METAL CONCENTRATIONS MEASURED IN SURFACE SOIL SAMPLES COLLECTED ON SEPETIBA BAY WATERSHED, RIO DE JANEIRO, BRAZIL

ALDO PACHECO FERREIRA

FIOCRUZ/ENSP/CESTEH - Fundação Oswaldo Cruz, Escola Nacional de Saúde Pública Sérgio Arouca, Centro de Estudos da Saúde do Trabalhador e Ecologia Humana, Rua Leopoldo Bulhões, 1480, Manguinhos, 21041-210, Rio de Janeiro - RJ, Brasil. E-mail: aldopachecoferreira@gmail.com

Recebido em abril de 2014. Aceito em novembro de 2014. Publicado em dezembro de 2015.

ABSTRACT – Environmentalists all over the world are concerned about how to cope with the increased disposal of pollutants in rivers, lakes, and landfills surrounding cities. In response to this concern, a survey was conducted to determine metal concentrations in surface soil samples collected in the Sepetiba Bay watershed, Rio de Janeiro, Brazil. Soil samples were collected in representative points in the study area. For control, samples from presumably unpolluted zones outside the direct influence of the chemical industries were used. In Brazil, in 2001, the State of São Paulo through the Environmental Company (CETESB) pioneered the publication of guidance values for pollutants in soils and groundwater. Concentrations of arsenic, chromium, copper, nickel, lead, zinc, cobalt, and cadmium were determined in the samples. Soils samples showed detectable concentrations for all the chemicals analysed. However, even though deserving attention, the pollutant levels for these chemicals in the soil still present levels below the maximum allowed concentrations established by the 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.

KEY WORDS:* *Sepetiba bay Watershed; soil, chemical industries; environmental toxicology.

CONCENTRAÇÕES DE METAIS MEDIDOS EM AMOSTRAS DE SOLO DA BACIA HIDROGRÁFICA DA BAÍA DE SEPETIBA, RIO DE JANEIRO, BRASIL

RESUMO – Ambientalistas em todo o mundo estão preocupados sobre como lidar com o aumento da disposição de poluentes em rios, lagos e aterros vizinhos as cidades. Em resposta a esta preocupação, foi feito uma investigação para determinar a concentração de metais em amostras da superfície de solo da Bacia Hidrográfica da Baía de Sepetiba, Rio de Janeiro, Brasil. As amostras de solos foram coletadas em pontos representativos do local de estudo. Para o controle, algumas amostras foram utilizadas em zonas não poluídas presumivelmente fora da influência direta das indústrias químicas. No Brasil, em 2001, o Estado de São Paulo através da Companhia Ambiental (CETESB) foi pioneiro na publicação de valores de orientação para solos e águas subterrâneas. As concentrações de arsênio, cromo, cobre, níquel, chumbo, zinco, cobalto e cádmio, foram determinadas nessas amostras. As amostras de solo apresentaram concentrações detectáveis para todos os produtos químicos analisados. Ainda que mereçam atenção, no entanto, os níveis de poluentes para esses produtos químicos no solo ainda se apresentam em níveis abaixo das concentrações máximas permitidas estabelecidas por referência brasileira. Os resultados deste estudo podem ser usados para intervirem na poluição nesta bacia hidrográfica, orientando ações diretas na descarga de efluentes por indústrias, assim como o controle ambiental.

PALAVRAS CHAVE:* *Bacia Hidrográfica da Baía de Sepetiba; solo; indústrias químicas; toxicologia ambiental.

CONCENTRACIONES DE METALES MEDIDOS EN MUESTRAS DE SUELO DE SUPERFICIE RECOGIDOS EN LA CUENCA DE LA BAHÍA DE SEPETIBA, RÍO DE JANEIRO, BRASIL

