

Anthropogenic heavy metal signatures for the fast growing urban area of Natal (NE-Brazil)

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Abstract In this study the effect of anthropogenic discharges on the heavy metal content in the Potengi–Jundiaí river system near the fast growing city of Natal, NE-Brazil, is investigated. Due to the multiple anthropogenic source character without any predominating anthropogenic heavy metal discharge the area of Natal may serve as a characteristic place for the study of the impact of the fast growing Brazilian cities on the environment. In general the sediments of the Rio Potengi–Jundiaí river system in the studied area are not severely polluted. However, close to waste water drain pipes a characteristic anthropogenic heavy metal signature is visible in enhanced Zn, Pb, Cu and Cd values relative to reference elements such as Al and Fe. Sources are domestic and animal waste, combustion products and hydrocarbons. These heavy metals are probably mainly bound to organic matter. The elements Sn, Hg and Ag in part also belong to the anthropogenic heavy metal signature. The elements Cr, Ni and V are characteristic of weathering heavy minerals in crystalline rocks exposed in the catchment

area of the river system and are not significantly added from anthropogenic sources. These heavy metals are most likely predominantly bound to oxides and represent the pristine geogenic background of the system. They can thus be used as reference elements to monitor incipient accumulation of Zn, Pb, Cu and Cd due to anthropogenic input. The element characteristics found here match with those found in other fast growing urban areas such as the São Paulo metropolitan area.

Keywords Heavy metals · Anthropogenic enrichment · Potengi river · Brazil

Introduction

Highly urbanized areas are affected by the diffuse anthropogenic release of hydrocarbons, combustion products and waste water to the environment. Such processes are mirrored in changes in heavy metal concentrations in river- and sea sediments. That diffuse anthropogenic emissions characteristically affect concentrations of Pb, Zn, Cu and Cd, as these appear in gasoline, lubricants, tyres or plastic materials, was shown for various places worldwide (e.g. East China Sea, Lin et al. 2002; Hong Kong, Li et al. 2001; Europe, Austria, Müller et al. 1983; Spain, Cobelo-García and Prego 2004; India, Balachandran et al. 2005; Callender 2003). Huang et al. (1994) showed for the Piratininga Lagoon, Rio de Janeiro, Brazil, that Pb, Cu and Zn are enriched in the upper parts of sediment cores. Another example for heavy metal enrichment in a Brazilian river system is given by da Silva et al. (2002) who pointed out that mainly Zn and Ni next to Cu are

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enriched in the Tietê-Pinheiros river system downstream of Sao Paulo city.

Anthropogenic enrichment can be revealed by heavy metal concentrations exceeding the range of background concentrations. Such concentration data may be related to particle size, normalized to Al- or K-, to Fe- or Mn- or to C_{org} -concentrations in order to account for available particle surface, for abundance of silicates and especially clay mineral, for oxide or for organic matter, respectively, which all control the concentrations of heavy metals (e.g. Chen et al. 2004; Lin et al. 2002; Rosales-Hoz et al. 2003; Soto-Jiménez and Páez-Osuna 2001). If certain heavy metals predominate in anthropogenic discharges to sea- and river sediments, the first indication of such process should be a shift in concentration ratios between different heavy metals.

This study seeks to investigate how shifts in element ratios indicate incipient effects of anthropogenic discharges and to define characteristic anthropogenic sediment heavy metal signatures for the fast growing city of Natal, NE-Brazil. This area is not affected by specific mining and heavy industry activity and therefore may serve as characteristic example of the Brazilian cities along the coast of the country.

Study area and sample locations

The city of Natal, capital of the state Rio Grande do Norte, and its surrounding towns (Fig. 1) have more than 1,000,000 inhabitants and are characterized by fast growth of approx. 30,000 pers./year (Petta and Medeiros 2004). In the last years the pressure of

urbanization has led to inefficient waste water treatment and thus caused problems for ground- and surface water (Guedes et al. 2005; Medeiros et al. 2004; Petta and Araujo 2004).

