



TRACE METAL CONCENTRATIONS AND GEOCHEMICAL PARTITIONING IN ARROYO CARRASCO WETLANDS, MONTEVIDEO, URUGUAY

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ABSTRACT

A survey of trace metal concentrations and geochemical partitioning in sediments and their distribution in sediment cores was carried out in the Arroyo Carrasco wetlands, Montevideo metropolitan area, Uruguay. The results showed that the area is heavily contaminated with Cr from tanneries, with maximum concentrations reaching 1,224 $\mu\text{g}\cdot\text{g}^{-1}$ and 807 $\mu\text{g}\cdot\text{g}^{-1}$ in suspended particles and bottom sediments respectively. The results also show a moderate contamination with Zn and Pb from various diffuse sources entering the wetlands through surface runoff. Suspended particles are the major carriers of heavy metals from the wetlands to the Rio de la Plata fluvio-marine complex, being enriched in trace metals relative to bottom sediments. Geochemical partitioning showed that Zn, Pb and Cu are associated with reducible phases, whereas organic matter is the major substrate for Cr. Distribution of pollutant metals in sediment profiles, showed a decrease in metal contamination in recent years, probably as a result of enforcement of pollution control policies.

RESUMO

Foi realizado um levantamento das concentrações e da partição geoquímica em sedimentos superficiais e da distribuição em testemunhos de sedimentos de metais pesados, na área do Arroyo Carrasco, região metropolitana de Montevideo, Uruguai. Os resultados mostraram que a área apresenta-se bastante contaminada por Cr, originado em cortumes, com as concentrações máximas atingindo 1.224 $\mu\text{g}\cdot\text{g}^{-1}$ e 807 $\mu\text{g}\cdot\text{g}^{-1}$ no material particulado em suspensão e nos sedimentos de fundo, respectivamente. Os resultados também mostraram uma contaminação moderada de Zn e Pb, oriundos de diversas fontes difusas e que atingem o arroio através do escoamento superficial (runoff). O material particulado em suspensão é o principal carreador de metais pesados a partir do Arroyo Carrasco para o complexo fluvio-marinho do Rio de La Plata. A partição geoquímica dos metais estudados nos sedimentos mostrou que Zn, Pb e Cu estão preferencialmente associados a fases redutíveis, enquanto a matéria orgânica é o principal substrato para o Cr. A distribuição dos metais estudados em perfis de sedimentos mostrou um decréscimo em suas concentrações em anos recentes, provavelmente como resultado da aplicação por parte das autoridades ambientais de políticas de controle ambiental.

INTRODUCTION

Surveys on the trace metal contamination in coastal environments of Latin America still cover only a small percentage of the continent's coastline and are mostly restricted to the industrialized coasts of Brazil, Argentina, Colombia and Chile (Seeliger & Lacerda, 1988). Many important sites have never been the subject of intensive studies. Among them, is the Plata River fluvio-marine complex, the most important estuarine area of the continent south of the Amazon River and the major contributor of continental materials to the western south Atlantic Ocean. Despite its importance, this region has been nearly totally neglected in trace metal contamination studies.

The estuarine waters along the metropolitan area of Montevideo, Uruguay, receive significant inputs of trace metals from various sources, reaching the area through creeks draining contaminated wetlands adjacent to the estuary. Important metals are Cr, released from tanneries, at an approximate rate of 660 t.yr^{-1} (Agudo, 1990); Pb, mostly from gasoline combustion and batteries and the paint industry, with an estimated input of 0.36 t.yr^{-1} ; and Cu and Zn, from untreated urban and domestic effluents of over 1.2 million inhabitants (Moyano *et al.*, 1993).

Preliminary surveys in the area reported extremely high concentrations of Cr (over $11,000 \mu\text{g.g}^{-1}$) and Pb (over $900 \mu\text{g.g}^{-1}$) in coastal sediments close to the Montevideo Harbor and along the west coast

of the city (Carrasco *et al.*, 1993). However, no study has investigated the transport and geochemical partitioning of trace metals in the major wetland areas adjacent to the fluvial-estuarine complex of the Plata River, which are the major sources of these pollutants to the coastal area.

Most trace metal inputs, entering the estuarine area, comes from the Arroyo Pantanoso and the Arroyo Carrasco wetland basins. The Arroyo Carrasco wetlands (Fig. 1) deteriorated in the late 1970's, when they were channeled for sanitary purposes, resulting in major hydrological changes of many areas (Arocena & Pintos, 1988; Arocena *et al.*, 1992). Simultaneously, local environmental authorities enforced stricter control of trace metal