RESUMEN – Los ecologistas de todo el mundo se preocupan sobre cómo hacer frente al aumento de la eliminación de contaminantes en ríos, lagos y rellenos sanitarios de ciudades cercanas. En respuesta a esta preocupación, se hizo una encuesta para determinar las concentraciones de metales en muestras de suelo de superficie recogidos en la cuenca de la Bahía de Sepetiba, Río de Janeiro, Brasil. Las muestras de suelo se recogieron en puntos representativos en el lugar de estudio. Para el control, se utilizaron muestras en zonas no contaminadas presumiblemente fuera de la influencia directa de las industrias químicas. En Brasil, en 2001, el Estado de São Paulo a través de la Compañía Ambiental (CETESB) fue pionera en la publicación de los valores limites para los suelos y las aguas subterráneas. Se determinaron las concentraciones de arsénico, cromo, cobre, níquel, plomo, zinc, cobalto y cadmio en las muestras. Muestras de suelos mostraron concentraciones detectables de todos los productos químicos analizados. A pesar de la atención que merece, los niveles de contaminantes de estos productos químicos en los niveles del suelo se encuentran por debajo de las concentraciones máximas permitidas establecidas por referencia brasileña. El resultado de este estudio se puede utilizar para intervenir en la contaminación de la cuenca de la bahía de Sepetiba, guiando las acciones directas en los efluentes vertidos por las industrias, así como en la gestión ambiental.

PALABRAS CLAVE:* *Cuenca de la Bahía de Sepetiba; suelo; química; toxicología ambiental.

INTRODUCTION

Pollution is considered here as the introduction into the aquatic environmental of manufactured substances, which are harmful to life and to human or animal health and the increase to toxic levels of naturally-occurring elements (i.e., metals). Continental inputs of trace metals, oil, oil derivatives and xenobiotics are rapidly increasing due to economic development of most countries of the continent. Diverse areas of the coastline, especially protected shores, are continually under pressure. These key ecosystems are exposed to contaminants transported by rivers and can convey contaminants through food chains to the human population (Li et al. 2013a).

The society has been growing concern about the management of water resources and their interaction with the environmental aspects of their watersheds (Temmerman et al. 2013). This phenomenon has brought benefits such as technical scientific, the best knowledge of the hydrological cycle in atmosphere, hydrosphere and lithosphere. Another benefit comes from awareness of lack for regional hydrological information, which leads groups to deepen research studies, developing techniques that may enable the sustainable use of water (Ferreira 2011).

Industrial development and population growth in recent decades, in particular, growth in sectors linked to the production of energy are related to a large number of actions that endanger the environment, within which the man inserts (Slatin 2011). The energy issue is the foundation for the development plans of the nations, however, governments, society, research institutions and companies themselves need to be responsible for generating a responsible and sustainable natural resources management (Cahen 2006).

The management of water resources is difficult. 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. 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 (Leal Neto et al. 2006). The environmental impacts arising from various pollution sources cited evidence the urgency of concrete actions to prevent, control, preservation and water quality restoration (Freitas et al. 2001). In this context, scientific researches guide the actions to mitigate impacts on water resources, increasing their effectiveness.

Changes in the coastal zone result from both local human activities and biophysical properties. Thus, on a global scale, regional coastal zones will show differences in their response to a similar human activity (Wang et al., 2013). The regional systems are subject to outside pressures and drivers including climate change and global socio-economic trends and alterations (Gray and Shadbegian 2004).

In order to develop a global assessment of the importance of changes in river catchments and impacts on coastal seas by applying a systems approach, using the Sepetiba bay watershed as a model, the Figure 1 denotes a framework at this study area, focusing on the horizontal flux of substances within the catchment coastal zone system. This systems approach, integrating the natural and social sciences, addresses issues such as critical concentrations and loads, resilience and carrying capacity.

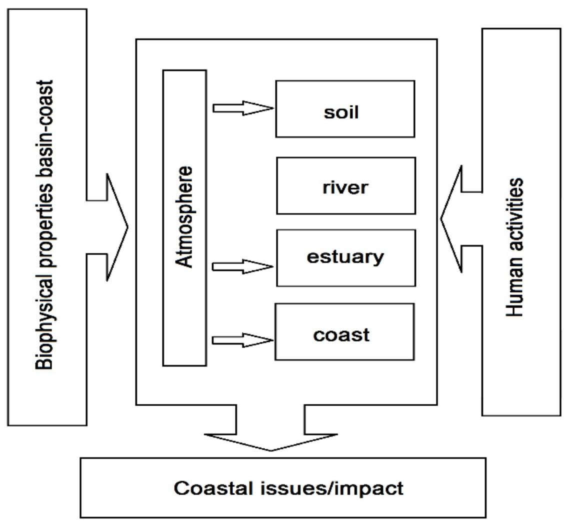

Figure 1. The framework impact on coastal zone system: environmental pressures.

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 (Li et al. 2013b). This is particularly important for metals, whose cycles include a significant atmospheric component. Even relatively remote areas shows abnormal concentrations. Accelerated land-use changes in coastal basins also contribute to the remobilization of deposited pollutants on soils (Landrot et al. 2012).

