Journal of
Coastal Zone Management
ISSN: 2473-3350

Ferreira and Moreira, J Coast Zone Manag 2015, 18:3
http://dx.doi.org/10.4172/2473-3350.1000404

Research Article Open Access

Metals Pollution Status in Surface Sediments along the Sepetiba Bay Watershed, Brazil

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Abstract

Coastal areas provide important benefits to humans in terms of food resources and ecosystem services. At the same time, human activities can have significant negative impacts on the health of ecosystems. Thus, control of pollution of watersheds, as well as necessary, it is essential to reduce and systematically eliminate today impactful consequences that are evident in marine and estuarine ecosystems. The present study investigated the extent of metals distribution at Sepetiba bay watershed. Five sampling sites were selected for the analysis of surface sediments. Samples were collected from February 2013 to September 2014 and analysed for the concentrations of As, Cd, Zn, Cu, Pb, Cr, Ni, and Co, using ICP. For control, some samples were used in uncontaminated areas outside the direct effect from chemical industries. The data indicate that the sediments in the research sites are contaminated. However, the levels found, although near the limits are shown below the maximum permitted concentrations established by Brazilian reference. The result of this study can be used to intervene in the pollution Sepetiba bay watershed, guiding direct actions in the effluents discharged by industries as well as in environmental management.

Keywords: Metals; Sediment; Sepetiba bay watershed; Pollution

Introduction

The presence of metals from anthropogenic sources in the marine environments has become an important environmental and human health apprehension. Once are deposited in sediments, they suffer a series of physical, chemical and biological processes. Metals occur in a number of different forms, principally in the dissolved and in the solid state (adsorbed onto surfaces of clays, element oxides, organic material, co-precipitated with sediment phases and incorporated into organic matter) [1].

Metals are among the most common environmental contaminants and their behavior noteworthy stay for long periods in the environment, mainly sediments, and therefore represent potential threat to biodiversity and ecosystems. In addition, in aquatic ecosystems, these elements can undergo chemical transformations that make them even more harmful to environment. High concentrations of Cd, Hg, Pb, Zn, Cu, Ni and semimetals such as As, for example, may have harmful effects on own aquatic organisms or predators, since these are biomagnified in the food chain [2,3].

Sediments provide habitats for many aquatic organisms and also a major repository for many of the more persistent chemicals that are introduced into surface waters. In the aquatic environment, most anthropogenic chemicals and waste materials including toxic organic and inorganic chemicals eventually accumulate in sediments. In aquatic environments, many metals are transported predominantly in association with particulate matter, and consequently, a high concentration of metals is often detected in sediments in many industrialized harbours and coastal regions around the world [4-7].

The management of water resources is difficult [8,9]. The establishment of effluent load to be thrown into a water body shall consider two extremes. Firstly, the cost of effluent treatment facilities, which increases with the degree of treatment required, and secondly, the capacity of the receiving water body to absorb this surplus pollution, making the final treatment [10,11]. Wastewater from domestic and industrial effluents into rivers, the use of fertilizers and pesticides, soil degradation caused by deforestation, landfills and mining are the major drivers impacting on water resources in the country [12,13]. The environmental impacts arising from various pollution sources cited evidence the urgency of concrete actions to prevent, control, preservation and water quality restoration [14]. In this context, scientific researches guide the actions to mitigate impacts on water resources, increasing their effectiveness.

Metals are favourably transferred from the dissolved to the particulate phase and these results reflect in its elevation of concentration in marine sediments. Consequently, concentrations frequently surpass those in overlying water by several orders of magnitude [15]. Once sediments can store metals, concentrations can be great and become potentially toxic. Exposure and uptake of even a small fraction of sediment-bound metal by organisms could have significant toxicological meaning, particularly where circumstances favour bioavailability. In addition, increased metal concentrations in pore water may subsidise expressively to sediment toxicity [16].

