Assessment of two species of macrophytes as biomomitors of heavy metals in rivers of Córdoba, Argentina.

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INTRODUCTION

Direct discharge or wet and dry air depositions of contaminants increase the concentrations of trace elements in aquatic systems, thus resulting in their accumulation in sediments [1]. Aquatic plants absorb elements through roots and/or shoots and in water quality studies they may be useful biomonitors. In aquatic systems, where pollutant inputs are discontinuous and pollutants are quickly diluted, analysis of plant tissues provide time-integrated information about the quality of the system. The province of Córdoba has a large number of rivers and lakes in its geography, but also presents major urban centers in which industrial, mining and agricultural-livestock activities are the most directly involved in the production of waste, effluents and air emissions containing heavy metals. Within the diverse sources of emission at the Suquía river it is important to refer to the city of Córdoba, where there is significant vehicular traffic, and numerous metallurgical and metal-mechanical companies. In addition, there is an industrial park in Río Tercero city, that can be considered an important source of pollution for the Ctalamochita river. The aim of this study was to evaluate two macrophytes species, *Stuckenia filiformis* and *Potamogeton pusillus* as bioindicators of heavy metal pollution and their spatial variation in rivers of the province of Córdoba.

EXPERIMENT

The sampling was carried out in the rivers Ctalamochita and Suquía of the province of Córdoba and three sampling sites were selected according to the presence of the aquatic plants, *Stuckenia filiformis* and *Potamogeton pusillus*. a) In the Ctalamochita river, the sites selected were located before, during and after of Río Tercero (RT) city, named pre-RT city, RT city and post-RT city respectively. The Río Tercero city is an area with chemical, petrochemical and military factories of great magnitude with a population of c. 45,000 inhabitants. b) In the Suquía river, the sites selected were located before, during and after of Córdoba (Cba) city, named pre-Cba city, Cba city and post- Cba city respectively. The city of Córdoba is characterized by a strong presence of metallurgical industries, agricultural fields and intense vehicular traffic due to the presence of major roads with a population of c. 1,500,000 inhabitants. Sampling digestion and analysis. The dry material was ground and reduced to ashes at 500 ^{o}C for 4 hours. The ashes were digested with HNO_3 and filtered. The volume was adjusted to 10 ml with Milli-Q water, and 10 ppm of a Ga solution was added as an internal standard. Aliquots of 5 μL was taken and deposited on an acrylic reflector surface. The blank preparation followed the same procedure. Solutions with known elements at different concentrations were prepared to determine a calibration curve. The elemental composition of *S. filiformis* and *P. pusillus* leaves was determined using Total Reflection X-ray Fluorescence with Synchrotron Radiation (SR-TXRF), with polychromatic bean approximately 5 mm wide and 0.1 mm high being used for excitation. For X-ray detection, a Si(Li) detector was used with an energy resolution of 165 eV at 5.9 keV.

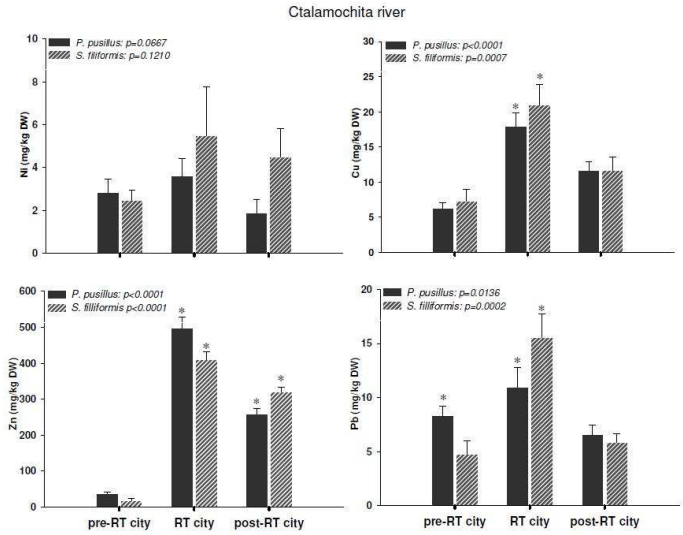

FIG. 1: Average concentrations and standard deviation of heavy metals in leaves of two aquatic plants measured in three sampling sites of the Ctalamochita river. ($*$ show significant differences: $p<0.05$; ANOVA test). Note: before Río Tercero (RT) city (pre-RT city); during of the city (RT city); after of the city (post-RT city)