In Brazil, there is a lack of information about pollutant emissions 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 2001, the State of São Paulo through the Environmental Company (CETESB) pioneered the publication of guidance values for soils and groundwater in 2001, updating them in 2005 (CETESB 2005). The value of prevention was defined as the concentration in the soil of a substance above which there can be changes detrimental to soil quality. This value indicates the soil quality capable of supporting their primary function, protecting the ecological receptors. The intervention value is the concentration of a substance in the soil beyond which there are potential direct and indirect risks to human health, considered a generic exposure scenario. Toxic components and / or substance included in the list of Guiding Values for soil are presented in **Table 1**.

Table 1. Toxic elements and / or substance of Guiding Values for Soil (mg.kg^{-1})

Element	Quality reference value	Intervention	
		Residential	Industrial
As	3.5	55	150
Cd	<0.5	8	20
Zn	60	60	300
Cu	35	400	600
Pb	17	300	900
Cr	40	40	75
Ni	13	100	130
Co	13	65	90

Data source: Cetesb, 2005

In economic terms, there is the strategic location of Sepetiba Bay: a radius of 500 km has about 70% of Gross National Product - GNP (FIRJAN 2005). 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.

MATERIAL AND METHODS

Study site: Sepetiba bay watershed

Sepetiba Bay is located in the State of Rio de Janeiro, Brazil, (22°54'06" and 23°04'18" S and of 43°03'42" and 44°02'03" 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 ($89m^3.s^{-1}$), Guarda River ($6.8m^3.s^{-1}$), Ita channel ($3.3m^3.s^{-1}$), Piraquê River ($2.5m^3.s^{-1}$), Portinho River ($8.8m^3.s^{-1}$), Mazomba River ($0.5m^3.s^{-1}$) and Cação River ($1.1m^3.s^{-1}$). 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.

The Sepetiba Bay basin has an estimated population of 1,295,000 inhabitants, which generate an output of sewage of about 286,900 m^3/day. The majority of the municipalities included in this basin do not have services of solid waste collection and the release is made commonly in landfills, much of which are located on the banks of rivers close to urban areas, resulting in serious environmental degradation. The uncontrolled increase of population without a corresponding expansion of infrastructure and adequate sanitation generates a large volume of domestic and industrial waste and the use, though moderate, of pesticides in agricultural activities, are sources of pollution to waters in the basin. About 1.7 million inhabitants live in this region concentrated mainly in urban area (Cunha et al., 2006). The average annual rainfall in the study area is between 1000 and 1,500 mm, with most of the rain falling in the summer (between December and April) south of the Equator.

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).

Between February 2013 and September 2014, 05 soil samples were collected at each sampling stations preliminary identified at Hydrographic basin of Sepetiba bay. 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 (Chang et al. 1984). That more than 90% of applied toxic trace metals in soils are found at a depth of 15 cm from the surface. However, there are many authors who report maximum toxic trace metal concentration in the surface layer from up to 6 cm (Iwegbue et al. 2006; Haiyan and Stuanes 2003). Generally content of toxic trace metals is significantly higher in top soils than in subsoil with a very few exceptions as they have little downward movement because of their strong affinities with soil solid phase (Banuelos and Ajwa 1999; Sterckeman et al. 2000). 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 <2mm fraction. Before and after sieving, the samples were homogenized and quartered and then grinded in an agate mortar (Figure 2).