Apart from direct inputs to rivers, atmospheric deposition of pollutants on basins and transport by runoff also contributes significantly to increasing metal concentrations in coastal seas [17]. This is particularly important for metals, whose cycles include a significant atmospheric component. Even relatively remote areas show abnormal concentrations of these two metals. Accelerated land-use changes in coastal basins also contribute to the remobilization of deposited pollutants on soils [18].

In Brazil, there is a lack of information about pollutant emissions

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Received April 09, 2015; **Accepted** May 20, 2015; **Published** June 02, 2015

Citation: Ferreira AP, Moreira MDFR (2015) Metals Pollution Status in Surface Sediments along the Sepetiba Bay Watershed, Brazil. J Coast Zone Manag 18: 404. doi: 10.4172/2473-3350.1000404

by industrial activities. Moreover, there is no national inventory of potentially polluting industries, with data on the amount of pollutants and their location. The monitoring systems at the emission source are poor and/or absent. These systems require specialized personnel and should be performed continuously making the costly procedure. In this context, where data are scarce and pollution emission monitoring is not performed, the methodologies for estimating emissions of pollutants are present as an extremely important tool. Through these methodologies is possible to define critical areas of pollution and rank the most polluting industrial typologies, where the government can focus its efforts on mitigation of pollutants.

In economic terms, there is the strategic location of Sepetiba Bay: a radius of 500 km has about 70% of gross national product - GDP [19]. The federal government also predicts new industrial complexes installation in the region. The Growth Acceleration Program (GAP), among its objectives, seeks to expand the Sepetiba port, connection to the main federal highways, investments in the Petrochemical programs, local housing and sanitation. Therefore, the goal of this paper was to study the possibility of soil contamination by metals in comparison to pristine soils (control areas) within the industrial zone related to Sepetiba bay watershed, Rio de Janeiro, Brazil.

Materials and Methods

Study site: Sepetiba bay watershed

Sepetiba Bay is located in the State of Rio de Janeiro, Brazil, (22º55' and 23º 05'S / 43º40' and 44º40'W) with an area of 450 km^2. This region present its northern and eastern area limited by the continent, a sandbank vegetation on southern limit, and Ilha Grande Bay on the west. Its greatest length is 42.5 kilometres from east to west and its greatest width is 17.2 kilometres from north to south, with a perimeter of 122 km.

The watershed contributing to Sepetiba bay has two main sources: the Serra do Mar mountain chain and an extensive area of lowland, crossed by many rivers, consisting of 22 sub-basins. The main rivers within the catchment area of the Sepetiba bay and its respective average flow are Gandu River, also known as channel of San Francisco (89 m^{3}s^{-1}), Guarda River (6.8 m^3 s^{-1}), Ita channel (3.3 m^3 s^{-1}), Piraquê River (2.5 m^3 s^{-1}), Portinho River (8.8 m^3 s^{-1}), Mazomba River (0.5 m^3 s^{-1}) and Cação River (1.1 m^3 s^{-1}). The other rivers are water bodies of smaller basins, with very low flows. Guandu River is the most important contributor of the basin and it is responsible for supplying water to several cities, being the main source of Rio de Janeiro city [20].

Sampling

Initially the data were collected from 261 industrial occupants of the site study and listed in Federation of Industries of Rio de Janeiro (FIRJAN); however, for this research, we selected only those representatives of the metallurgical sector (16), chemical (40) and plastic and rubber (19), totalling about 75 industries, concatenating those most polluting. The five sampling stations represent the sectors occupied by these industries in the area investigated. Its coordinates recorded with the aid of a GPS device are: P1 (22º36'03"S / 43º32'21"W), P2 (22º36'12"S / 43º49'24"W), P3 (22º38'22"S / 43º43'20"W), P4 (22º40'48"S / 43º33'11"W) and P5 (22º54'20"S / 43º43'23"W).