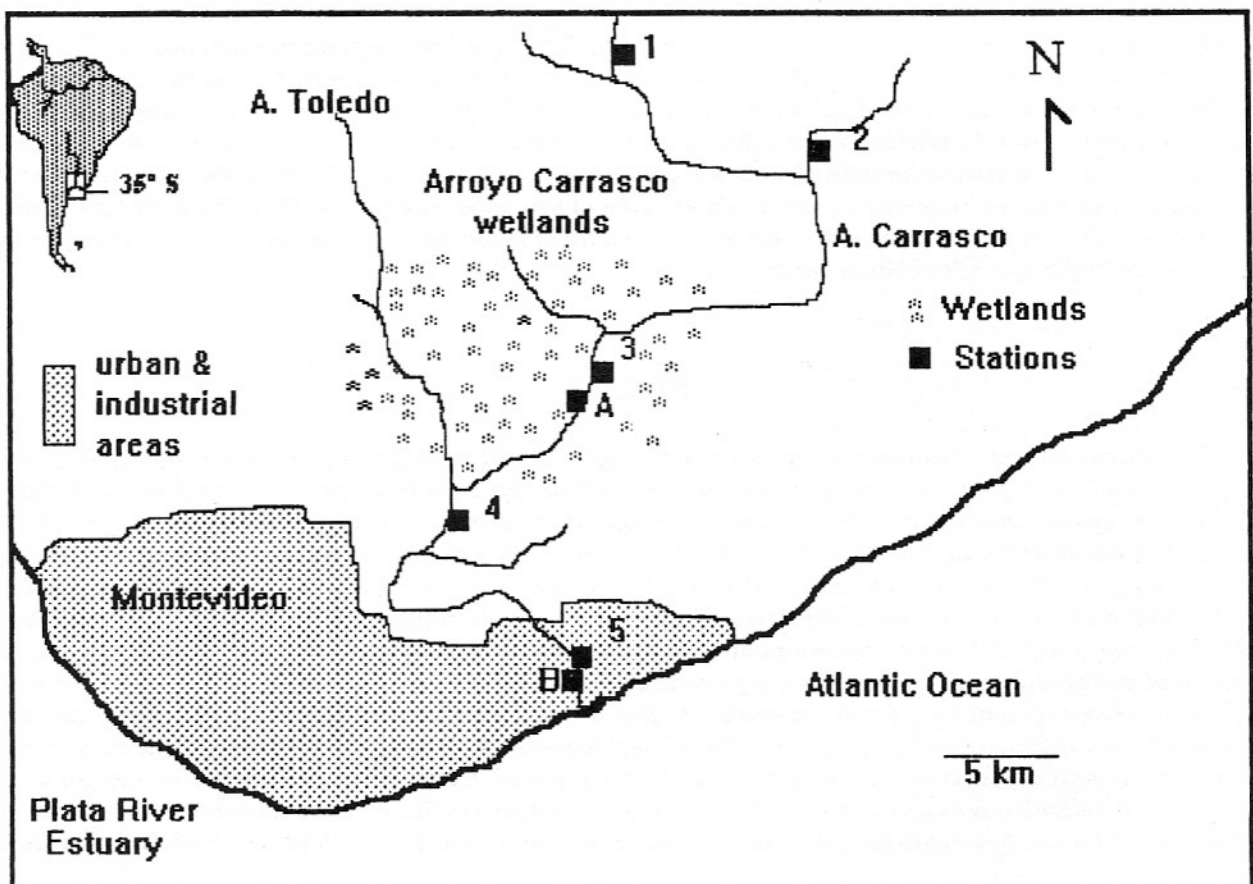


Figure 1 - Schematic map of sampling points along the Arroyo Carrasco wetlands, Montevideo, Uruguay.

emissions from industries. These two factors may have affected the inputs of trace metals and their transport through the Arroyo Carrasco. However, up to now, no study reported on the fate of trace metals in the area.

The present study reports on the spatial distribution and geochemical partitioning of selected trace metals (Zn, Pb, Cu and Cr) in bottom and suspended sediments along the Arroyo Carrasco wetlands. We also report on their distribution in sediment cores from the area, to evaluate the recent history of trace metal contamination in the Montevideo metropolitan area. Although of a descriptive nature, this study provides the basis for further evaluations of trace metals loading and geochemical behavior in this key coastal area of the western South Atlantic Ocean.

STUDY AREA

The Arroyo Carrasco drains an area of nearly 214 km² along the East Coast of Montevideo metropolitan area. It originated from eustatic sea level change and sand ridge formation during the quaternary, resulting in a choked lagoon without significant link to the Plata River fluvio-marine complex. A 0.3 to 2.0-m silt and clay layer presently covers the quaternary marine sands. Freshwater macrophytes, in particular *Cyperaceae*, *Typhaceae* and *Gramineae* (Legrand, 1959; Arocena & Pintos, 1988) dominate the Arroyo.

Water and sediments brought into the wetlands are mostly due to surface runoff of the basin and no seasonal pattern of water and sediment loads were reported for the area (Arocena *et al.*, 1992).

Estimates of sedimentation rates are, unfortunately, not available for these wetlands, but these type of ecosystems typically undergo sedimentation rates

ranging from 0.1 to 0.3 -cm.yr⁻¹ (Long & Mason, 1983; Nichols & Boon, 1992). This range is suitable for the study of recent variability in trace metal loading rates in the area, as relatively small cores would comprise somewhere from 30 to 100 years of recent sedimentation history.

Previous studies in the Montevideo metropolitan area showed strong contamination by Cr, Pb and Zn, derived from diffuse domestic effluents, scattered chemical industries, tanneries and probably atmospheric deposition (Moyano *et al.*, 1993; Carrasco *et al.*, 1993).

Five sampling stations (1 to 5) were established in the study area for the collection of water, suspended matter and surface bottom sediments, and two stations (A and B) for the collection of sediment cores (Fig. 1). Station 1 is located at the headwaters of Arroyo Carrasco, in a primarily agricultural area with little urban and no industrial development. Data from this station are considered background for the region. At Arroyo Carrasco Basin, chemical and metallurgic industries are located upstream the Arroyo Carrasco wetlands, between stations 2 and 3 in Figure 1. Tanneries and food industries, as well as most urban development, are located downstream the wetlands, between stations 4 and 5 in Figure 1.

