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Levels of Heavy Metals in Waters from the La Plata River, Argentina: An Approach To Assess Bioavailability

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The La Plata River is one of the most important aquatic systems of South America. It is formed by the confluence of the Parana and Uruguay rivers, and drains to the Atlantic Ocean through a wide estuary. Industrial and domestic waste disposal and harbor activities take place along the coast of the La Plata River, which provides the freshwater supply for Buenos Aires, the capital city of Argentina. In addition, it is considered that most discharges into rivers settle in estuaries and nearshore areas.

Chemicals discharged into an aquatic system are distributed within the soluble phase, the suspended or bottom sediments, and in biota (Connell 1987). This complex process is governed not only by the physicochemical properties of the chemicals, but also by hydrological, weathering, and geological factors (GESAMP 1987). With trace metals, only a small proportion remains in the soluble fraction, while the major fraction is removed and becomes associated with the suspended or bottom sediments (Luoma 1988). However, the load of metals bound to sediments may also affect the water quality when desorption processes occur, caused by changes in acidity, complexing agents, and turbulence of water, among others (Lietz and Galling 1989).

For these reasons, the purpose of the present work was to assess the levels of cadmium, cobalt, nickel, lead, and iron in water samples from coastal zones of the La Plata River. The analyses of metals in water were performed on the so-called **recoverable fraction**, according to the definitions from the US Environmental Protection Agency (US EPA 1979). The recoverable fraction is obtained treating the unfiltered sample with mineral acid. This pretreatment may provide one

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means for assessing the reactivity and availability of metals present not only in the dissolved phase, but also in the suspended particulate matter. Most aquatic monitoring programs include analyses of the dissolved fraction, suspended, and bottom sediments. We suggest that analysis of the recoverable fraction might constitute a better approach to assessing the total potential bioavailability of elements by biota, conducting only one analysis.

MATERIALS AND METHODS

Replicate sub-surface water samples from 5 sites in the La Plata River (Fig. 1) were collected in acid-washed polyethylene bottles (2 L each) during summer and winter 1989.

The pH of all samples was measured with a pH-meter and the samples were acidified to $pH < 2$ with concentrated ultrapure nitric acid. The samples were filtered 24 hr later using filter paper (blue band) to remove particulate matter, and the filtrate stored at 4°C.

The metals Cd, Co, Fe, Ni, and Pb were determined in the filtrate essentially according to the method of Subramanian and Méranger (1979), but using a chelation mixture consisting of ammonium pyrrolidine dithiocarbamate (APDC) and sodium diethyldithiocarbamate (DDC), 2 % each in distilled water, as recommended by Bruland et al. (1979). This dual carbamate system provides a broader working pH range than either of the two reagents alone (Ashton and Chan 1987). Briefly, 10 mL of ammonium citrate buffer 20%, pH 7.2, were added to 100 mL of water samples. The pH was adjusted to 4-6, followed by the addition of 10 mL of chelating mixture and 10 mL of methylisobutyl ketone (MIBK). The mixture was shaken for 10 min and the MIBK layer separated.

Metal concentrations were determined in the MIBK layer with an AA-575 Varian flame atomic absorption spectrophotometer (AAS), with deuterium lamp background corrector. Due to its accuracy, the chelation-extraction system, followed by AAS, has been widely used, including intercalibration studies (Ashton and Chan 1987; Flegal and Coale 1989).

Standard addition methods were used to compensate for matrix effects. Appropriate standard solutions of metals, in 1% nitric acid, were prepared by serial dilutions of 1,000 mg L^{-1} stock solutions. All samples were analyzed in triplicate. All metals were quantitatively extracted since complete transfer from the aqueous to the organic phase occurred in a single