From February 2013 to September 2014, soil samples (5) were collected at each sampling stations Sepetiba bay watershed. For control, a few samples were used in presumedly uncontaminated areas outside the direct effect of the chemical industries. Duplicate soil samples (depth 0-20 cm) were collected along the sampling stations by using a polyethylene tube with 4 cm diameter and were stored in plastic bags. Most of the soil samples were collected from the upper surface of the soil with depth ranging from 5-10 cm. It has been demonstrated by [21] that more than 90% of applied toxic metals in soils are found at a depth of 15 cm from the surface. However, there are many authors who report maximum toxic metal concentration in the surface layer from up to 6 cm [22,23]. Generally content of toxic metals is significantly higher in top soils than in subsoils with a very few exceptions as they have little downward movement because of their strong affinities with soil solid phase [24,25]. The two pristine soil samples (C1 and C2) were collected from sites 5 to 30 km away from study site, which showed no evidence of human disturbance. In the laboratory, the samples were dried at 40-50ºC and were sieved through plastic-only sieves into <2 mm fraction. Before and after sieving, the samples were homogenized and quartered and then grinded in an agate mortar (Figure 1).

Soil parameters

The values of pH and organic matter content of the soil samples were also determined. Fifteen grams of sample were dissolved in 15 ml of deionized water, and after mixing for 24 h the measurement of pH was done with a pH-meter. Inorganic matter content was evaluated according to the Loss on Ignition (LOI) method. Samples were dried in order to eliminate water content. Subsequently, they were heated for 2 h at 600ºC and the weight loss was assessed.

Metals

Metals determined in this study were selected based on the degree of toxicity [26]. For each sampling location, composite samples were collected approximately 200 g of soil collected with the aid of stainless steel at a depth of 0.2 m. For laboratorial analyses, 0.5 g of dried samples of soil was treated with 5 ml of nitric acid (65% Suprapur, Merck, Darmstadt, Germany) in Teflon vessels for 8 h at room temperature. Subsequently, they were heated at 80ºC in a stove for 8 h. After cooling, solutions were filtered and made up to 25 ml with deionized water. The determination of the elements (As, Cd, Zn, Cu, Pb, Cr, Ni, and Co) was performed by the method of optical emission spectrometry in inductive plasma (Inductively Coupled Plasma-Optical Emission Spectrometry, ICP) with physical flame of argon. For definition of wavelengths in the ICP, we tested initially, all the possibilities offered by the device, both the axial view and in the radial plane. For each element, the design spectrum of a solution containing only the chemical species was determined in order to identify and adjust the emission peak of the element. A reading of the blank was made in a sample and the maximum point of the calibration curve in order to investigate possible spectral interferences and, if possible, minimize them, by making adjustments to the baselines, delimiting the peak area. After these adjustments, a reading of the calibration curve was made by selecting the wavelengths that showed the coefficient of determination of the linear model (R2) closer to 1 and with minimal spectral interference. Accuracy and reproducibility of the methods were tested using muscle (DORM-2, National Research Council, Canada) certified material. Standards and blanks were analysed along with each set of samples. Concentrations are expressed as μg g^{-1} dry weight.

Statistical analysis

Statistical analysis was undertaken using an Origin 7.5 software package (OriginLab Corporation). The average distribution of the pollutants throughout the soil was assessed using analysis of variance (ANOVA). In order to determine which organ was significantly