For detection of anthropogenic heavy metal discharge, sediments of the Potengi- and Jundiaí rivers, which catch the surface waters of the coastal region of Natal (Fig. 1), were sampled. Both rivers combine and empty into the Atlantic ocean in an estuarine area characterized by mangrove swamps. Due to their predominantly fine grained sediments and high abundance of organic matter they can act as sinks for anthropogenic contaminants (e.g. Rosales-Hoz et al. 2003).

Different locations were chosen to get samples representative of various surface water contributions to the Jundiaí and Potengi rivers. Samples M0, PO1 and PO2 were taken upstream in a distance of several km to Natal and Macaíba (Fig. 1). In these places the rivers are not reached by the tides and only affected by minor agricultural activities. This is confirmed by low NH_4^+ , NO_3^- and NO_2^- -concentrations (Table 1). The relatively high conductivities are due to the high rates of evaporation in the area during the period of sampling in the dry season (September–October, 2005). The samples M0 (river Jundiaí), PO1 and PO2 (river Potengi) are considered to be closest to the geogenic background and to represent the natural input to the Jundiaí and Potengi estuarine system which is dominated by weathering of the crystalline basement exposed in the region (Fig. 1).

Also, the location RD1 at the mouth of the Rio Doce into the Potengi estuary, represents a sweet water contribution to the system which is not affected by the tides (conductivity 237 $\mu S/cm$, Table 1). However,

Fig. 1 Geological sketch map of the area of Natal with sample locations along the Rio Potengi–Jundiaí river system

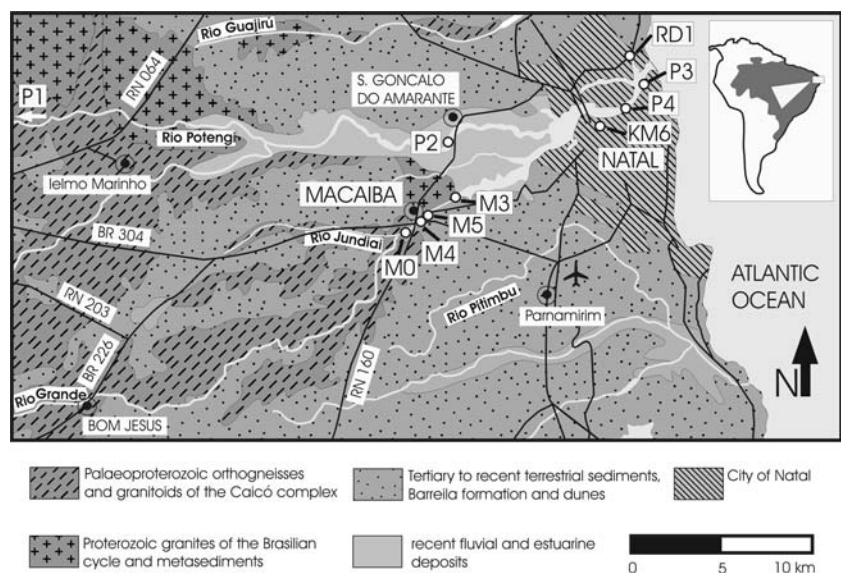


Table 1 Metal and total organic (TOC) and total inorganic carbon (TIC) concentrations of fluvial and estuarine sediments of the Potengi and Jundiai rivers