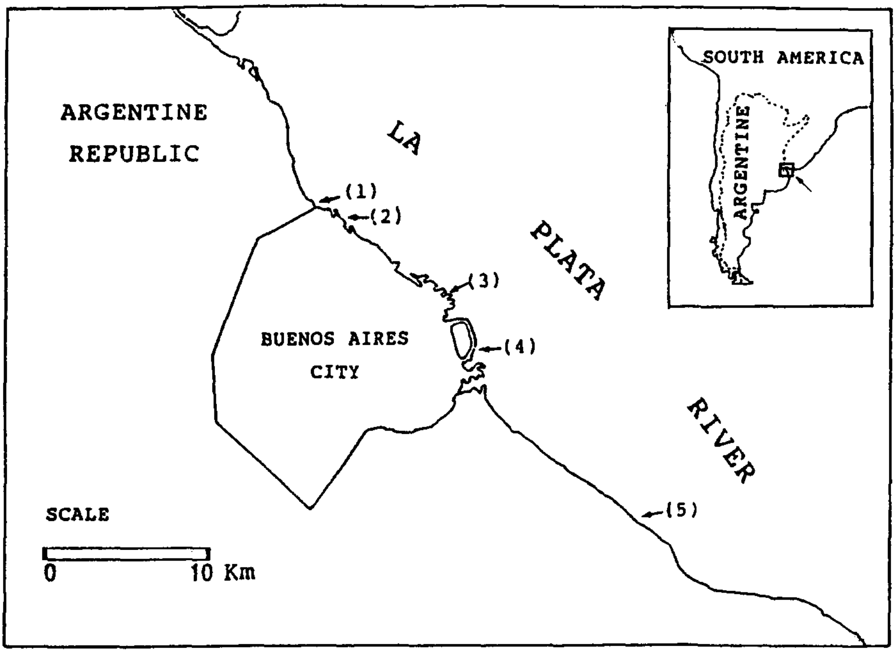

Figure 1. Map of the sampling stations along the La Plata River: (1) Olivos Port, (2) University City, (3) Buenos Aires Port, (4) Fishing Club, (5) Quilmes Beach. Inset: The square encloses the sampling zone, and the arrow indicates the La Plata River.

extraction, as it was previously shown (Verrengia Guerrero and Kesten 1993). The precision of the method was tested in spiked river water samples (n=6) and expressed in terms of the coefficient of variation. Their values were 3.3%, 4.8%, 4.2%, 5.5%, and 6.5% for Cd, Co, Fe, Ni, and Pb, respectively.

Reagent blanks were analyzed to detect any possible contamination during the procedure. Their values were negligible for all the elements analyzed.

All glassware was cleaned by soaking it in 10% nitric acid and thoroughly rinsed with ultrapure distilled water, as previously described by Ashton and Chan (1987).

RESULTS AND DISCUSSION

Table 1 shows the levels of trace metal concentrations in water samples collected during summer and winter, 1989, from the La Plata River. Cd and Co were only detected in sampling station (3), Buenos Aires Port,

Table 1. Ranges, mean values and standard deviations of metal concentrations in the recoverable fraction of waters from the La Plata River, Argentina.

		pH	Cd (ppb)	Co (ppb)	Ni (ppb)	Pb (ppb)	Fe (ppm)
Station 1: Olivos Port							
S*	(n=5)	7.0	<0.2	<2.0	<0.5	8.8-12.9	0.28-0.42
#						10.8± 2.1	0.35±0.07
W*	(n=4)	7.3	<0.2	<2.0	1.9-3.6	6.1- 8.0	0.32-0.52
#					2.5±0.8	7.0± 1.0	0.41±0.10
Station 2: University City							
S	(n=4)	7.5	<0.2	<2.0	8.2-9.7	4.9- 8.9	0.56-0.69
					9.0±1.1	6.9± 2.8	0.64±0.07
W	(n=4)	7.0	<0.2	<2.0	3.5-3.9	16.7-19.6	1.05-1.63
					3.7±0.3	18.2± 2.1	1.34±0.41
Station 3: Buenos Aires Port							
S	(n=4)	6.8	<0.2-0.4	<2.0-3.0	1.8-7.3	2.4-58.6	0.68-1.26
			0.3±0.2	2.5±0.7	4.3±2.4	28.1±28.6	0.97±0.27
W	(n=6)	6.0	<0.2	<2.0	0.6-3.7	4.2-18.4	0.57-0.77
					2.0±1.2	9.4± 6.5	0.70±0.11
Station 4: Fishing Club							
S	(n=4)	6.0	<0.2	<2.0	<0.5	12.5-16.4	0.93-1.01
						14.5± 2.8	0.96±0.04
W	(n=4)	6.0	<0.2	<2.0	<0.5-2.8	9.9-13.7	0.86-0.98
					1.6±0.9	11.3± 1.8	0.92±0.08
Station 5: Quilmes Beach							
S	(n=6)	8.0	<0.2	<2.0	0.5-1.3	6.1- 6.7	0.53-0.64
					0.9±0.6	6.4± 0.4	0.57±0.06
W	(n=8)	6.5	<0.2	<2.0	1.1-4.6	9.6-23.7	1.29-1.31
					3.0±1.6	19.1± 7.4	1.30±0.02

S: summer 1989; W: winter 1989; *: ranges; #: mean ± SD; n= number of samples during summer 1989. For Ni, Pb, and Fe the results were variable. Indeed, it is well known that metal concentrations in river waters may vary over wide ranges (Lietz and Galling 1989). These variations may be due to the fact that the sampling stations are subjected to the effects of many industrial and anthropogenic activities, since this area is one of the most densely populated in the country. Olivos Port is mainly a recreational port. Nearby University City, several industrial effluents are discharged. Buenos Aires Port is one of the most important commercial ports in the country. Next to it, the Fishing Club is located, where refilling processes have taken place. Around Quilmes Beach, domestic and industrial wastes are discharged, most of them untreated. In addition, the estuary of the La Plata River has a complex hydrodynamic, influenced by a large load of inputs from the Parana and Uruguay rivers, and the marine currents from the Atlantic Ocean. The estuary also receives large amounts of discharges and wastes from minor tributaries, such as the Reconquista and Riachuelo rivers (among others), which are heavily polluted.

