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Natural Background Assessment and Its Anthropogenic Contamination of Cd, Pb, Cu, Cr, Zn, Al And Fe in the Sediments of the Southern Area of Patos Lagoon

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ABSTRACT

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The Patos Lagoon, located in Southern Brazil, is the world's largest choked coastal lagoon with an approximately 151000 km2 watershed. It receives untreated domestic, agricultural and industrial wastes associated with the populations living along its margins. This study examined the distribution of Cd, Pb, Cu, Cr, Zn, Al and Fe in 15 sediment cores of the lagoon in an attempt to establish natural background levels of these metals and to assess anthropogenic influences on them. Al and Fe were tested as normalizes among which Al was chosen as the most appropriated for the sampling sites. In some stations anomalous concentrations for Cd, Pb and Cu were found and contamination of sediments with Zn, Cr, Al and Fe was also observed.

ADDITIONAL INDEX WORDS: *Background assessment, anthropogenic contamination, metals*

INTRODUCTION

Many heavy metals (e.g., Co, Cu, Fe, Zn, etc.) are essential to some biological processes at low concentrations; however, any of them can be toxic to estuarine and marine organisms when available above a threshold level. Other elements, such as Cd and Pb, have no known biological function and at high concentrations may affect biological communities (KENNISH, 1997).

Growing concern regarding the impact of heavy metal discharges from municipal and industrial sources in coastal environments has compelled researchers to asses and to monitor metal distributions in coastal aquatic environments. Because of their particle reactivity, most metals discharged in estuarine and coastal areas tend to accumulate in coastal sediments and thus their distributions there provide a record of metal pollution (FORSTNER, 1979).

For the last 30 years sediment analysis has provided important information about metal contamination in marine coastal environments. Contamination of harbours and living marine resources, and in some cases, threats to human health by heavy metals have been documented by many workers (LORING and RANTALA, 1992; REIMERS, 1991; HANSON *et al*., 1993; BOTHNER *et al*., 1998; CELO *et al*., 1999; VAN GEEN, 1999). High levels of trace metals in sediments, however, do not necessarily reflect anthropogenic influence, but instead may be of a diagenetic origin (ZWOLSMAN *et al*., 1993) or due to grain size effects (LORING and RANTALA, 1992). Since metals from natural and anthropogenic sources both accumulate in sediments, it is often difficult to determine what fraction of the sedimentary metal load comes from which source. A crucial step for pollution assessment of sediments is establishing the expected natural background concentration levels of heavy metals, from which various approaches can be used to quantify anthropogenic inputs. Metal concentrations are often normalized to a conservative component whose levels are unaffected by contamination inputs. Examples of such geochemical normalizers are Al, Fe, Li, etc (LORING and Rantala, 1992; WINDOM, 1987; LORING, 1990). These serve as tracers of the dominant natural metal-bearing phases in sediments.

Up to now, there have been few assessments of metal levels in Patos Lagoon sediments in relation to anthropogenic inputs (BAISCH *et al*., 1988). An attempt to assess the anthropogenic contribution to particulate metal concentrations in the estuarine region of Patos Lagoon, however, has been made by NIENCHESKI *et al*., (1994).

Patos Lagoon (10360 km2) and Mirim Lagoon form the largest lagoonal system of South America and the watershed discharging into these lagoons is about 202,000 km2, of which 75% is associated with the Patos Lagoon (Figure 1). The only contact with the sea is through an inlet at the southern end of Patos Lagoon. Geomorphologically the southern region of the lagoon has the characteristics of a bar-built estuary with a 30 km wide upper limnic part which gradually, over 50 km, narrows into a 700 m wide access channel. Within the estuarine area of the lagoon there is a navigation channel of ca. 12 m depth. Almost 80% of the lagoon is less than 2 m deep. Like many coastal lagoons, Patos Lagoon is affected by various human activities related to population expansion, material waste disposal, engineering works, lack of watershed management, etc. At present it receives untreated domestic, agricultural and industrial wastes (HARTMANN, 1988; NIENCHESKI *et al*., 1999).

We attempted to assess background levels of Pb, Cd, Zn, and Cr in sediments of the southern part of Patos Lagoon. For this purpose, cores were collected from 15 stations during 1996 and from 11 stations during 1997. To assess background metal concentration, samples from the deeper parts of the cores were analyzed and Al and Fe were used as indicators (i.e. normalizers) of natural metal bearing phases. Finally, an assessment of anthropogenic influence in the study area was carried out under the assumption that the deep sediment provide an indication of natural metal levels.