RESULTS AND DISCUSSION

The average concentrations of heavy metals in two aquatic plants in the Ctalamochita river are showed in the Figure 1. In all cases significant differences were found between the sampling sites, except for Ni concentrations. *S. filiformis* and *P. pusillus* accumulated the highest levels of Cu, Pb and Zn in the city of Río Tercero (RT). Moreover, Zn concentrations were significantly higher in the site located after the city (post-RT

city) for both species. As for the Suquía river; all elements, except for Ni, showed significant differences between sampling sites in the two macrophytes (Figure 2). The highest values of Cu, Pb and Zn were found after the city of Córdoba (post-Cba city) where metallurgical industries are situated. The levels of heavy metals were similar in the two

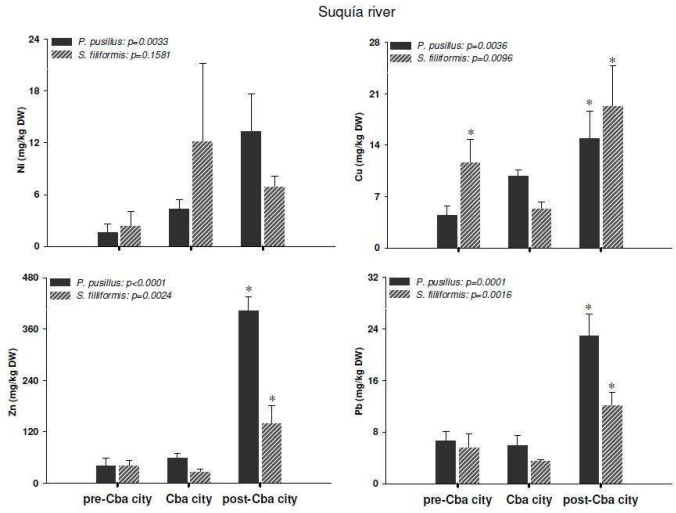

FIG. 2: Average concentrations and standard deviation of heavy metals in leaves of two aquatic plants measured in three sampling sites of the Suquía river. (∗ show significant differences: p<0.05; ANOVA test). Note: before Córdoba (Cba) city (pre-Cba city); during of the city (Cba city); after of the city (post-Cba city)

macrophytes under study (Figure 3) and the average concentrations of elements did not change significantly. Therefore, both species may response in a similar manner to changes within aquatic ecosystems. On the one hand, the highest content of Zn was found in the Ctalamochita river (Figure 3) and this result is in agreement with Rodriguez et al., [2], while Zn contents were higher in the metallurgical and chemical industries areas, among others. On the other hand, Ni concentrations were higher in the Suquía river and this result is in consonance with those obtained by Gaiero et al., [3], where high Ni levels in sediment might originate from stormwater of the drainage systems of Córdoba city.

	River			Species		
	Ctalamochita	Suquía	*p*-Value	*P. pusillus*	*S. filiformis*	*p*-Value
Ni	3,5 ± 1,6	**6,8 ± 5,8**	0,0248	4,6 ± 4,4	5,7 ± 4,7	0,4771
Cu	12,7 ± 5,7	11 ± 5,9	0,4071	10,9 ± 5,1	12,8 ± 6,4	0,3440
Zn	**256,7 ± 183,9**	119,5 ± 137,8	0,0161	216,5 ± 189,8	159,7 ± 158,3	0,3011
Pb	8,7 ± 3,9	9,5 ± 7	0,6553	10,3 ± 6,3	7,9 ± 4,7	0,2263

FIG. 3: Average concentrations and standard deviation of heavy metals in leaves of two aquatic plants measured in two rivers of Córdoba province. Note: Concentrations are in mg/kg dry weight. Significant differences between sampling site are in bold letters (p<0.05; ANOVA test)

CONCLUSION

The species *S. filiformis* and *P. pusillus* behaved as effective biomonitors of aquatic quality. The response of both biomonitors for heavy metal accumulation was similar. This behavior is related to polluting activities altering the stability of the aquatic ecosystems under studied. The accumulation of heavy metals in the biomonitors in two rivers of the province of Córdoba showed a reduced environmental quality due to anthropogenic activities. If we consider that these areas are mainly for recreational use and drinking water, risk assessment toxicological studies should be performed in these sites located in proximity of industrial activities.

ACKNOWLEDGEMENTS

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[1] Baldantoni D, Maisto G, Bartoli G, Alfani A. 2005. Aquatic Botany 83: 48-60.
[2] Rodriguez JH, Weller SB, Wannaz ED, Klumpp A, Pignata ML. 2011. Ecological Indicators 11: 1673-1680.
[3] Gaiero DM, Roman Ross G, Depetris PJ, Kempe,S. 1997. Water, Air, and Soil Pollution 93:303-319.