	M0	M3	M4	M5	KM6	PO1	PO2	PO3	PO4	RD1
Sediment										
Al	4.41	8.11	1.23	3.89	1.51	5.03	5.12	2.20	2.31	0.72
V	13.0	54.0	8.0	9.3	8.0	14.3	12.7	23.3	18.0	1.7
Cr	22.8	95.3	12.3	17.3	9.2	13.1	7.2	30.0	23.0	1.9
Fe	0.613	2.700	0.340	0.497	0.453	0.563	0.477	1.210	0.873	0.833
Ni	11.8	61.7	7.8	12.6	4.8	8.3	3.8	15.4	11.9	0.9
Cu	3.6	30.7	6.7	6.0	12.7	3.7	1.6	28.4	21.0	0.6
Zn	11.2	72.7	32.9	11.0	59.0	12.0	6.7	62.7	76.0	1.7
As	1.47	4.00	2.37	1.50	1.43	1.33	0.60	2.37	1.40	0.30
Mo	0.33	1.67	0.33	<0.30	0.67	<0.30	<0.30	1.33	2.00	<0.30
Ag	<0.003	0.080	0.027	0.023	<0.003	0.007	<0.003	0.120	1.700	<0.003
Cd	0.007	0.110	0.030	0.017	0.070	0.010	0.013	0.073	0.107	0.010
Sn	0.33	0.53	0.50	0.27	2.00	0.37	0.03	1.30	3.10	<0.03
Hg	<0.003	0.020	0.003	0.003	0.010	<0.003	<0.003	0.023	0.233	<0.003
Tl	ND	ND	ND	ND	0.17	ND	0.03	0.13	0.13	ND
Pb	4.67	24.70	4.67	4.00	13.67	1.77	1.67	11.00	19.70	0.70
TOC	0.09	2.38	0.56	0.29	0.51	0.20	0.05	1.22	2.21	0.10
TIC	0.01	0.38	6.27	0.06	0.06	0.17	0.08	0.67	0.16	0.01
Water										
NO ₃ ⁻	<1	<1	<1	<1	<1	<1	<1	<1	<1	5–10
NO ₂ ⁻	ND	<0.02	0.03	0.02	<0.02	ND	<0.02	<0.02	<0.02	0.05
NH ₄ ⁺	ND	3.5	5.0	1.0	25.0	ND	<0.2	30.0	5.0	<0.2
Cond.	3.32	8.06	1.58	1.51	0.51	4.83	2.73	38.60	39.90	0.24
Redox	94	-117	-142	50	93	176	122	-296	-181	162

Metal concentrations are given as mg/kg in dried (40°C) sediment fraction <0.5 mm. TIC, TOC, Fe and Al values as wt%

Carbon (TIC/TOC) analysed by total evaporation in LECO RC412 C-analyser. V, Cr, Fe and Ni analysed by ICP-OES (Perkin Elmer Optima 2000 DV). Cu, Zn, As, Mo, Cd, Ag, Sn, Tl and Pb analysed by Perkin Elmer Analyst 800 graphite furnace AAS. Hg determined by cold vapour technique in Perkin Elmer FIMS-100. Major element determination including Al was done by ED-XRF (Spectro XLab2000) using Co-, Al- and Ti-targets. Precision for concentration is better than 5% and 0.9% for analysis by ICP-OES/AAS and Al analysis by XRF, respectively. NO₃⁻, NO₂⁻ and NH₄⁺ were measured colorimetrically on site in the water of the sampling point and are given in mg/l. Cond. denotes conductivity in mS/cm and redox is redox-potential (Eh in mV), ND not determined

this location lies within a densely populated area in the suburbs of Natal and the catchment area of Rio Doce is in part intensively used for agriculture. Such anthropogenic burden is mirrored in enhanced NO₃⁻ and NO₂⁻-concentrations (Table 1).

In the vicinity of Macaiba the water of the Jundiai is affected by untreated wastewater. In a study of the Jundiai water composition Guedes et al. (2003, 2005) have shown that the biochemical demand of oxygen markedly exceeds the tolerable value of 5 mg/l for drinking-water (CONAMA 1986) and NO₂⁻ can reach values up to 0.83 mg/l, especially in the dry season (Guedes et al. 2005).

For this study sediment samples M3, M4 and M5 were taken along the river Jundiai within Macaiba or downstream close to this town such as M3 (Fig. 1). The latter sample represents the mangrove swamps characteristic of the estuarine area. High amounts of organic matter cause reducing conditions mirrored in low redox potential and elevated NH₄⁺-concentration (Table 1).

