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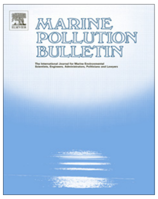

Background values for evaluation of heavy metal contamination in sediments in the Parnaíba River Delta estuary, NE/Brazil

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ABSTRACT

This study establishes regional background levels and upper thresholds (geochemical baseline) for Zn, Cu, Pb, Cr, Mn, and Fe from surface samples and profiles taken in 16 sedimentary environments of the Parnaíba River Delta estuary, NE–Brazil. Three approaches were applied to evaluate metal contamination: normalization to Fe, statistical analysis and sediment quality guidelines or environmental assessment criteria (TEL–PEL). Metal concentrations in sediments ranged from 2.4 to 31 mg Zn kg^{-1}, 1.5 to 48 mg Cu kg^{-1}, 1.3 to 28 mg Pb kg^{-1}, 1.5 to 38 mg Cr kg^{-1}; 145 to 1,356 mg Mn kg^{-1}, and 0.3% to 2.5% for Fe. All metals showed positive correlations with the <0.63 μm sediment fraction, indicating a significant association with rich lithogenic sources of iron oxide–hydroxides. Results suggest a low probability of adverse effects to the local aquatic biota. The background values of the area were lower than those reported for other areas of the northeastern coast of Brazil.

The relationship between natural processes and the changes caused by human action on the geochemical availability of metals is an issue with many implications in various fields of knowledge. Metallic pollutants have received considerable attention due to their persistence, biogeochemical recycling and environmental risk. It is a fact that the sediments transported by rivers play a key role in the absorption of trace metals and the ability of sediments to associate with metal species is related to the different geological materials of the drainage basin of origin (Chen et al., 2000; Luiz-Silva et al., 2002; Hortellani et al., 2008). In Brazil, several metal accumulation studies have sought to establish the geochemical basis for the assessment of natural and/or anthropogenic metal loads that may potentially reach the coastal environments in areas subject to urban and industrial pressure variables (Barcellos and Lacerda, 1994; Baptista et al., 2000; De Carvalho Gomes et al., 2009; Aprile and Bouvy, 2008; Luiz-Silva et al., 2002; 2006; Hortellani et al., 2008). However, only few studies related to this theme have been conducted in some impacted basins in the semiarid region of the Brazilian northeast (Marins et al., 2004; Sabadini-Santos et al., 2009; Passos et al., 2011).

Determining the natural levels of metals is essential to the accurate assessment of the degree to which a particular metal has been enriched in a given environment. These assessments provide an objective basis for decision making by public officials and for the proper use of natural resources. These values can be used as a relative measure to distinguish natural concentrations of trace metals (geogenic and/or biogenic) and the anthropogenic influence on their concentrations in soils and sediments (Reimann et al., 2005; Galuszka, 2007). The geochemical baseline reflects the natural concentration of one element in a particular material (e.g. soil, sediment, and rock). At the same time, it can be described as the threshold used to distinguish between geochemical backgrounds and anomalies (Salminen and Gregorauskiene, 2000). This term was introduced in 1993 in the framework of the International Geological Correlation Programme (IGCP, projects 259 and 360) in order to create a global reference network of national and regional geochemical data sets to be used as an international background database for environmental legislation (Darley, 1997). The methods most commonly used to determine geochemical background values for metals are direct, empirical geochemical methods or indirect, statistical ones (Reimann et al., 2005; Rodríguez et al., 2006; Galuszka, 2007).

The present study aims to establish regional background levels and upper thresholds (geochemical baselines) for metals in the sedimentary environment of the Delta of the Parnaíba River, NE Brazil. For this purpose, we have investigated the distribution of Zn, Cu, Pb, Cr, Mn and Fe in surface sediments and sediment cores

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(grain size <63 μm) using different data analysis methodologies. The TEL–PEL sediment quality guidelines or environmental assessment criteria were used to check if metal concentrations in sediments may occasionally be associated with adverse biological effects. We used the Geoaccumulation Index (I_{geo}) and the Enrichment Factor (EF) for the quantitative measurement of sediment contamination by Zn, Cu, Pb and Cr of anthropogenic origin.