MATERIAL AND METHODS

The sampling campaign was carried out during the beginning of the rainy season in November 1994. Surface waters, bottom and suspended sediments were collected at all 5 stations located along the Arroyo Carrasco drainage, from the incoming tributaries to the Plata River fluvio-marine complex (Fig. 1).

Upon arrival at each station, immersing acid washed 0.5-l polyethylene bottles against the water flux collected three (3) water samples. Major hydrochemical parameters (pH, temperature and conductivity) were determined in the field in these samples using portable electrodes. Variability among the triplicate determinations in the field was always less than 5%. These water samples were also used for the determination of total suspended solids (TSS) in the laboratory within 8 hours of sampling. Similarly, a 10-l water sample was also collected at each station with a Teflon® flask, for the separation of the TSS for trace metal analysis. Filtering the water samples through 0.45 µm Millipore® filters carried out determination of TSS. Similarly, the sample for trace metal analysis was separated in three (3) sub-samples in the laboratory prior to filtering through 0.45 µm Millipore® filters. The filters for TSS were put into an oven (60 °C) for 24h for drying and further weighting. The filters were kept in a freezer for trace metal analysis using the same procedure for bottom sediments described below.

At each station, from 1,000 to 2,000 kg of bottom sediments were collected using a plastic shovel at shallow areas. When deeper sampling was necessary, a large metallic shovel was used, but sediments were taken from the center of the shovel only, avoiding contact with any metallic surface. Samples were stored in plastic bags and transported under low temperature to the laboratory, where they were separated in three (3) sub-samples, sieved through 0.5-mm nylon sieves, and immediately put into an oven (60 °C) for drying. These procedures were carried out within 10 hours from the original sampling time.

Two sediment cores were collected at two stations; station A,

inside the wetlands proper and station B, at the Arroyo-estuary interface (Fig. 1). Inserting two 9.0 cm diameters, 1 m long, transparent acrylic tubes, into the sediment, by hand collected sediment cores. The tubes were closed with plastic caps and carefully transported to the laboratory within a maximum of 8h from sampling. In the laboratory, each sediment core was sliced in 0.5 cm layers through the superficial 2.0 cm of depth. Then in 1.0 cm slices, from 2.0 to 7.0 cm in depth, and at 5.0 cm intervals, from 7.0 cm down to the bottom of the core (16 cm and 40 cm at stations A and B, respectively). Each core slice sample was sieved through 0.5 mm nylon sieves to exclude large sand grains and detritus and dried at 60°C until constant weight.

Two grams of dried sediments from each bottom sediment sub-sample and from the core slices were used for trace metals analysis. For suspended particulates, however, the mass of samples retained in filters was variable, ranging from 0.2 to 1.5 grams of total suspended matter. Trace metals were extracted in all sediment samples through leaching with hot HCl 0.5 N after shaking for 8 hours and filtered. This treatment does not extract metals from refractory minerals of geological origin and serves to evaluate the incoming metals from natural weathering and from anthropogenic sources to the wetlands (Fizman *et al.*, 1984).

In the core slices, organic matter content was determined through loss on ignition at 450°C for 16 h; and the total Al and Fe concentrations were also determined after complete sample digestion with strong acid mixture (HCl:HNO₃:HF, 3:3:1) in Teflon® crucibles.

An additional duplicate sample of bottom sediments from each

station was used for sequential extraction of trace metals, following standard procedures (Souza *et al.*, 1986), for 1.0 g of dry sample.

a- exchangeable fraction: leaching with 20 ml 1N CH₃COONH₄, pH=7.0, after 2 h contact at room temperature,

b- oxidizable fraction: extraction with H₂O₂ 30% + HNO₃ 0.02 M (5:3) after 5h contact at room temperature and 1h at 98°C followed by leaching with 10 ml 3.5 N CH₃COONH₄,

c- reducible fraction: extraction with 35 ml 0.1 M NH₂OH.HCl + CH₃COOH 25% + HNO₃ 0.02 M, after 4h contact at room temperature and 1h at 98°C followed by leaching with 10 ml 3.5 N CH₃COONH₄,

d- residual fraction: digestion with 12 ml of hot HF_{conc} + HClO_{4 conc} + HNO_{3 conc} (5:1:1) till dryness and dissolved with 20 ml HNO₃ 10%.

All metal analyses were conducted through conventional flame atomic absorption spectrophotometry following standard procedures, at the National Environmental Authority (DINAMA) analytical facility, in Montevideo. Detection limits for the metals analyzed were Al: 5.0 µg.g⁻¹, Fe: 1.0 µg.g⁻¹, Cr: 2.0 µg.g⁻¹, Zn: 1.0 µg.g⁻¹, Cu: 0.5 µg.g⁻¹ and Pb: 1.0 µg.g⁻¹. Deuterium background correction was used for the determinations of Zn, Cu, Cr and Pb. Unfortunately, no reference standards were available, but variability among sub-samples determinations (n=3) was always less than 15% and whenever a sub-sample presented larger variability, it was discarded and a new one analyzed.