MATERIALS AND METHODS

Sampling

Cores were collected using the coastal research vessel LARUS between August 15th and September 30th, 1996 and between May 2nd and May 12th 1997 at several locations in the Southern portion of Patos Lagoon (Figure 1). Stations 1-12 were located near the urban and industrial center of Rio Grande City. In addition to harbor activities, an industrial complex is located in this area. Likely sources for metal contamination associated with this complex include fertilizer and refinery plants. Sampling site 13 is located in "Saco do Justino", which is a protected area for fish and shrimp cultivation (with an average depth of 1.5 m). Stations 14 and 15 are located near the cities of Pelotas and São Lourenço do Sul, at a distant of 45 and 90 km from the ocean inlet, respectively.

Sediment cores were collected using pre-cleaned plastic core

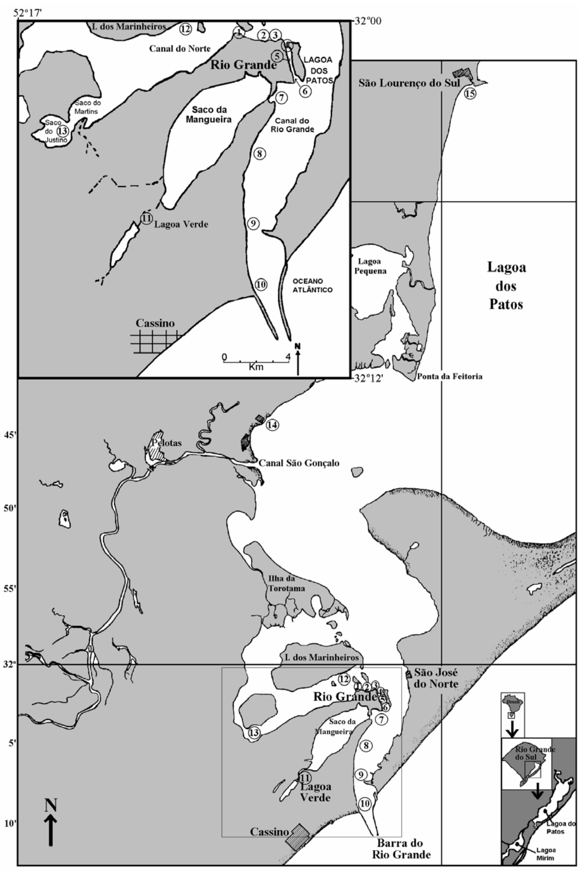

Figure 1. Map of the study area showing the sample locations in the estuarine region of Patos Lagoon.

tubes. During the first cruise 15 sediment cores were collected which penetrated about 10 cm. For stations 11 to 15 the collected sediment core depth was about 45 cm. During the second cruise 11 sediment cores of about 25 cm in length were collected. Sub-sampling was performed by extruding the sediment column in small intervals from the top of the core tube (0, 0.5, 1, 2, 5, 10, 15, 25, 35 and 45 cm). Individual sampling intervals were carefully collected from the extended core with a Teflon spatula. The sediment sections were dried for 24 hours at 80º C, after which they were ground to a powder and stored in glass bottles at 4º C. A total of 189 sediment sub-samples were analyzed.

Analytical Procedures

The procedure used for total sediment digestion was that recommended by UNEP (1990) with some modifications. Samples were placed in a Teflon vial and treated, overnight, with concentrated HNO_3. After that, the residues were digested with a 10 mL acid mixture (1:2:3) of HF-$HClO_4$-HNO_3 on a hot plate. After samples were completely digested, the solution was evaporated to dryness and the resulting residue taken up with 3 mL HNO_3 HCl (1:1). Samples were transferred to a 25 mL volumetric flask and brought to volume with distilled water. All reagents used were of ultra pure grade and Milli-Q water was used throughout the digestion procedure. A Flame AAS CG-AA 7000 and a GFAAS ZEISS model 5 were used for Fe, Cr, Zn and Al, and for Pb and Cd, respectively. A N_2O/C_2H_2 flame was used for determination of Al and Cr, as previously recommended, to eliminate interference (BARAJ *et al.*,1999).