The Parnaíba River Delta system is a complex and important ecosystem, having its own fluvial–marine dynamics and harboring important plant and animal communities. It has a wide coverage area of about 2,750 km^2. The Delta is embedded in the morphological unit known as the "Late Tertiary Barreiras Formation", comprised of unconsolidated iron-rich alluvial sediments encompassing the entire Brazilian eastern and northeastern shoreline. It is characterized by extensive fluvial–marine plains crisscrossed by canals that form islands resulting from the accumulation of terrigenous materials. The coastline and watercourses have their own perennial maritime influence, which makes the waters brackish. Extensive mangroves have developed under these environmental conditions, with significant phytoplankton primary productivity levels occurring in its coastal plume. This complex configuration of ecosystems transforms this environment into an important global conservation area (MMA, 2006). Due to its environmental importance, in 1996 the Delta was declared an Environmental Protection Area extending over three states in Northeastern Brazil (Ceará, Maranhão and Piauí). The Parnaíba River watershed (34400 km^2) is characterized by a low industrial development. The Delta has few point sources of contaminants and therefore diffuse pollution sources prevail, which are typically difficult to control and monitor. The two main river channels flowing into the Atlantic Ocean are the Parnaíba (P) and Igaraçu (Ig). A regional urban center (Parnaíba city) can be found on the western boundary of the environmental protection area, which is a possible source of metal loads to the Igaraçu River, mainly associated with specific emissions of domestic effluents and the presence of a leather processing industry (tannery).

Sampling of surface sediments and cores was randomly done at 16 points distributed along the two main channels of the Delta in February 2010, during the rainy season. A total of 129 samples, including 16 surface samples and 113 samples from sediment cores, were collected from muddy deposition areas (Fig. 1). Surface samples were taken with a Van Veen grab and the cores were taken with a manual piston corer and acrylic tubes. Cores with depths ranging between 50 cm and 95 cm were obtained. Points P1 to P3 and Ig1 to Ig3 are under fluvial influence, P4 and Ig4 represent the end of the river and points P5 to P8 and Ig5 to Ig8 are located along the estuarine gradient. After collection, surface samples were initially stored in sealed polyethylene bags and transported to the laboratory. At the Coastal Biogeochemistry Laboratory of the Institute of Marine Sciences of the Federal University of Ceará, the cores were split at 5.0 cm intervals. One portion was used for chemical and the other for physical testing. Samples intended for chemical testing were oven-dried at 105 °C and the muddy fraction (<63 μm) was separated by passing the sediment through a nylon mesh sieve. Regional comparisons of elemental concentrations can only be made using texturally equivalent sediments and/or size fractions. This is necessary to normalize for the "grain size effect" (Loring and Rantala, 1992). Metals were extracted with *aqua regia* in a microwave oven, according to USEPA method 3051A (USEPA, 1998). Concentrations were determined by Flame Atomic Absorption Spectrometry (FAAS) (Shimadzu AA 6200) and a background correction with a deuterium lamp. All samples for this study were analyzed in three replicates. The validation of this method was performed by testing a certified estuarine sediment standard material (Material 1646a – The National Institute of Standards and Technology). Recovery rates for the metals were 92% for Zn, 84% for Cu, 83% for Pb, 72% for Cr, 81% for Mn, and 99% for Fe. Statistical procedures involved the establishment of normality using the Shapiro–Wilk test, Pearson correlation, Box–Whisker plots and cumulative distribution plots of metal concentrations with the Statistica 8.0 software (StatSoft, Inc. 1984–2007). Organic carbon (OC) content was determined with the Walkley and Black titration method (Nelson and Sommers, 1982).

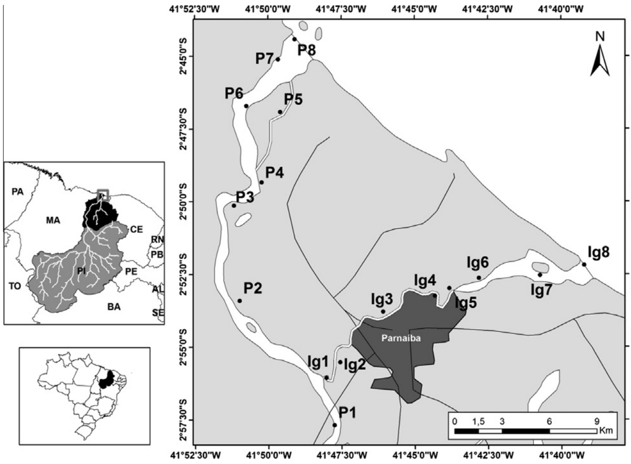

Fig. 1. Sampling points distributed along the two main channels of the Parnaíba River Delta estuary.