RESULTS AND DISCUSSION

Hydrochemistry

Table 1 shows values determined for the hydrochemical

variables along the Arroyo Carrasco. Waters presented neutral pH (6.9 - 7.1) through the region and relatively high electrical conductivity (367 - 1,117 µS.cm⁻¹), due to the presence of calcareous sandstones along the eastern and western border of the Arroyo (Arocena & Pintos, 1988). It is clearly shown by the extremely high conductivity found at the headwater station 1 (1,117 µS.cm⁻¹). Total suspended solids increased by a factor of 6, from the lowest value determined at the headwater station 1 (24 mg.l⁻¹), to station 2, where the maximum TSS was observed of 155 mg.l⁻¹. After station 2, at the border of the Arroyo wetlands proper, TSS showed a continuous decrease to station 5 (86 mg.l⁻¹), near the estuary. This result suggests that, at least, 50% of the suspended sediment load is retained in the wetlands. Seasonal variability of the hydrochemistry of Arroyo Carrasco has been shown previously to be small (Arocena & Pintos, 1988; Arocena *et al.*, 1992). Temporal variability of the TSS was related to changes in surface runoff from the basin (Arocena & Pintos, 1988; Arocena *et al.*, 1992).

In general, our data fit well into the range reported by earlier studies (Arocena & Pintos, 1988; Arocena *et al.*, 1992). However, those authors reported events of saline intrusion in the lower section of the Arroyo, at the estuarine interface, corresponding to station 5 of this study, but this was not detected in our survey.

Total trace metals concentrations

Mean trace metals concentrations in suspended particles are shown in Figure 2a. All trace metals in station 1 suspended particles showed concentrations below the detection limit of our

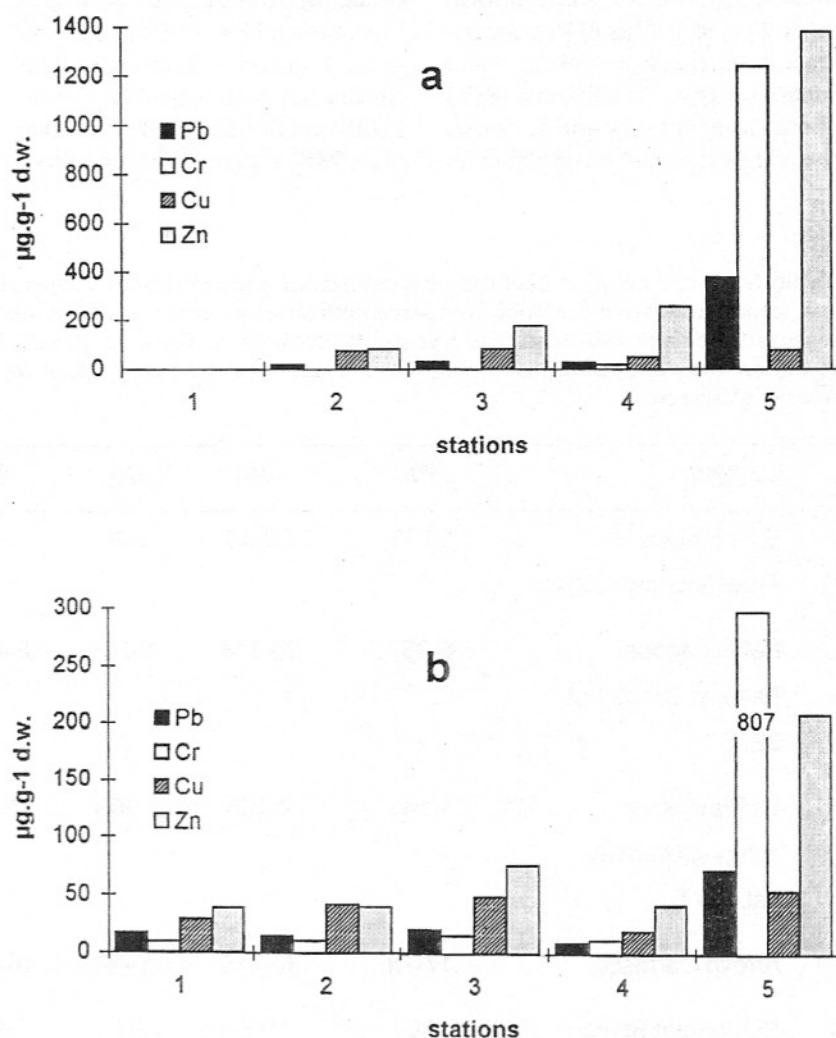
Table 1 - Hydrochemistry of the Arroyo Carrasco basin in November, 1994. Numbers are averages of three (3) determinations in each station. Variability among determinations were always less than 5% (n=3).

Station	Conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)	pH	Temperature ($^{\circ}\text{C}$)	Total Suspended Solids (TSS) ($\text{mg}\cdot\text{L}^{-1}$)
01	1,117	7.0	14.1	24
02	583	7.1	16.3	155
03	488	6.9	20.4	145
04	367	6.9	17.6	117
05	526	6.9	19.4	86

methods, Cr concentrations remained undetectable also at stations 2 and 3, and very low ($21.4 \mu\text{g}\cdot\text{g}^{-1}$) at station 4. At station 5, however, Cr concentrations increased by a factor of 58, reaching a maximum value of $1,244 \mu\text{g}\cdot\text{g}^{-1}$. Lead showed similar behavior to Cr, with low and uniform concentrations from station 2 to 4 (17.1 to $30.1 \mu\text{g}\cdot\text{g}^{-1}$) and a 14-fold increase at station 5 ($385 \mu\text{g}\cdot\text{g}^{-1}$). Zinc showed a continuous increase from station 2 ($79.0 \mu\text{g}\cdot\text{g}^{-1}$) to station 5 ($1,381 \mu\text{g}\cdot\text{g}^{-1}$), whereas Cu presented relatively constant concentrations (76.2 - $84.4 \mu\text{g}\cdot\text{g}^{-1}$) across all stations.