M4 was taken directly at the outlet of a wastewater pipe which is high enough not to be reached by the tides. Despite of low organic carbon in the sediment, the redox potential is low and the NH₄⁺ and NO₂⁻ concentrations in the water are high, indicating that this sediment is affected by waste water. Sample M5 represents the sediment of the Jundiai river in the area marking the maximal reach of the high tide. Though M5 was taken within the town of Macaiba, the lower NH₄⁺ and NO₂⁻-concentrations (Table 1) show that here the water is less affected by waste water than at sampling point M4. M3 and M5 sediment samples were taken during low tides in areas of low flow velocity close to the river banks.

The locations PO3 and PO4 are close to large waste water drain pipes into the Potengi estuary in the city of Natal within the harbour (PO3) and close to it (PO4). Samples PO3 and PO4 were collected from depths of 9 and 1 m, respectively, using a van Veen dredge. High conductivities point to the high amount of sea water close to the mouth of the Potengi river. The contri-

bution of waste water in both sites is reflected by high NH_4^+ and low redox potential (Table 1). Sample KM6 was taken in the canalized rivulet “Córrego das Quintas” in the quarter Quintas of Natal, an area of low social standard. Different to all the other samples which have components entirely <0.5 mm, sample KM6 contained cm sized rock and concrete components. Many waste pipes from private houses contribute untreated waste water to the rivulet which is, as can be noticed by smell, high turbidity, the occurrence of domestic waste and high NH_4^+ concentration, highly polluted.

In summary one can thus define a group of samples (i.e. M4, KM6, PO3, PO4) which are clearly affected by waste water and can consequently be taken to investigate the anthropogenic influence on the sediment composition. Another group (i.e. M0, PO1, PO2) represents the geogenic background. A third group (i.e. RD1, M3, M5) may, to an unknown extent, be anthropogenically affected which will be discussed.

Materials and methods

The sediment samples were dried at 40°C and sieved. The fraction <0.5 mm which predominates in all samples was taken for aqua regia digestion ($\text{HCl}:\text{HNO}_3 = 3:1$). The concentration of heavy metals (including Fe) and As were determined by ICP-OES and graphite furnace AAS (see Table 1 for details). Hg was analysed by cold vapour technique. Total inorganic carbon (TIC) and total organic carbon (TOC) were analysed after total evaporation in an analyser equipped with IR-detector (see Table 1 for details). Major element composition, of which Al is given in Table 1, was determined by ED-XRF.

Results and discussion

The heavy metal and As concentrations of the sample fractions <0.5 mm (Table 1) are variable but in general lower or in the same range as average concentrations of natural river muds or estuarine sediments (Calender 2003; DePaula and Mozeto 2001). Concentrations of Pb, Zn and Cu are mainly lower than those of European estuaries (Seine, Medway, Cundy et al. 2005). Except for sample PO4 Hg-concentrations are <0.023 ppm. Thallium is <0.17 ppm and will not be considered further.

Table 2 shows the Spearman rank correlation coefficient (r_s) matrix for concentration data of the sediment samples studied here. One can see that Cr, V, Ni and, less well pronounced, Fe are correlated. Also, Cu, Zn, Mo, Cd, Sn, Hg, Ag and Pb are correlated ($r_s = 0.81$ – 0.99) indicating that these elements, too, may have a common source. Different to Cr, V and Ni the latter group has a clear affinity to organic matter as indicated by the correlation with TOC. Except for Sn and Hg, r_s of these elements and TOC is >0.83.

If normalized to the abundance of elements such as Al and Fe, which serve to represent the geogenic mineral composition (clay minerals, oxides) controlling the geogenic abundance of heavy metals, one can see (Table 3) that for Cr, V and Ni the samples M4, KM6, PO3 and PO4 which mirror the anthropogenic impact do not differ significantly from the other samples. These elements, thus, are derived from geogenic sources, among which mafic and ore minerals from the crystalline rocks exposed in the catchment area of the Potengi and Jundiá rivers (Fig. 1) are most probable sources. These elements may form oxide phases. However, a clear control of their distribution by Fe

Table 2 Spearman rank correlation coefficient matrix for concentration data of sediment samples of the Rio Potengi–Jundiá river system