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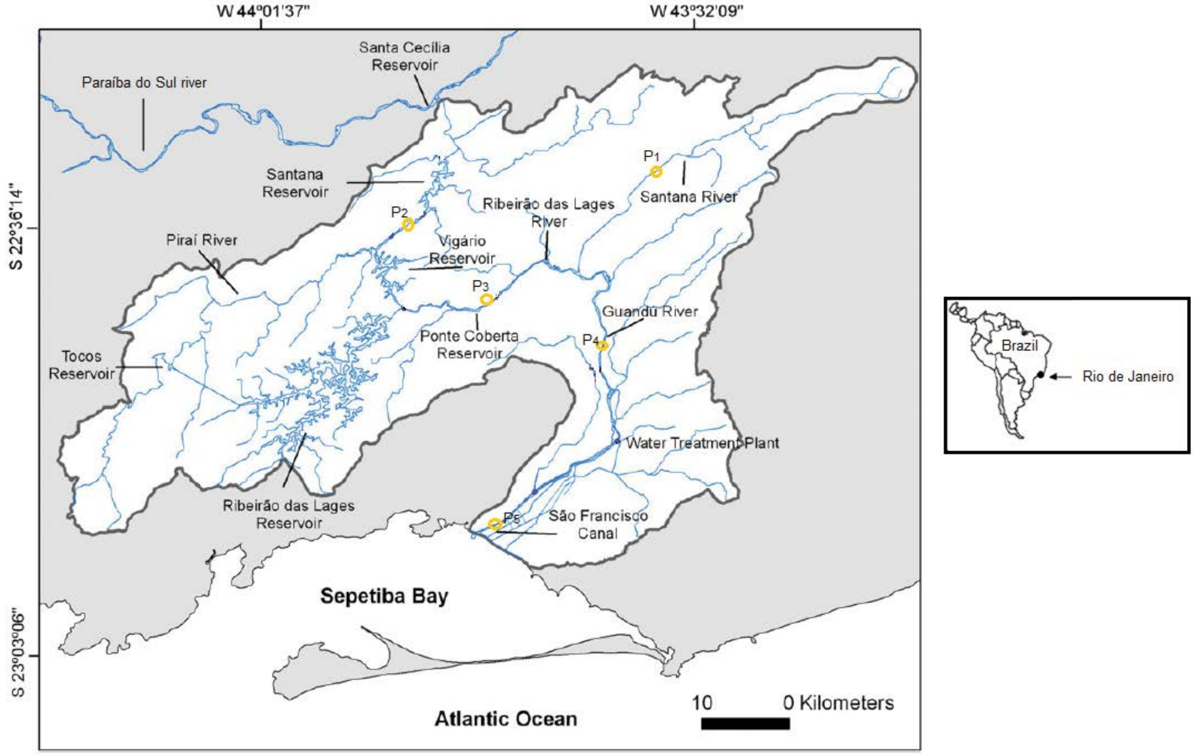

Figure 1: Study site: Sepetiba Bay Watershed. P indicates sampling stations, 2013-2014.

different from the other, a post-hoc comparison was carried out using Turkey's multiple comparison test. For all the tests, p-values of <0.05 were used to determine significant differences.

Results and Discussion

The transport and accumulation of organic matter, nutrients, metals and their biogeochemical cycles are strongly affected by land uses, including agriculture, industrial and urban uses. In relation the results of soil fertility, based in soil particle size analysis in the study area, was revealed a high proportion of sand with small percentages of silt and clay.

The metals may have their levels of occurrence in soils related to its source material and therefore are considered naturally occurring both by the standard Dutch as CETESB. There is a value of background to Brazilian soils, which complicates the interpretation of data obtained from sampling campaigns for research, because many factors can influence the occurrence of metals in soils, making it difficult to quantify the levels found in anthropogenic. These elements considered naturally occurring have their global averages referenced by Rose et al. [27], and Kabata-Pendias and Pendias [28], the target values of New Netherlands List and the Orientations Values for Soil and Groundwater of São Paulo state (CETESB), Brazil, which relate the values on which the soil is considered clean (Table 1).

The possibility of seasonal variation of pollutant levels demonstrated reinforces the need for soil monitoring in the area. The soil contamination can vary over time depending on the frequency of release of contaminants in the environment. Typically in industrial contaminants tend to have this behaviour because their addition to the medium vary with the product being manufactured, problems in operating procedures, climatic and economic factors.

Treatments used in many cases of contaminated soils, as in abandoned industrial areas, may include the removal of contaminated soil and its rearrangement in controlled landfills or opt for their treatment. In general, are not indicated in this case, that having different functional characteristics. Other alternatives need to be traced, such as in situ remediation, efficient monitoring system, re-evaluation of the containment system and operating procedures more safe and controlled.