These results cannot be easily compared with data reported in the literature. In a previous study (Verrengia Guerrero and Kesten 1993), we found that the values obtained using this pretreatment were intermediate between those from the dissolved fraction and the total metal content.

Most workers perform trace metal determinations in the dissolved fraction (obtained by filtering the water samples through a 0.45 um pore filter). It is considered that those analyses reflect the metal load that can be readily incorporated into potable water supplies (Smith et al.1987). Despite the modern methodologies, marked discrepancies are still found in the literature in relation to the levels of trace metal concentrations in the dissolved fraction from natural waters (GESAMP 1987; Portmann et al. 1987; Flegal and Coale 1989). These differences are often attributed to a possible contamination of the samples. However, they may be also attributed to the particular characteristics of each aquatic system, as well as the methodologies employed during the collection, preservation, storage, pre-treatment , treatment and analysis.

Ashton and Chan (1987) consider that the analysis of the dissolved fraction is not always the best approximation in all the studies, since sometimes the suspended material ought to be included.

As we have seen before, sorption and desorption processes of metals bound to sediments influence water quality. In addition, the trace metal uptake by biota (specially benthic biota) may not only occur through the soluble phase, but also via the suspended or bottom sediments (Landner 1988; Luoma 1988). Taking into account the high acidity of the digestive systems in most aquatic organisms, the effective load of trace metals absorbed by biota would exceed the levels present in solution. In fact, McConchie and Lawrance (1991) reported that the high cadmium concentrations found in bivalve molluscs from Shark Bay, Western Australia, did not correlate with the cadmium concentrations found in the waters (soluble phase) or in substrate sediments. Their study revealed, however, that suspended particles, specially those rich in iron-oxides, ingested by the molluscs effectively released cadmium as consequence of the low digestive pH.

According to Gibbs (1973) trace metals in solution are readily bioavailable, whereas if they are adsorbed on organic materials or metallic hydroxides they are less available, but can be made available by means of chemical changes to release them. Therefore, in relation to the analytical procedure presented in this work, during the contact time of the unfiltered water samples with nitric acid, part of the elements associated with the suspended material would be released and solubilized. Other authors have conducted similar procedures to assess the reactivity and biological availability of trace metals from sediments (Trefry et al. 1985).

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REFERENCES

Ashton A, Chan R (1987) Monitoring of microgram per litre concentrations of trace metals in sea water: the choice of methodology for sampling and analysis. Analyst 112: 841-844

Bruland KW, Franks RP, Knauer GA, Martin JH (1979) Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in sea water. Anal Chim Acta 105:233-245

Connell DW (1987) Ecotoxicology-A framework for investigations of hazardous chemicals in the environment. Ambio 16:47-50

Flegal AR, Coale KH (1989). Trends in lead concentrations in major US rivers and their relation to historical changes in gasoline-lead consumption. Wat Res Bull 25: 1275-1277

GESAMP (1987) Land / sea boundary flux of contaminants: Contributions from rivers. UNESCO Rep Stud nº 32, 171 p

Gibbs RJ (1973) Mechanisms of trace metal transport in rivers. Science 180:71-73

Landner L(1988) Hazardous chemicals in the environment. Some new approaches to advanced assessment. Ambio 17: 360-366

Lietz W, Galling G (1989) Metals from sediments. Wat Res 23:247-252

Luoma SN (1988) Bioavailability of sediment-bound metals. US Geological Survey, Circular 969:32-56

McConchie DM, Lawrance LM (1991) The origin of high cadmium loads in some bivalve molluscs from Shark Bay, Western Australia: A new mechanism for cadmium uptake by filter feeding organisms. Arch Environ Contam Toxicol 21:303-310

Portmann J, Harper D, Balls P, Pattinson P, Head J, Parker J, Ramsay RJ (1987) Aquat Environ Monit Rep, MAFF Direct Fish Res, Lowestoft (17), United Kingdom

Smith R A, Alexander R, Wolman M G (1987) Water-quality trends in the nation's rivers. Science 235:1607-1615

Subramanian KS, Méranger JS (1979) APDC-MIKB graphite furnace atomic absorption system for some trace metals in drinking water. Intern J Environ Anal Chem 1:25-40

Trefry JH, Metz S, Trocine RP, Nelsen TA (1985) A decline in lead transport by the Mississippi River. Science 230: 439-441

US EPA (1979) Methods of chemical analysis of waters and wastes. US Environmental Protection Agency. Cincinnati, OH

Verrengia Guerrero NR, Kesten EM (1993) Influencia de algunas variables metodológicas en la determinación de metales pesados en aguas de río. Actas 1º Jornada de Investigación Científica en Materia de Contaminación de las Aguas. Montevideo, Uruguay (in press)