Accuracy of analytical results was checked by analyzing reference sediment material IAEA-356. Three blanks and three replicate of the reference material were digested with every set of 20 samples. Replicate analysis of the IAEA-356 were within 9% of reported values for all analyses.

RESULTS

To assess the relative contributions of natural and anthropogenic metal inputs to sediments, it is necessary to have some idea of what natural concentrations are expected to be in sediments from a given region. As discussed in the introduction, researchers often collect and analyze samples from areas remote from anthropogenic inputs to establish metal to normalizer relationships. These relationships usually take the form of a given metal concentration plotted against a normalizer (e.g. Al) over a range of sediment textures resulting in a direct correlation of metal to normalizer. A regression curve is then established from the data with 95% confidence bands. Thus if this population of samples reflects natural conditions, then there is a 95% probability that data from new samples, from the general region, will fall outside (i.e. above) the upper confidence band if it contains a significant anthropogenic input.

In the present study, we do not have a sufficient number of sampling sites which we can say are not likely to receive anthropogenic inputs. But, because we have collected cores we argue that the deeper portions of the cores have the highest probability of being uncontaminated. Thus for the purpose of assessing anthropogenic input to sediments in this region, we use data from samples taken at the bottoms of cores to establish metal-normalizer relationships to which the data in the remaining parts of the cores are compared.

We compared metal data in samples from the bottoms of cores to two normalizers, Al and Fe. Regression analyses of metal on normalizer generally show weak relationships but those using Al as the normalizer were best and are presented in Figure 2. Also shown in this figure are lines which represent the metal:Al ratio for average soils (MARTIN and WHITFIELD, 1982). Although the regressions are not tight, the results shown in Figure 2 at least compare reasonably well with average soils for all metals except Pb and Cr. These latter two metals appear to be depleted in sediments of the region in comparison to average soils.

Figure 3 presents all the data from the cores along with the regression curves from Figure 2. From this presentation of the data, it is clear that the upper layers of the sediment cores are significantly enriched in cadmium and copper relative to expected "natural" concentrations assumed to be reflected in deeper layers. Some sediments also appear to be enriched in Pb, Cr and Zn, but the scatter in data, including those from the lower sections of the core, make such an interpretation more tenuous.

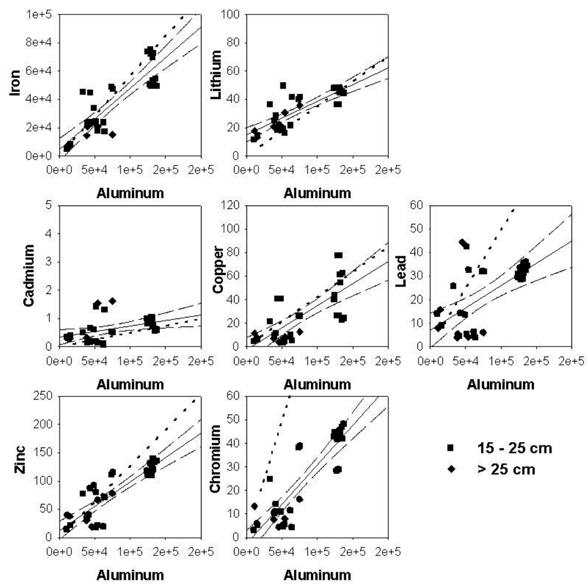

Figure 2. Metal concentration plotted against a normalizer (Al). Data obtained from depth below 15 cm. A regression curve is established from the data with 95% confidence bands. Dotted lines represent the metal:Al ratio for average soils (MARTIN and WHITFIELD, 1982).

