**	-0.08	0.80***	0.76***

\* Significant at the 0.05 probability level; \*\* Significant at the 0.01 probability level; \*\*\* Significant at the 0.001 probability level.

pointed out the importance of the macrophytes in the cycling of elements in aquatic ecosystems. In the present study for Co, a significant and negative correlation was observed between the sediment and macrophyte (Table 6). In general terms, Co in sediments revealed a trend to increase its levels in the direction of the flow of the river (Table 3), although the accumulation of this metal shown by the aquatic plants had no major changes in the same direction (Table 5). These results suggest that in *S. filiformis*, the translocation of this metal may have been restricted to the upper parts of their tissues through its uptake and accumulation in the roots or by rhizosphere precipitation. This mechanism has already been observed in different species of plants for various metals [49]. However, as the analysis of the current study was carried out in plant leaves, in order to evaluate this situation it would be convenient to perform an analysis of the accumulation of this metal in the different tissues.

**Table 5**  
Mean values and standard deviation ( $\pm$ SD) of the concentrations of Co, Cu, Fe, Mn, Ni, Pb and Zn in *S. filiformis* leaves in 2006 and 2009 from the Suquia river, Córdoba, Argentina. Results of the variance analysis (Kruskal–Wallis) between sampling sites for each year are shown with values in each vertical column followed by the same letter not differing significantly at  $p < 0.05$  (pairwise comparisons of means).

Site	<i>S. filiformis</i> (mg kg <sup>-1</sup> DW)							
	Co [2006]	Co [2009]	Cu [2006]	Cu [2009]	Fe [2006]	Fe [2009]	Mn [2006]	Mn [2009]
1	-	2.80 $\pm$ 0.06 b	-	5.90 $\pm$ 0.50 c	-	1327 $\pm$ 33 d	-	209 $\pm$ 16 c
2	2.96 $\pm$ 0.57 a	3.15 $\pm$ 0.14 b	11.73 $\pm$ 2.52 ab	9.43 $\pm$ 0.36 b	7351 $\pm$ 2438 a	3098 $\pm$ 132 c	2607 $\pm$ 644 a	1347 $\pm$ 198 a
3	1.22 $\pm$ 0.11 b	2.97 $\pm$ 0.12 b	8.65 $\pm$ 0.45 b	4.56 $\pm$ 0.14 c	3051 $\pm$ 313 b	4683 $\pm$ 870 b	1107 $\pm$ 77 bc	338 $\pm$ 17 c
4	0.98 $\pm$ 0.11 b	3.84 $\pm$ 0.18 a	5.14 $\pm$ 1.66 b	9.61 $\pm$ 0.38 b	3164 $\pm$ 197 b	8896 $\pm$ 86 a	2099 $\pm$ 266 ab	817 $\pm$ 25 b
5	1.06 $\pm$ 0.52 b	3.82 $\pm$ 0.07 a	5.47 $\pm$ 0.62 b	11.31 $\pm$ 2.05 b	1598 $\pm$ 97 b	7614 $\pm$ 485 a	2439 $\pm$ 454 a	437 $\pm$ 24 c
6	-	-	-	-	-	-	-	-
7	2.79 $\pm$ 0.70 a	3.53 $\pm$ 0.03 a	19.45 $\pm$ 4.44 a	19.72 $\pm$ 0.34 a	7310 $\pm$ 952 a	2598 $\pm$ 60 cd	91 $\pm$ 17 c	1470 $\pm$ 74 a
Kruskal–Wallis	*	***	***	***	**	***	***	***
Site	<i>S. filiformis</i> (mg kg <sup>-1</sup> DW)							
	Ni [2006]	Ni [2009]	Pb [2006]	Pb [2009]	Zn [2006]	Zn [2009]		
1	-	6.28 $\pm$ 0.55 b	-	5.18 $\pm$ 0.85 b	-	25.7 $\pm$ 0.5 e		
2	2.43 $\pm$ 1.30 b	8.33 $\pm$ 1.03 b	5.61 $\pm$ 1.73 b	7.90 $\pm$ 1.60 b	42.4 $\pm$ 9.0 b	38.7 $\pm$ 2.6 d		
3	0.81 $\pm$ 0.49 c	6.63 $\pm$ 0.43 b	13.60 $\pm$ 0.71 a	4.90 $\pm$ 1.02 b	35.5 $\pm$ 1.8 b	23.6 $\pm$ 2.7 e		
4	5.98 $\pm$ 1.78 a	6.31 $\pm$ 0.97 b	4.58 $\pm$ 0.36 b	7.48 $\pm$ 0.54 b	16.5 $\pm$ 5.8 b	55.9 $\pm$ 1.0 c		
5	12.22 $\pm$ 7.30 a	8.59 $\pm$ 0.87 b	3.58 $\pm$ 0.15 b	6.47 $\pm$ 0.29 b	27.1 $\pm$ 5.2 b	67.8 $\pm$ 2.0 b		
6	-	-	-	-	-	-		
7	6.94 $\pm$ 1.00 a	19.66 $\pm$ 1.47 a	12.24 $\pm$ 1.54 a	17.62 $\pm$ 1.81 a	141.3 $\pm$ 32.8 a	148.3 $\pm$ 5.4 a		
Kruskal–Wallis	**	***	***	***	***	***		

\*, significant at the 0.05 probability level; \*\*, significant at the 0.01 probability level; \*\*\*, significant at the 0.001 probability level. DW, dry weight.

Significant and positive correlations for Cu, Ni, Pb and Zn were found between surface water samples and *S. filiformis* leaves (Table 6). Because this macrophyte has rhizomatous stems and long filiform and submerged leaves [25], these elements could have been taken from the water column by the plant.

Macrophytes are biological filters and have a strong influence on the movement of chemicals in the aquatic ecosystem; in this sense, they may be able to accumulate substances in concentrations exceeding their contents in a particular environment [44]. In this study, high levels of heavy metal accumulation in *S. filiformis* (Table 5) were recorded at the same sites of the Suquía river, with the greatest heavy metal concentrations being observed in surface waters (Table 2) and sediments (Table 3). These results are in agreement with Demirezen and Aksoy [50], who postulated that the aquatic flora reflects the metal content of its environment.

In previous studies on the Suquía river, the aquatic environment has been presented as a sink surface runoff, leaching and/or effluent discharges from human activity [13,14,23], as it is known that industrial activities and wastewater discharges that reach rivers can have a significant impact on the water quality and biota living there [24,51]. Finally, the Cu, Pb and Zn incorporated as pollutants in surface waters and sediments were able to be removed by *S. filiformis* in self-purification processes. Therefore, this species could be proposed as a suitable heavy metal bioindicator for the early stages of river pollution.

#### 4. Conclusions

In general, higher concentrations of heavy metals in sediment samples in this study were observed in 2006, during the dry season, than in 2009 during the rainy season, but these differences were not as great in surface water samples. The average concentrations of the heavy metals were within the limits established by national and international organizations for the protection of aquatic life, except for Cu and Pb in surface waters for both sampling campaigns and for Zn in sediments of 2006, which occurred primarily downstream of Córdoba city.

The aquatic plant *S. filiformis* revealed a high capacity to accumulate heavy metals in its tissues in this study, especially in areas of the river where higher values of heavy metals were observed in the abiotic compartments, surface water and sediments. This species might have an influence on nutrient recirculation in the Suquía river and, in turn, even be able to accumulate higher concentrations of metals than those found in the aquatic environment.

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