Grain size analyses showed that the <63 μm fractions (silt and clay) were prevalent in the sediments, ranging from 32% to 98%. Metal concentrations in the <63 μm fraction of surface sediments and sediment cores ranged from 2.4 to 31 mg Zn kg^{-1}, 1.5 to 48 mg Cu kg^{-1}, 1.3 to 28 mg Pb kg^{-1}, 1.5 to 38 mg Cr kg^{-1}, 145 to 1,356 mg Mn kg^{-1}, and 0.3% to 2.5% for Fe. Organic carbon (OC) concentrations ranged from 0.8% to 19%. Positive correlations were found between metals and the <63 μm fraction with OC (Fe: $r = 0.78$; Zn: $r = 0.76$; Cu: $r = 0.59$; Pb: $r = 0.55$; Cr: $r = 0.54$ and <63 μm fraction: $r = 0.55$; $n = 129$, $p < 0.01$). Positive significant correlations were also found between OC and metals, with the exception of Fe, with the <63 μm (OC: $r = 0.53$; Zn: $r = 0.60$; Cu: $r = 0.59$; Pb: $r = 0.29$; Cr: $r = 0.37$; $n = 129$, $p < 0.01$). All metals including Fe showed positive correlations with the <63 μm fraction, indicating a significant association with rich lithogenic sources of iron oxide–hydroxides from the watershed, where Oxisols prevail (EMBRAPA, 2006). Therefore, iron is the most appropriate conservative element in the region for the normalization procedure, since it was the only metal not correlated with OC in accordance with similar studies from other rivers in northeastern Brazil (Aprile and Bouvy, 2008; Sabadini-Santos et al., 2009).

Two interpretation criteria were used to assess sediment quality with regard to metallic contaminants, in accordance with guideline values developed by NOAA (Buchman, 1999). TEL (Threshold Effect Level) is the limit under which no adverse effects on the biological community are observed, and PEL (Probable Effect Level) is the probable level where adverse effects in the biological community would occur. The TEL and PEL reference values for brackish and saline sediments adopted by Brazilian legislation (CONAMA 344/04) are as follows: 150 and 410 mg kg^{-1} for Zn, 34 and 270 mg kg^{-1} for Cu, 48 and 218 mg kg^{-1} for Pb, and 81 and 218 mg kg^{-1} for Cr. In terms of PEL and TEL, Zn, Cu, Pb and Cr concentrations were below the reference values, even considering that our concentrations are for the <63 μm fraction, thus overestimating the bulk sediment concentrations. The low trace metal concentrations found in the sediments of the Parnaíba River Delta estuary suggest a low probability of adverse effects to the local aquatic biota. For the analysis of normality made for each metal, a subset of data was truncated based on the heuristic procedure proposed by Reimann et al. (2005), keeping in mind that the upper layers of the sampled sediments may reflect recent contamination events. Thereby, far outliers related to sampling points subject to a higher influence of point source emissions from the Parnaíba urban center were removed. This procedure was applied by Rodríguez et al. (2006) to determine the background sediment levels in the Basque country in Spain. The distribution of truncated data for each metal, according to the Shapiro–Wilk test, showed unimodal distributions of Zn, Cu, Pb, Cr, Mn and Fe.

One way to determine the natural geochemical (lithogenic) background for the study area is from the mean concentrations of elements in the lower layers of sediment. The geochemical method, based on the testing of known, manmade samples free of interference and background concentrations usually provides mean or median values. (Swennen et al., 1998; Horckmans et al., 2005). The levels of metals available in sediments deposited in sedimentary basins during the pre-industrial period are used to evaluate background concentrations. Therefore, it is necessary to know the sedimentation rates of the different basins to determine the depth at which these sediments are located. Low sedimentation rates (<0.3 cm yr^{-1}) are typical of estuaries of the northeast coast of Brazil (Marins et al., 2004). Thus depths between 30 cm and 100 cm integrate depositions that are optimal for the determination of background values in view of the late industrialization of the country. The basic assumption is that the deeper layers of overbank sediments represent pre-industrial times and hence the background situation of the catchment area of the river under study. Table 1 presents the main statistical descriptors for the data obtained from these deeper sediments.