	Al	V	Cr	Fe	Ni	Cu	Zn	As	Mo ^a	Cd	Sn	Hg ^a	Pb	Ag ^a
TOC	−0.067	0.512	0.685	0.442	0.673	0.939	0.891	0.670	0.843	0.912	0.794	0.729	0.839	0.829
Al		0.658	0.418	0.261	0.418	0.103	0.091	0.130	0.443	0.039	−0.079	0.271	0.136	−0.314
V			0.876	0.718	0.803	0.633	0.658	0.439	0.700	0.491	0.476	0.643	0.579	0.543
Cr				0.685	0.964	0.770	0.733	0.718	0.643	0.567	0.564	0.586	0.742	0.600
Fe					0.612	0.406	0.406	0.203	0.729	0.361	0.212	0.671	0.379	0.543
Ni						0.758	0.636	0.767	0.643	0.567	0.467	0.329	0.664	0.371
Cu							0.927	0.755	0.814	0.912	0.855	0.757	0.912	0.771
Zn								0.567	0.986	0.833	0.952	0.929	0.930	0.886
As									−0.100	0.570	0.446	−0.186	0.670	0.329
Mo										0.871	0.757	0.900	0.886	0.800
Cd											0.761	0.814	0.818	0.829
Sn												0.814	0.882	0.943
Hg													0.700	0.975
Pb														0.829

^a Limited database as several samples have concentrations < lower limit of determination, see Table 1

Table 3 Ranges of element concentrations (in ppm, see Table 1) normalized to Al and Fe (in wt.-% of the element)

	Geogenic	Anthropogenic		Geogenic	Anthropogenic
V/Al	2.4–6.7	5.3–10.6	V/Fe	18.7–26.6	17.6–23.5
Cr/Al	1.4–11.8	6.1–13.7	Cr/Fe	15.1–37.2	20.3–36.2
Ni/Al	0.7–7.6	3.2–7.0	Ni/Fe	8.0–25.4	10.6–22.9
Cu/Al	0.3–3.8	5.4–12.9	Cu/Fe	3.4–12.1	19.7–28.0
Zn/Al	1.3–9.0	26.7–39.0	Zn/Fe	14.1–26.9	51.8–130.0
As/Al	0.1–0.5	0.6–1.9	As/Fe	1.3–3.6	1.6–7.0
Mo/Al ^a	0.1–0.2	0.3–0.9	Mo/Fe ^a	0.5–0.6	1.0–3.6
Ag/Al ^b	<0.1–1.0	2.0–74.0	Ag/Fe ^b	0.5–5.0	8–194.0
Cd/Al ^c	0.2–1.4	2.4–4.6	Cd/Fe ^{a,c}	1.0–4.0	6.0–15.0
Sn/Al ^c	0.6–7.0	41.0–134.0	Sn/Fe	0.1–0.7	1.1–4.4
Hg/Al ^{c,d}	0.1–0.3	0.2–10.1	Hg/Fe	0.6–0.7	0.9–26.7
Pb/Al	0.3–3.1	3.8–9.0	Pb/Fe	3.1–9.2	9.1–30.2

The group of samples representing geogenic signatures comprises M0, M3, M5, PO1, PO2 and RD1 unless otherwise noted. The samples representing anthropogenic impact are M4, KM6, PO3 and PO4

^a M5, PO1, PO2, RD1 excluded due to Mo concentrations < lower limit of determination

^b Multiplied by 100, M0, KM6, PO2, RD1 excluded due to Ag concentrations < lower limit of determination

^c Multiplied by 100

^d M0, PO1, PO2, RD1 excluded due to Hg concentrations < lower limit of determination

oxides is not mirrored in the data as r_s between Cr, V, Ni and Fe only varies between 0.61 and 0.72 (Table 2).

Relative to Al and Fe the elements Zn, Pb, Cd and Cu are clearly enriched in the samples M4, KM6, PO3 and PO4 (Table 3), making clear that these elements are derived from anthropogenic sources. The samples M5 and RD1, taken within densely populated areas but characterized by less polluted water, fall into the range defined by samples considered to represent geogenic background. The anthropogenic enrichment is less pronounced for As and Mo, though the latter element correlates with Zn, Pb, Cd and Cu.