Comparisons with trace metals concentrations in suspended matter from other areas of the Southwestern Atlantic coast are impossible, since no other study has reported on trace metals in suspended particles from this region.

In general, concentrations in bottom sediments increased from station 1, at the headwater of Arroyo Carrasco, to station 3, inside the wetlands proper, decreasing to station 4 and increasing again at station 5 (Fig. 2b). This pattern is in

**Figure 2** - Trace metal concentrations in suspended particles (a) and bottom sediments (b) from Arroyo Carrasco, Montevideo.

agreement with the concentration of total suspended solids observed at these sites, suggesting that Arroyo Carrasco acts as a trap to trace metals brought into the wetlands associated with suspended particles, as have been shown to occur in other coastal wetlands, such as salt marshes and mangroves (Nixon, 1980; Lacerda, 1994).

The increase in trace metals concentrations in station 5 is due to the presence of many industries and urban developments and a municipal sewage treatment plant located between this site and station 4. The highest total concentrations among all metals were observed for Cr at station 5 ($807 \mu\text{g.g}^{-1}$). This high concentration confirms previous trace metals surveys of sediments of the Plata River estuary and is due to the release of non-treated effluents

from tanneries, which concentrate in metropolitan Montevideo region (Carrasco *et al.*, 1993; Moyano *et al.*, 1993). Indeed, Cr concentrations are the highest reported for coastal sediments from this part of the South Atlantic Ocean (Table 2). The highest concentrations of Zn ($210 \mu\text{g.g}^{-1}$) and Pb ($73 \mu\text{g.g}^{-1}$) were also measured at station 5. These values for Zn and Pb are comparable to other moderately polluted areas, in the region, and are, probably, due to incoming surface runoff.

Lowest trace metals concentrations in bottom sediments were found at station 1 at the headwaters of Arroyo Carrasco (Table 2). The concentrations of Cr, Pb and Zn in this station are similar to background concentrations reported for similar areas in Argentina (Villa, 1988) and South Brazil (Baisch *et al.*, 1988) and for the Plata river

sediments (Moyano *et al.*, 1993) (Table 2), the only available data for this part of the South American coast. The concentrations of Cu, however, are consistently higher than those reported for other areas in the Southwestern Atlantic Ocean coast. The scarcity of data on the regional geochemistry, however, prevents further comparisons.

Suspended particles contained much higher trace metals concentrations than bottom sediments, particularly for Zn and Pb at station 5, which showed high relative enrichment in suspended particles. While the Zn/Cr and Pb/Cr ratios in bottom sediments are only 0.26 and 0.09, respectively, they increase to 1.1 and 0.3, respectively in suspended particles, suggesting that suspended particles are the major transport pathways of these metals through the Arroyo Carrasco.

Table 2 - Trace metal concentrations, minimum and maximum values reported, in bottom sediments ($\mu\text{g.g}^{-1}$ d.w.) from the Arroyo Carrasco compared with similar environments in the South Western Atlantic and with sub-recent Rhine river sediments. For this study, the first number in ranges are background concentrations observed at station 1 in Arroyo Carrasco, whereas second number is the highest reported concentrations for station 5 in Arroyo Carrasco.

Location	Pb	Zn	Cu	Cr	Author
Baía Blanca, Argentina, Lat. 39° S	13-17	30-39	6-9	----	Villa (1988)
Patos Lagoon Estuary, Brazil, Lat. 32° S	8-267	20-214	1-20	8-337	Baish <i>et al.</i> (1988)
La Plata River estuary, Uruguay, Lat. 35° S	1-141	2-105	1-109	1-57	Moyano <i>et al.</i> (1993)
Arroyo Carrasco	17-73	40-210	30-56	10-807	This study
Sub-recent Rhine river Sediments, Germany	30	115	51	47	Novotny (1995)

It has been suggested that the major source of suspended particles to the Arroyo Carrasco is the superficial runoff from the basin (Arocena *et al.*, 1992). Enrichment of trace metals in suspended particles have been reported for other situations, where urban runoff is a significant source of trace metals (Novotny, 1995). The role of suspended matter as the major transport pathway of trace metals in coastal areas has been reported for other coastal areas (Barcellos & Lacerda, 1993). Since the distribution of TSS suggests strong retention of particles inside the Arroyo Carrasco, an accumulation of trace metals is also expected and consistent with the commonly observed trend of high associated trace metal loads with urban derived suspended particles.

Geochemical partitioning

Several studies have stressed the importance of geochemical partitioning to understand trace metal mobilization and bioavailability on aquatic sediments. In summary, sequential geochemical extractions used for this partitioning are intended to mobilize trace metals from a particular substrate using a specific extractor assuming that only that particular substrate is affected. Although many criticisms of this procedure have been published related to its geochemical significance, these methods have proved of significance for pollution studies, since they are able to characterize the fraction of the total metal concentration potentially available for remobilization and biological uptake (Fernandes, 1997). A discussion of the advantages and disadvantages of such methods, however, is not in the scope of this study and a critical review of the various analytical procedures can be found in Kersten & Förstner (1989).