Different statistical techniques have been proposed to identify anomalous geochemical values, yielding a wide range of thresholds that can be estimated depending on the chosen method and transformation. Geochemical values within the range $[\text{mean} \pm 2\sigma]$ were often defined as the "geochemical background", acknowledging that the background is a range of values and not a single value (Hawkes and Webb, 1962; Reimann et al., 2005), although it is usually defined as the central value (mean, median or 95% confidence of the mean) or the upper limit value of the range or threshold (Rodríguez et al., 2006). Samples lying beyond the confidence interval (95%) will be regarded as "anthropogenically influenced".

Once regional background values are identified, the extent of anthropogenic contamination by metals in a certain area (anomalies) can be obtained through the standardization of data by a conservative element and Enrichment Factors (EF) (Aprile and Bouvy, 2008), as per the following equation: ([Metal]/Fe(%))/([Metal]/Fe$_{background}$(%)). The [Metal]/Fe$_{background}$ values were obtained by averaging the sampling points with a normal concentration of metals, or the samples that were within the 95% confidence level curve obtained by a regression band. Metal concentrations were normalized for the textural characteristic of sediments with respect to Fe. Iron was selected because it is a major sorbent in tropical soils and is a quasi-conservative tracer of the natural metal-bearing phases in fluvial and coastal sediments (Schiff and Weisberg, 1999). The I_{geo} reflects the relative enrichment of a given metal in a given system, its scale going from uncontaminated ($I_{geo} \leqslant 0$) to extremely contaminated ($I_{geo} > 5$) sediment. In this study, the average values of I_{geo} for surface sediments and profiles were graded as 0, that is, the sediments can be classified as not contaminated. Enrichment factor values between $0.5 \leqslant \text{EF} \leqslant 1.5$ suggest a relationship with the geological composition of the material and with weathering processes, whereas an EF > 1.5 shows areas with higher metal contamination levels. The average values determined for EF's of surface sediments were 1.3, 2.1, 1.4, 1.5, and 0.4 and those of the cores were equal to 1.1, 0.6, 0.5, 0.5 and 1.2, respectively, for Zn, Cu, Pb, Cr, and Mn. These results show a relative enrichment in the lower layers down to 30 cm (basal muds), reflecting a possible additional contribution as they are downstream to a regional urban center and under the influence of a port. The reduced EF of Cr may be related to the decline of the local leather industry and consequently the reduction of specific Cr effluent emissions in the region.

A graphic review of the empirical data distribution using a variety of exploratory data analysis tools is thus essential in order to estimate threshold values or define background concentrations (Reimann et al., 2005). Moreover, Box–Whisker element concentration plots were presented to evaluate the variation in the sediment samples of the Parnaíba River Delta (Fig. 2). This graphic approach allows the identification of extreme values, based on the accumulated frequency of a given element. It provides a graphical data summary relying solely on the inherent data structure and not on any data distribution assumptions (Tukey, 1977). Boxplots divide the data values sorted into four parts, median (second quartile), upper and lower quartiles, often referred to as upper and lower hinges defining a central box which contains about 50% of the data. The interquartile range (IQR) is defined as the distance

Table 1
Statistical descriptors of the background concentrations of metals in fluvial and estuarine sediments, integrated layers between 30 and 100 cm deep, in the Parnaíba River Delta (mg kg^{-1}, except Fe (%)).

	Range	Mean	Median	SD[a]	Background value[b]
Zn	2.6–23	13.4	13.7	5.4	11.5–18.6
Cu	1.5–14	6.8	7.0	2.9	5.9–9.9
Pb	1.5–11	5.9	5.7	2.4	4.7–8.1
Cr	1.5–38	18.0	16.8	8.7	11–20
Mn	155–1269	633	622	231	408–829
Fe	0.3–2.0	1.4	1.4	0.6	1.1–1.8

[a] Standard deviation (SD).
[b] Represent the 95% confidence level.