Tin, Hg and Ag are anthropogenically enriched (Table 3). Hg shows highest enrichment in PO3 and PO4. Sample M3 is characterized by a relatively high Hg/Al ratio of 0.3. This may be due to anthropogenic enrichment, too. Guedes et al. (2003) report Hg concentrations up to 0.355 ppm in the fine fraction (<63 μm) of sediment from Jundiá River near the sample location M3. As such concentrations are neither found upstream nor downstream of this area, Guedes et al. (2003) conclude that there must be an anthropogenic source of Hg near Macaiba. Silver, which is clearly enriched in samples M4, PO3 and PO4 (Tables 2, 3) is thus also an element indicative of anthropogenic emission supporting findings of other authors (e.g. Baldwin et al. 2004; Matthai et al. 2002; Szefer et al. 1998).

The anthropogenic input of Zn, Pb, Cd and Cu can also be illustrated using ratios of these elements with Cr and Ni (Fig. 2). The four most affected samples (M4, KM6, PO3 and PO4) tend to significantly higher Cu/Cr-, Zn/Cr- but also Cd/Ni- and Pb/Ni-ratios than found in the other samples.

Anthropogenic components admixed to an initial geogenic composition in M4, PO3, PO4 and KM6 may be sewage sludge but also animal waste (Fig. 2). The latter can be expected in particular for KM6 from the Quintas quarter of Natal where inhabitants keep animals (poultry, horse).

The element ratios of coal and fly ash (Fig. 2) may represent the signatures of combustion products and hydrocarbons which thus can also contribute to the trend of anthropogenic influence. High amounts of Zn in urban areas, especially in street dusts, can also be derived from vehicle tyres (Li et al. 2001).

The slightly enhanced concentrations of Sn and Hg in samples PO3 and PO4, taken in and near the area used as harbour in Natal may be derived from Sn- and Hg-organic complexes used in antifouling bottom paint from ships. The absence of Ag in sample KM6 which represents an area in which domestic waste predominates makes clear that Ag is rather derived from industrial sources (electrochemical industry, disposed electronic devices, photochemicals, X-ray applications, e.g. Ravizza and Bothner 1996; Baldwin et al. 2004).

Sample RD1, representing a sweet water river in a densely populated area, is characterized by a Cd/Ni-ratio which points to admixtures of combustion products or animal waste. Element ratios of samples M3 and M5, taken in the mangrove swamps downstream of Macaiba (M3) and within the town (M5), are within the range given by the unpolluted sediments (Fig. 2) and do not show enhanced concentrations relative to Al or Fe. This makes clear that despite of anthropogenic heavy metal discharges in the area—such as represented by sample M4 situated upstream of M3