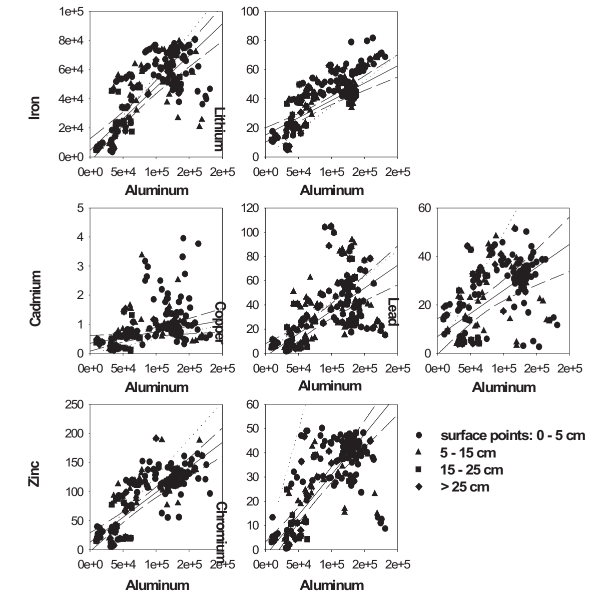

Figure 3. All the data from the cores along with the regression curves shown in Figure 2. Dotted lines represent the metal: Al ratio for average soils (MARTIN and WHITFIELD, 1982).

Table 1. *Enrichment Factor: (Me:Al) surface layers / (Me/Al) deep layers. The numerator is for mean data for upper centimeters of cores. The denominator is the slopes shown in Figure 2.*

Stations	Fe/Al	Cd/Al	Cu/Al	Pb/Al	Zn/Al	Cr/Al
1	1.53	4.45	1.57	1.72	1.58	0.93
2	1.38	6.45	1.15	2.35	1.20	1.31
3	1.32	2.80	0.94	1.24	1.30	1.01
4	1.56	2.42	2.25	1.59	1.38	1.17
5	1.28	2.21	1.39	1.42	1.20	1.00
6	1.25	2.25	1.35	1.89	1.31	0.99
7	1.13	1.82	0.78	1.89	1.38	0.85
8	1.11	2.26	0.75	1.68	1.37	1.08
9	1.52	1.51	0.94	1.92	1.65	1.53
10	1.91	2.98	0.89	1.84	1.81	1.52
11	0.67	1.46	0.37	0.27	1.04	0.41
12	1.15	8.46	1.49	6.98	2.07	1.11
13	0.90	2.53	0.53	0.77	1.11	0.53
14	0.42	1.40	0.23	3.34	0.33	0.16
15	0.67	0.83	0.38	1.06	0.32	0.34

DISCUSSIONS

Using data from the surface layers of the cores, metal enrichment factors can be calculated based on the regression of data from the bottom layers of the core (Table 1). If we arbitrarily assume that an enrichment factor of 2 or more is indicative of metal enrichments above natural levels, only cadmium, lead and copper appear to be significantly enriched in surface sediments. In the following, we suggest possible Sources for these metals:

Cadmium: its enrichment is observed in cores near the seaport (stations 1, 2, 3, 11 and specially 12) and may result from discharges associated with fertilizer plant activities over the past 25 years. Relatively high concentrations of Cd have been found in the raw minerals used in the fertilizer production (BECKER, 1985) resulting in contaminated liquid and air discharges. Rainfall also exhibits elevated concentrations of Cd in Rio Grande City (unpublished data). Cadmium occurs in varying amounts in all sedimentary phosphate and concentrations of 150 ppm Cd in these rocks will generate, after processing, a phosphate fertilizer with 120 ppm / Cd (BECKER, 1985). Elevated ratio values found at station 14 are likely due to Pelotas City.

Lead: with the exception of the more remote stations 11, 13 and 15, sediments analyzed appear to be influenced by discharges from the main cities located in the southern region of Patos Lagoon. It's interesting to point out that sampling sites 12 and 14 had lead enrichment greater than all other stations. This might be explained by the population growth and concomitant increase in the number of automobiles, especially in the Pelotas City, which has been an important commercial center in Rio Grande do Sul State and which has twice the population of the Rio Grande City. Transport is likely atmospheric (see below). Since in Brazil lead has not been added to gasoline for more than 10 years, the high EF's are likely the result of past activities.

Copper: the contamination of surface sediments at stations 4, 5, and 6, in Rio Grande Harbour, suggests port activity as a probable source. The values from these stations are in the upper part of the plot of copper vs. aluminum in Figure 3.

Transport Pathways: Station 12 is far from likely sources such as Rio Grande City but has the highest EF for most metals considered. This suggest an atmospheric transfer pathway driven by the dominant winds and sea breezes, which are from the South (BRAGA, 1997), that carry the urban / industrial aerial emissions northward.

The stations near the harbor are not as enriched as we might expect due to dilution of contaminated sediments by natural sediments transported through the main channel of Patos Lagoon.

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