Sediments play a major role in identifying the pollution pattern of aquatic systems. They act as both carriers and sink for contaminants and therefore reflect the history of pollution and provide a record of catchment inputs into aquatic ecosystems [29]. Table 2 shows the levels of metal distributions at Sepetiba bay watershed (2013-2014).

Exposure to chemicals is often connected with probabilities of causing negative health effects [14]. The character and harshness of these effects depend on the inherent properties of the substances and the exposure situation [30]. Most legislation regarding environmental conservation, management and the sustainable use of coastal natural resources fails to consider human activities in catchment basins; activities that are sometimes far from the coast. As well, many socio-economic driving forces acting on river catchments may be completely different from those acting on coastal areas. A general problem is a scaling mismatch between legal instruments and coastal issues as well as with drivers of change and legislation, rather than low quality environmental laws. As a result, despite a strengthening of environmental regulations for many coastal areas around the world, potential beneficial effects of these regulations on the quality of coastal environments are being overtaken by detrimental impacts generated

Parameters	Samples zone						
	P1	P2	P3	P4	P5	C1	C2
pH	5.2	4.7	4.9	5.0	5.1	5.3	5.4
Al (g.kg^{-1})	6.34	4.44	2.45	4.56	3.3	0.31	0.22
Ca (g.kg^{-1})	0.18	0.22	0.25	0.19	0.17	0.23	0.19
Mg (g.kg^{-1})	0.11	0.14	0.08	0.05	0.07	1.2	1.0
Na (g.kg^{-1})	0.02	0.04	0.02	0.02	0.03	0.03	0.04
N (g.kg^{-1})	6.33	5.67	3.45	4.41	2.99	9.38	9.77
K (g.kg^{-1})	1.22	1.18	1.43	1.26	1.461	2.15	2.67
P (g.kg^{-1})	0.09	0.03	0.06	0.15	0.18	0.16	0.21
Carbon (%)	0.12	0.23	0.45	0.32	0.66	0.37	0.68

Table 1: Mean data of granulometry and soil fertility analysis from Sepetiba bay Watershed and pristine control, 2013-2014.

Sampling stations	Elements (µg.g^{-1})							
	As	Cd	Zn	Cu	Pb	Cr	Ni	Co
P1	5.8	12.7	76.2	22.6	34.7	19.6	4.5	8.5
P2	4.9	23.6	62.7	11.4	16.3	45.4	9.3	13.4
P3	6.7	16.6	43.9	5.8	29.6	25.8	14.5	12.8
P4	7.1	34.7	47,8	33.6	34.3	22.5	22.4	17.3
P5	6.6	19.2	38,5	19.7	41.2	22.3	11.2	14.6
Control	As	Cd	Zn	Cu	Pb	Cr	Ni	Co
C1	1.5	3.3	12.8	4.9	11.2	11.4	2.3	4.5
C2	1.2	6.8	4.3	5.7	8.6	5.3	1.7	1.6

Table 2: Results obtained in laboratorial analyses performed for metal distribution at Sepetiba bay Watershed sediment, 2013-2014.

in catchment basins.

Conclusion

Both contamination and pollution involve the disturbance of the natural state of the environment by anthropogenic activity. The two terms are distinguishable by the severity of the effect: pollution induces the loss of potential resources. In the marine environment, human-induced disturbances take many forms. Owing to source strengths and pathways, the greatest effects tend to be in the coastal zone. Waters and sediments in such regions bear the main blow of industrial and sewage discharges and are subject to spoil dumping.

Indeed the magnitude of the industrialization in the area under evaluation, the current results suggest that chemical facilities located in the industrial complexes of Rio de Janeiro would mean a relevant source of pollution by metals. Moreover, the presence of these industries pose a notable risk for the health of the population living in the vicinity. Thereby, a surveillance program is clearly desirable, while some efforts should be focused on decreasing the environmental levels of polluter elements.

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