The geochemical partitioning of trace metals in the Arroyo Carrasco sediments is presented in Figure 3. As expected, most trace

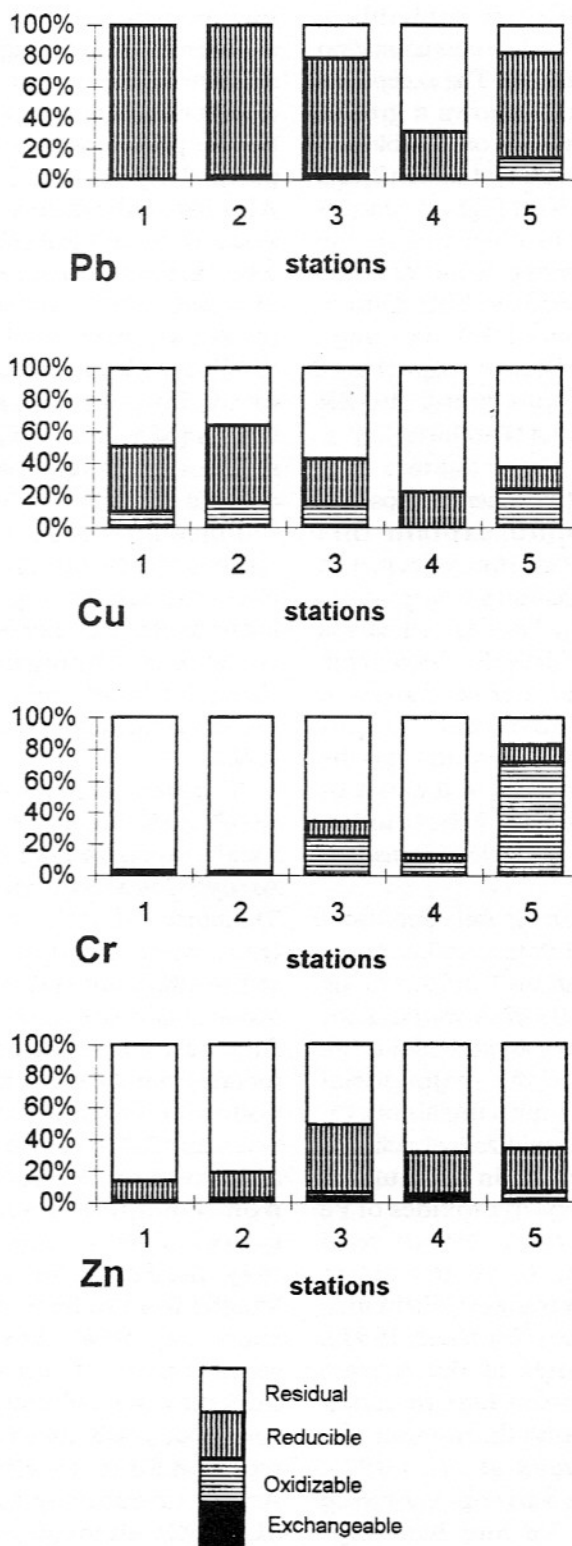


Figure 3 - Geochemical partitioning from sequential chemical extractions of trace metals in bottom sediments of Arroyo Carrasco, Montevideo.

metals are preferably associated with inert geochemical phases in sediments (>50% of the total concentration), at stations 1, 2 and 4. This result is probably a reflection of the low contamination status of the region. The exceptions are Cu, which shows a greater contribution of the oxidizable and reducible fractions at station 2, and Pb, for which the highest concentrations were observed in the reducible phase at all stations, except at station 4. This distinct distribution of Pb has been reported for bottom sediments of coastal lagoons along the SE Brazilian coast (Patchineelam *et al.*, 1988). Those authors suggested that atmospheric deposition of PbO could explain this distribution, since the major source of Pb in those areas was gasoline combustion. This hypothesis is consistent with the Pb distribution found in the Arroyo Carrasco, where runoff and direct atmospheric deposition are the major Pb sources to the metropolitan area of Montevideo (Moyano *et al.*, 1993; Carrasco *et al.*, 1993).

Potentially mobile sediment phases dominate metal concentrations at stations 3 and 5. Among the potentially mobile fractions, the reducible (oxy-hydroxides of Fe and Mn) are the major metal substrates for most metals but Cr, for which the oxidizable fraction is more important, in particular at station 5. Oxy-hydroxides of Fe and Mn have been well documented to be the major substrate for trace metals in oxic environments (Förstner, 1991). Earlier studies in the Arroyo Carrasco showed that oxic conditions are found throughout the year (Arocena *et al.*, 1992), favoring the scavenging of trace metals by Fe and Mn oxy-hydroxides.

At the contaminated station 5, over 75% of the total Cr is

associated with the oxidizable phase. Since oxic conditions dominate at all stations (Arocena *et al.*, 1992) and sulfides, which may be generated by bacterial sulfate reduction during events of salt intrusion, do not affect Cr distribution, organic matter should be the principal carrier of Cr, particularly at stations 3 and 5. Also, during the field sampling, no evidence of sulfide formation was found in the area. The preferential distribution of Cr in the organic phase is in agreement with the type of effluent released in the drainage, mostly from tanneries and urban wastes (Moyano *et al.*, 1993) at station 5, and the accumulation of organic matter in the wetland's sediments (station 3), which reaches 16.3% d.w. Similar geochemical partitioning of Cr has been reported for other urban areas contaminated by organic matter along the South Atlantic coast (Souza *et al.*, 1986; Baish *et al.*, 1988).