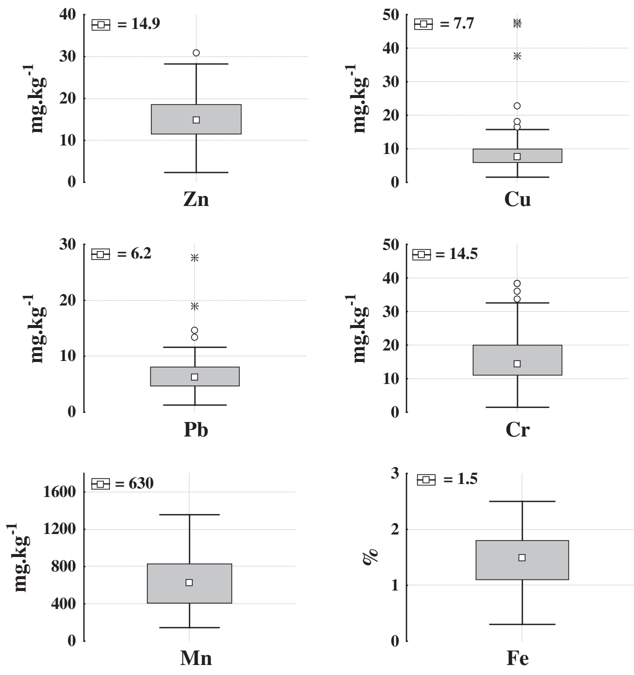

Fig. 2. Box–Whisker plots of Zn, Cu, Pb, Cr, Mn and Fe concentrations in the <63 μm fraction of surface sediments and cores of the Parnaíba River Delta estuary, NE Brazil. Median concentrations are indicated in the top left corner. Gray squares included 50% of the concentration data; horizontal bars represent the 25% and 75% interval. (∘) – represents outliers >1.5–3.0 times the 75% percentile, whereas (∗) – represents outliers >3.0 times the 75% percentile value.

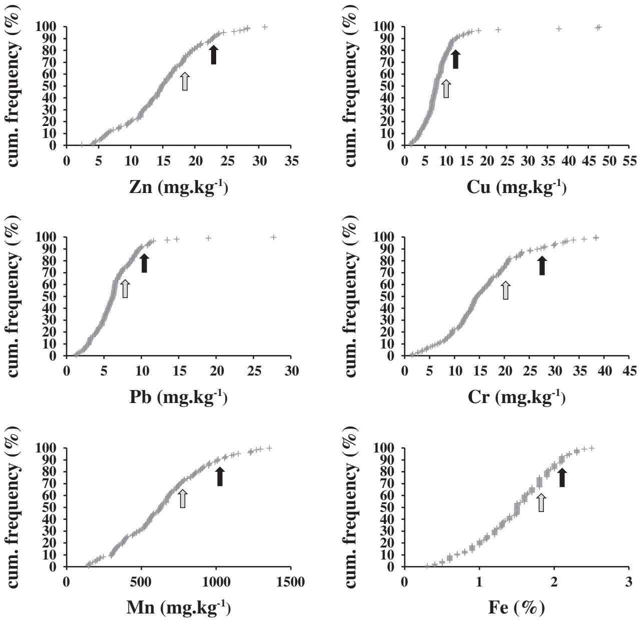

Fig. 3. Empirical cumulative distribution plots of metal concentration data for Zn, Cu, Pb, Cr, Mn and Fe in muddy fraction (<63 μm) samples of surface sediments and sediment cores of the Parnaíba River Delta estuary. The two arrows point at two turning points that separate the "background" values (gray arrow), from samples which may not be influenced by human impacts, and those influenced by anthropogenic activities (black arrow).

between the first and the third quartile (75th percentile – 25th percentile). The inner fence is defined as the box extended by 1.5 times the length of the box towards the maximum and the minimum (IQR) and is used in the identification of outliers. The upper and lower whiskers are then drawn from each end of the box to the farthest observation inside the inner fence. Extreme or out of range values, are represented by circles (outliers – up to 3 times the IQR) and stars (far outliers – above 3 times the IQR). Rodríguez et al. (2006) used this methodology in determining the boundaries of the regional backgrounds for Cd, Cr, Fe, Ni, As, Cu, Mn, Hg, Pb and Zn in marine and estuarine sediments from the coast of the Basque country. This method was also used in Brazil by Lemos et al. (2001) for the determination of background values of trace metals in the State of São Paulo. In the latter case the values were set based on the upper quartile (75%) of the analytical results. The values used to determine the limits of the regional background for Zn, Cu, Pb, Cr, Fe and Mn in the Parnaíba River Delta were the upper and the lower whiskers. The following metal concentrations were obtained with this methodology: 11.5–18.6 mg Zn kg^{-1}, 5.9–9.9 mg Cu kg^{-1}, 4.7–8.1 mg Pb kg^{-1}, 11–20 mg Cr kg^{-1}; 408–829 mg Mn kg^{-1} and 1.1–1.8% for Fe.