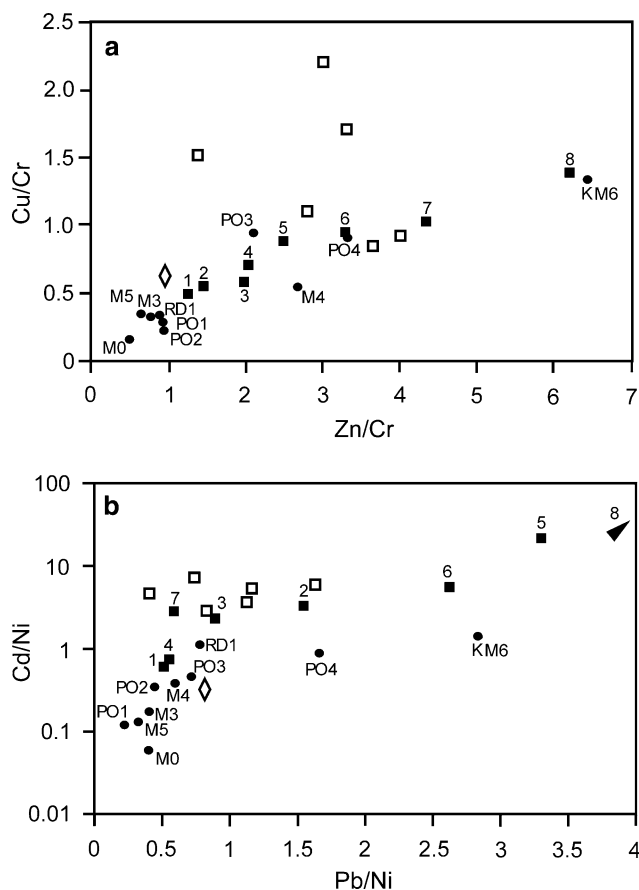


Fig. 2 **a** Zn/Cr–Cu/Cr plot, **b** Pb/Ni–Cd/Ni plot. Heavy metal ratios of sediments of the Rio Potengi–Jundiaí river system and average reference samples, 1 fly ash, 2 estuarine sediments, 3 coal, 4 lacustrine sediments, 5 sewage sludge, 6 recent lacustrine sediments, 7 animal waste, 8 fertilizers (1–8 taken from Callender 2003). Open squares show values of samples from the Tietê Pinheiros river system in the surroundings of São Paulo, Brazil (da Silva et al. 2002), see text for further explanation. Open diamonds indicate average values of four mangrove areas in the Arabian Gulf which are affected by oil spills, discarded wastes and petrol combustion (Shriadah 1999)

and M5—(also Guedes 2003; Guedes et al. 2003, 2005) these sediments (i.e. M3, M5) do not mirror the anthropogenic emissions, except for a slightly enhanced Hg/Al ratio in sample M3. The estuarine system is large enough and daily mixing with sea water and dilution during high tides at this stage of the urban development still prevents a significant accumulation of heavy metals. This can also be seen in mangrove sediments of the Arab Gulf which do not show significant relative enrichment of Zn, Cu and Cd despite of anthropogenic oil spills, solid wastes and petrol combustion (Shriadah 1999), Fig. 2. Only Pb shows enhanced values due to these anthropogenic emissions (Shriadah 1999).

The change towards higher Zn, Pb, Cd, Cu concentrations relative to Cr and Ni as a consequence of

urban discharges can in part also be seen in other Brazilian rivers such as the Tietê Pinheiros river system in the surroundings of São Paulo City, Brazil (Fig. 2) where large loads of different kinds of industrial and domestic wastes are discharged (da Silva et al. 2002).

In the area of Natal City, there is no predominating heavy industrial source of metals. Rather, one has to expect several sources such as domestic and animal waste, combustion products and hydrocarbons as well as paints. The multiple source character supports the idea that the system studied here around Natal may serve as a characteristic place for the study of the impact of the fast growing Brazilian cities on the environment.

Conclusions

In general the sediments of the Rio Potengi–Jundiaí river system in the area of Natal (NE-Brazil) are not severely polluted. However, close to waste water outlets a characteristic anthropogenic heavy metal signature is clearly visible in enhanced Zn, Pb, Cu and Cd values relative to reference elements such as Al and Fe. Most probable sources are domestic and animal waste, combustion products and hydrocarbons. These heavy metals are predominantly bound to organic matter.

The elements Sn and Hg have slightly enhanced concentrations in samples from Potengi river in the city of Natal. They may be derived from antifouling bottom paint material used for ships. Silver also is an indicator-element for anthropogenic emissions, mainly from industrial sources.

Cr, Ni and V are elements characteristic of weathering heavy minerals in crystalline rocks exposed in the catchment area of the river system and are not significantly added from anthropogenic sources. These elements which may predominantly be bound as oxides represent the pristine geogenic background of the system and can therefore also be used as reference elements to monitor incipient changes in the heavy metal composition due to anthropogenic input in the course of urban development.

Due to the multiple anthropogenic source character without any predominating anthropogenic heavy metal discharge the area of Natal may serve as a characteristic place for the study of the impact of the fast growing Brazilian cities on the environment. The element characteristics found here match with those found in the surroundings of the São Paulo metropolitan area.

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