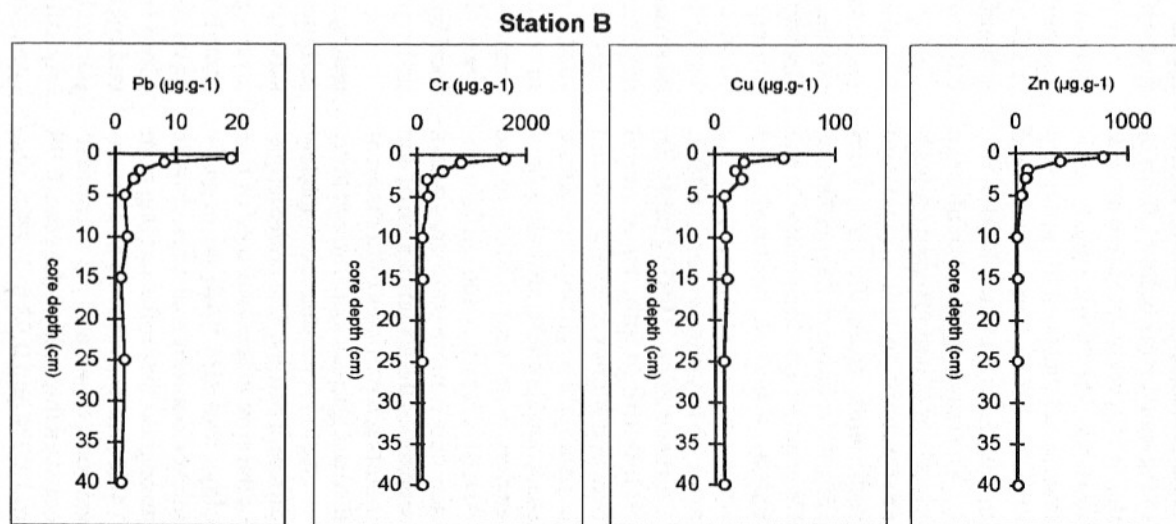
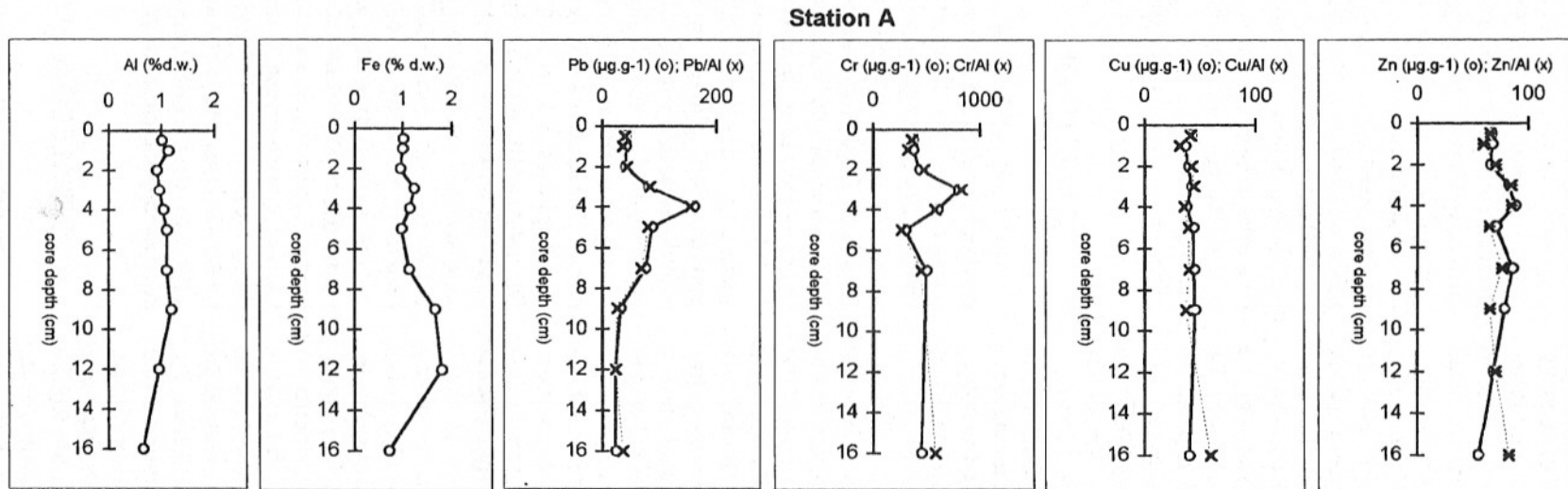
The increase in the importance of mobile fractions at station 5 and to a certain extension in the Arroyo Carrasco proper (station 3) suggests that the increase in trace metals content in the sediments of this station is due to accumulation of metal-enriched fine particles. Deposition of metals from the water column to bottom sediments may also be occurring. Still water conditions and stronger biological influence from emergent macrophytes typical of wetlands (station 3), may facilitate heavy metal transfer from water to sediments (Lacerda, 1994). At station 5, some transfer of trace metals from the water column may also occur due to salt intrusion events reported for this section of the Arroyo Carrasco by Arocena *et al.* (1992), although we did not measure any increase in conductivity at station 5 during our sampling campaign.