Another graphic display of the geochemical distribution are the empirical cumulative distribution plots (ECDF diagram). This technique does not require any assumption concerning the distribution function (Tennant and White, 1959; Lepeltier, 1969; Matschulla et al., 2000). One of the main advantages of ECDF diagrams is that each single data value remains visible; however, ranges cannot be determined without a certain degree of subjectivity (Reimann et al., 2005). A deviation of the distribution can be seen as a shift in the upper part of the curve. Fig. 3 presents the cumulative distribution plots of metal concentration data in the muddy sediment fraction (<63 μm) of surface samples and sediment cores in the Parnaíba River Delta estuary. The two arrows point at two turning points that separate the "background" values (0–70%), from samples which may be either influenced by human impacts (>90–100%) or not (70–90%). The inflexion of the curves in Fig. 3 shows a relatively accumulative density of the concentration of the element, representing the boundary line between the background value and the abnormal value (Lepeltier, 1969; Matschulla et al., 2000; Reimann et al., 2005).

In the cumulative metal distribution plots, the arrows indicate inflexion or breaking points that most likely reflect the presence of multiple populations and outliers. The lower one may represent the upper limit of the baseline of the chemical elements and the upper one may represent the lower limit of the anomaly, i.e., the influence of human activity on the two inflexions. The following metal concentrations were obtained with this methodology: 18.2–22.7 mg Zn kg^{-1}, 9.3–12.7 mg Cu kg^{-1}, 7.3–9.9 mg Pb kg^{-1}, 19.1–27.3 mg Cr kg^{-1}; 764–1,007 mg Mn kg^{-1} and 1.8–2.1% for Fe. Wang and Zhang (2012) established an Environmental Geochemical Baseline for Hg, Cd, As, Pb, Cr, Cu, Ni and Zn in surface soils of Guiyang City, Guizhou Province, China, by using cumulative probability plots. Likewise, Luiz-Silva et al. (2006) determined geochemical anomalies for trace metals in sediments of the Santos-Cubatão estuarine system in the coast of São Paulo, southeastern Brazil.

The results obtained using different methodologies propose threshold ranges for the tested metals (Table 2) and compares them to metal background concentrations reported in sediments from different tropical estuaries in Latin America and the world.

Metal concentrations are on the lower side of the range reported for the São Francisco and Tapacurá tropical estuaries, also located in northeastern Brazil, and indicate that any minor metal contamination is probably restricted to rice plantation effluents from small urban agriculture communities (Aprile and Bouvy,

Table 2
Concentration of heavy metals in sediments of different rivers of Latin America and the world (mg kg^{-1}, except Fe (%)).

Region	Zn	Cu	Pb	Cr	Mn	Fe
Parnaíba River Delta (Brazil)[a]	2.6–31	1.5–48	1.3–28	1.5–38	145–1356	0.3–2.5
Tapacurá river (Brazil)[b]	4–55	1–57	<0.01–1.3	0.04–5.9	14–158	0.6–3.3
São Francisco estuary (Brazil)[c]	1–57	1–26	4–16	10–82	10–82	0.4–4.3
Santos – São Vicente estuary (Brazil)[d]	6–312	–	2–205	5–112	–	0.3–8
Jurujuba bay (Brazil)[e]	21–132	6.3–18	15–40	30–49	50–200	1.4–3.0
Almendares and San Francisco river (Cuba)[f]	86–709	72–421	39–189	84–210	390–1630	1.7–4.5
Montevideo Harbor (Uruguay)[g]	174–491	58–135	44–128	79–253	–	–
World average[h]	95	45	20	90	850	4.7

[a] This work: full range of metal concentrations from entire sediment cores.
[b] Aprile and Bouvy (2008).
[c] Sabadini-Santos et al. (2009).
[d] Hortellani et al. (2008).
[e] Baptista Neto et al. (2000).
[f] Olivares-Rieumont et al. (2005).
[g] Muniz et al. (2004).
[h] Salomons and Forstner (1984).