Trace metals distribution in sediment cores

The distribution of trace metals through sediment cores collected from lakes, marshes and wetlands, notwithstanding some limitations, has been successfully associated with trace metals loading rates to a given area (Johnson, 1987; Rasmussen, 1994), in particular when the most significant sources of trace metals are diffuse sources (Lacerda *et al.*, 1991). The distribution of trace metals observed through a core can be a strong instrument to study the evolution of trace metal contamination through time and the impact of increasing industrialization or the effectiveness of emission control policies. For a proper interpretation of trace metal distribution in sediment cores, it is important to determine the distribution of tracers of natural processes simultaneously, to rule out variations in trace metals concentrations due to erosion/sedimentation effects, changing natural metals sources among others. Aluminum and to a lesser extent iron, have been extensively used as tracers of natural metals sources (Sinex & Helz, 1981; Pachineelam *et al.*, 1988; Förstner, 1991).

The distribution of Al, Fe and trace metals in the cores collected at stations A and B is shown in Figure 4. The two cores contained sediments of different texture and organic matter content. At station B, only the surface layer of the sediment (0.0-1.0 cm) was rich in organic matter (>50% d.w.) and was constituted of a very fine, fluid, organic mud. Below this depth the sediment was basically composed of fine (<1.0 mm) sand grains and was very poor in organic matter and clay content (<2%). No data are available on Fe and Al concentrations in this core; therefore historical evaluation of changes in trace metals

Figure 4 - Distribution of trace metals and iron and aluminum concentrations (dry weight basis) along sediment cores from Arroyo Carrasco, Montevideo.



concentrations is impossible for this station. The textural and organic matter characteristics of this core suggest that the distribution of trace metals in the core from station B does not necessarily reflect trace metal load to the sediment. Rather it reflects the larger capacity of the fine, organic surface sediments, relative to the sand layers below 1.0 cm of depth to accumulate trace metals, in particular at this highly contaminated station. This grain size effect has been largely discussed in literature (Förstner, 1991).

The concentrations of all trace metals at station B show a high enrichment in the superficial sediments, from 0.0 to 1.0 cm (Fig. 4), relative to deeper layers. Concentrations are similar to the values found in contaminated surface sediments throughout the area (Moyano *et al.*, 1993; Carrasco *et al.*, 1993) (Table 2). Below this depth, trace metal concentrations were very low and constant through the core. Since suspended particles are particularly enriched in trace metals in the Arroyo Carrasco, the surface enrichment is more consistent with a scenario of the accumulation of fine metal-rich particles rather than of increasing metal load through time.

Station A presented completely different results. The entire length of the core was constituted of fine clays and silt, with an organic matter content that varied little throughout the profile, ranging from 14.6% to 16.3% *d.w.* The concentrations of Al and Fe were also constant throughout the core (0.98 to 1.03% and 0.98 to 1.28%, respectively). These elements, due to their natural abundance, relative to anthropogenic sources, are good tracers of changing natural inputs of trace metals. Therefore, if variations related to Al or Fe occur, they are most probably due to variations in the anthropogenic inputs (Förstner, 1991). At station

A, the uniform distribution of organic matter and clay content, and of the Al and Fe concentrations, suggest that any variations in trace metals concentrations in different core layers are most probably due to variations in trace metals loading rates to the Arroyo Carrasco and can be used to historically characterize the trace metal contamination of the area.

At station A, the absolute metal concentrations and the relative concentrations to Al and Fe (Fig. 4) indicated a peak in subsurface sediments (from 2.0 to 6.0 cm), in particular for Pb, Cr and Zn, to a lesser extent. Copper has not shown the same behavior, remaining constant throughout the profile. The first three metals have already been identified as contaminants to the coastal areas of Montevideo (Carrasco *et al.*, 1993; Moyano *et al.*, 1993). As discussed earlier, the somewhat high and constant Cu concentrations, found in this core, and the spatially uniform distribution of Cu in bottom sediments through the area suggest that Cu concentrations, observed in this study, reflect local background values rather than anthropogenic influences.

The decrease in the concentrations of Cr, Zn and Pb in surface sediments, relative to sub-surface sediments strongly suggest that the anthropogenic inputs of these metals to Arroyo Carrasco may have decreased in recent years (from 10 to 30 years, depending on sedimentation rates). This is supported by the lack of evidence of any natural disturbance through the cores, attested by constant Al, Fe and organic matter concentrations in the cores. In particular the diversion of most industrial and sewage effluents to a submarine outfall in the early 90's may have been largely responsible for the observed decrease (Moyano *et al.*, 1993). We cannot specify the causes, but suggest that the

enforcement of environmental policies during the late 80's and the regional economic drawback may have contributed to the decrease observed in trace metals concentrations. Dredging and channeling in the 70's, resulting in the flushing out of fine, richer surface sediments, is unlikely to have caused the decreasing concentrations of Zn, Cr and Pb in surface sediments relative to subsurface ones, since no change was detected either in organic matter content or in the concentrations of Cu, Fe and Al.

CONCLUSIONS

The results of this first survey on the fate of trace metals in the Arroyo Carrasco, Montevideo, show heavy contamination of the area by Cr and, to a lesser extent, Zn and Pb. Copper concentrations, although relatively high, seem to represent local background values. The majority of metal content in sediments is associated with inert geochemical phases or more mobile reducible phases, with the exception of Cr, which showed strong association with organic matter. The relative importance of mobile phases, at least for Pb and Cr, may result in the release of large amounts of trace metals in case of significant changes in the wetlands geochemical conditions. Presently, trace metals concentrations are decreasing in the wetlands proper. However, continuous monitoring is necessary to follow hydrochemical changes in these wetlands and to evaluate further decrease of metal contamination, due to the enforcement of the control policies adopted.

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