2008; Sabadini-Santos et al., 2009). On the other hand, our results are up to one order of magnitude lower than the world's average metal values (Salomons and Forstner, 1984) and up to two orders of magnitude lower than those reported for other regions of Brazil and Latin America subjected to a more intensive land use (Muniz et al., 2004; Olivares-Rieumont et al., 2005).

Finally, this study shows that the sediments of the Parnaíba River deltaic system have not yet reached multi-element concentration levels able to affect the balance of the local ecosystem. The geochemical results presented in this case study are intended to contribute to a database for future environmental monitoring studies of the Parnaíba estuarine system, supporting the implementation of public policies aimed to ensure the sustainability of the activities developed in the region.

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References

Aprile, F.M., Bouvy, M., 2008. Distribution and enrichment of heavy metals in sediments at the Tapacurá river basin, Northeastern Brazil. Braz. J. Aquat. Sci. Technol. 12, 1–8.

Baptista Neto, J.A., Smith, B.J., McAllister, J.J., 2000. Heavy metal concentrations in surface sediments in a near shore environment, Jurujuba Sound, Southeast Brazil. Environ. Pollut. 109, 1–9.

Barcellos, C., Lacerda, L.D., 1994. Cadmium and zinc source assessment in the Sepetiba bay and basin region. Environ. Monit. Assess. 29, 183–199.

Buchman, M.F., 1999. NOAA Screening Quick Reference Tables, NOAA. HAZMAT. Report 99-1, Seattle WA. Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration, p. 12.

Chen, J.S., Wang, F.Y., Li, X.D., Song, J.J., 2000. Geographical variations of trace elements in sediments of the major rivers in eastern China. Environ. Geol. 39, 1334–1340.

Conselho Nacional do Meio Ambiente – CONAMA, 2004. Resolução CONAMA n° 344, 25 March, 2004. <http://www.mma.gov.br/port/conama/res/res04/res34404.xml> (assessed 10.11.13).

Darley, A.G., 1997. A global geochemical reference network: the foundation for geochemical baselines. J. Geochem. Explor. 60, 1–5.

De Carvalho Gomes, F., Godoy, J.M., Godoy, M.L.D.P., de Carvalho, Z.L., Lopes, R.T., Sanchez-Cabeza, J.-A., de Lacerda, L.D., Wasserman, J.C., 2009. Heavy metals in sediment profiles from Sepetiba and Ribeira Bays: a comparative study. Radioprotection 44, 243–250.

EMBRAPA, 2006. Empresa Brasileira de Pesquisa Agropecuária – National Research Center of Soils. Brazilian System of Soil Classification. 2. ed. – Rio de Janeiro, 306p.

Galuszka, A., 2007. A review of geochemical background concepts and an example using data from Poland. Environ. Geol. 52, 861–870.

Hawkes, H.E., Webb, J.S., 1962. Geochemistry in Mineral Exploration. Harper, New York.

Horckmans, L., Swennen, R., Deckers, J., Maquil, R., 2005. Local background concentrations of trace elements in soils: a case study in the Grand Duchy of Luxemburg. Catena 59, 279–304.

Hortellani, A.M., Sarkis, J.E.S., Abessa, D.M.S., Sousa, E.C.P., 2008. Assessment of metallic element contamination in sediments from the Santos – São Vicente estuarine system. Quim. Nova 31, 10–19.

Lemos, M.M.G., Dias, C.L., Rocca, A.C.C., Casarini, D.C.P., 2001. Methodology used to establish the values of quality reference for soil and groundwater in the State of São Paulo. In: Prevention and Control of Pollution Soil and Groundwater. 1st Joint World Congress on Groundwater, Fortaleza, Brazil. <file:///C:/Users/Prof.%20Francisco%20Jos%C3%A9/Downloads/23477-85064-1-PB.PDF>.

Lepeltier, C., 1969. A simplified treatment of geochemical data by graphical representation. Econ. Geol. 64, 538–550.

Loring, D.H., Rantala, R.T.T., 1992. Manual for the geochemical analysis of marine sediments and suspended particulate matter. Earth Sci. Rev. 32, 235–283.

Luiz-Silva, W., Matos, R.H.R., Kristosch, G.C., 2002. Geoquímica e índice de geoacumulação de mercúrio em sedimentos de superfície do Estuário de Santos-Cubatão (SP). Quim. Nova 25, 753–756.

Luiz-Silva, W., Matos, R.H.R., Kristosch, G.C., Machado, W., 2006. Spatial and seasonal variability of trace-element concentrations in sediments from the Santos-Cubatão estuarine system, São Paulo, Brazil. Quim. Nova 29, 256–263.

Marins, R.V., Paula Filho, F.J., Maia, S.R.R., Lacerda, L.D., Marques, W.S., 2004. Total mercury distribution as a proxy of urban and industrial pollution along the brazilian coast. Quim. Nova 27, 763–770.

Matschulla, T.J., Ottenstein, R., Reimann, C., 2000. Geochemical background- can we calculate it? Environ. Geol. 39, 990–1000.

MMA, 2006. Ministério do Meio Ambiente do Brasil. Caderno da Região Hidrográfica do Parnaíba. Secretaria de Recursos Hídricos, Brasília, 184 p.

Muniz, P., Danulat, E., Yannicelli, B., García-Alonso, J., Medina, G., Bícego, M.C., 2004. Assessment of contamination by heavy metals and petroleum hydrocarbons in sediments of Montevideo Harbour (Uruguay). Environ. Int. 29, 1019–1028.

Nelson, D.W., Sommers, L.E., 1982. Total carbon, organic carbon, and organic matter. In: Page, A.L., Miller, R.M., Keeney, D.R. (Eds.), Methods of Soil Analysis: Part 2. Chemical and Microbiological Properties, second ed. Agronomy Series 9. American Society of Agronomy, Madison, WI, pp. 539–579.

Olivares-Rieumont, S., de La Rosa, D., Lima, L., Graham, D.W., Alessandro, K.D., Borroto, J., Martínez, F., Sánchez, J., 2005. Assessment of heavy metal levels in Almendares River sediments, Havana City Cuba. Water Res. 39, 3945–3953.

Passos, E.A., Alves, J.P.H., Garcia, C.A.B., Costa, A.C.S., 2011. Metal fractionation in sediments of the sergipe river, Northeast, Brazil. J. Braz. Chem. Soc. 22, 828–835.

Reimann, C., Filzmoser, P., Garrett, R.G., 2005. Background and threshold: critical comparison of methods of determination. Sci. Total Environ. 346, 1–16.

Rodríguez, J.G., Tueros, I., Borja, A., Belzunce, M.J., Franco, J., Solaun, O., Valencia, V., Zuazo, A., 2006. Maximum likelihood mixture estimation to determine metal background values in estuarine and coastal sediments within the European Water Framework Directive. Sci. Total Environ. 370, 278–293.

Sabadini-Santos, E., Knoppers, B.A., Oliveira, E.P., Leipe, T., Santelli, R.E., 2009. Regional geochemical baselines for sedimentary metals of the tropical São Francisco estuary, NE-Brazil. Mar. Pollut. Bull. 58, 601–634.

Salminen, R., Gregorauskiene, V., 2000. Consideration regarding the definition of a geochemical baseline of elements in the surface materials in areas differing in basic geology. Appl. Geochem. 15, 647–653.

Salomons, W., Forstner, U., 1984. Metals in the Hydrocycle. Springer-Verlag, Berlin, 396 p.

Schiff, K.C., Weisberg, S.B., 1999. Iron as a reference element for determining trace metal enrichment in southern California coastal shelf sediments. Mar. Environ. Res. 48, 161–176.

Swennen, R., Van der Sluys, J., Hindel, R., Brusselmans, A., 1998. Geochemistry of overbank and high-order stream sediments in Belgium and Luxembourg: a way to assess environmental pollution. J. Geochem. Explor. 62, 67–79.

Tennant, C.B., White, M.L., 1959. Study of the distribution of some geochemical data. Econ. Geol. 54, 1281–1290.

Tukey, J.W., 1977. Exploratory Data Analysis. Reading: Addison-Wesley.

USEPA, 1998. United States Environmental Protection Agency –. Method 3051a – Microwave assisted acid digestion of sediments, sludges, soils, and oils. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods; Office of Solid Waste, U.S. Environmental Protection Agency: Washington, DC, 1998.

Wang, J., Zhang, Y., 2012. Characteristics of Baseline and Analysis of Pollution on the Heavy Metals in Superficial Soil of Guiyang, Geochemistry – Earth's System Processes. Intech, Rijeka, pp. 429–456.