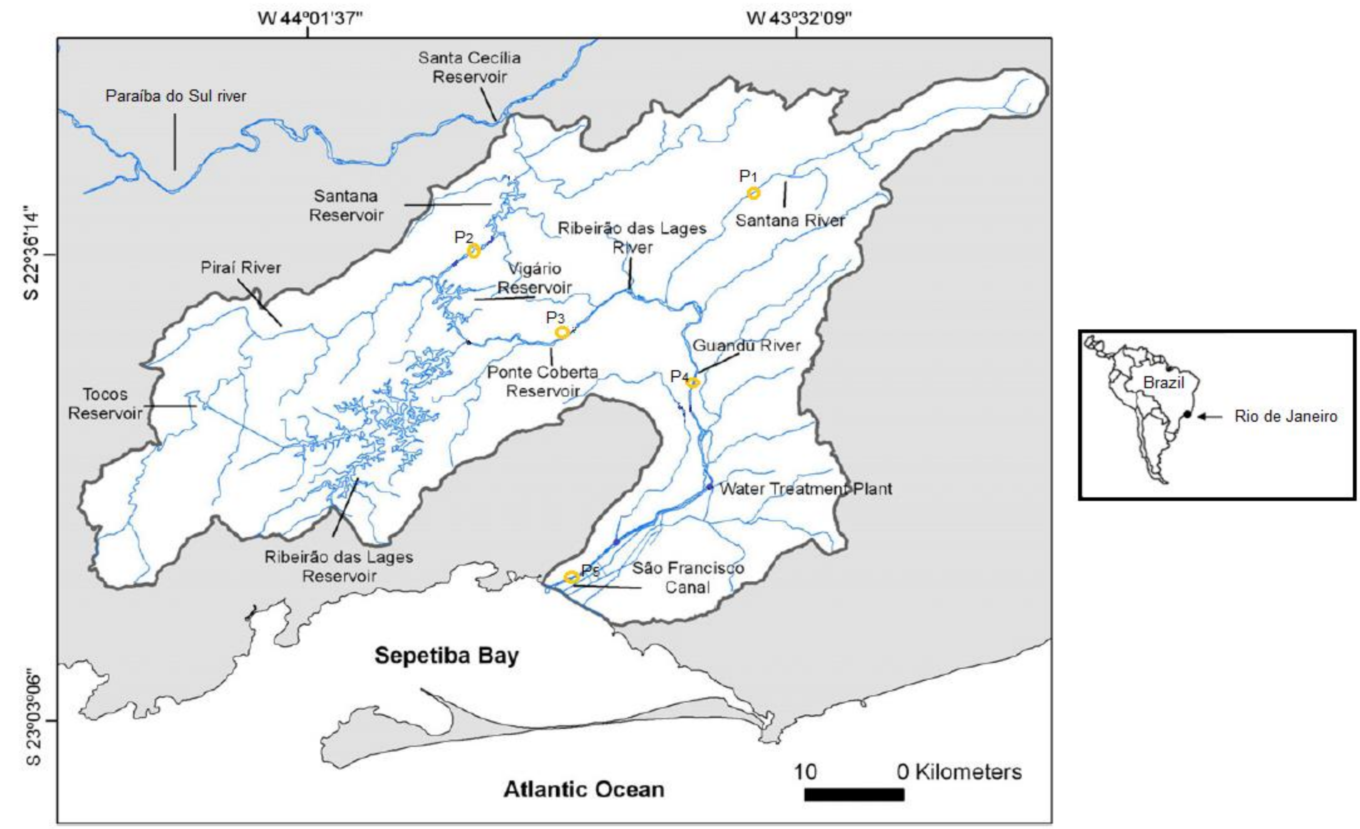

Figure 2. Study site: Sepetiba bay Watershed. P indicates sampling stations, 2013-2014.

Reagents and materials

All glassware was washed with extran (5% v/v), with HNO_3 solution 1:1 (v/v) and finally with deionized water. All solutions were prepared with "analytical grade" reagents (Merck or Sigma) and deionized water purified through the Milli-Q system (Millipore). The reference solutions to obtain the analytical curves for the determination of metals in sediment samples were prepared by serial dilution of stock solutions of 1000 mg L^{-1} (Qhemis) of As, Cd, Cr, Co, Pb, Cu, Ni and Zn in HNO_3 1.0 mol L^{-1}.

Metals determination

Metals determined in this study were selected based on the degree of toxicity (ATSDR 2007). 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 were treated with 5 ml of nitric acid (65% Suprapur, E. 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 (Souza et al., 2012). Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for the determination of arsenic, chromium, copper, nickel, lead, zinc, cobalt, and cadmium; with the advantage of determining multi-elements in larger amounts, and traces without any change in experimental parameters. 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 different from the other, a post-hoc comparison was carried out using Tukey`s multiple comparison test. For all the tests, p-values of <0.05 were used to determine significant differences.

RESULTS AND DISCUSSION

The pH values obtained ranged from 4.7 to 6.9. The transport and accumulation of organic matter, nutrients and trace 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 (Table 2).

Table 2. Mean data of granulometry and soil fertility analysis from study site and pristine control, 2013-2014

Parameters	Samples zone						
	P1	P2	P3	P4	P5	C1	C2
pH	5.2	4.7	6.9	5.0	6.1	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

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 behavior because their addition to the medium vary with the product being manufactured, problems in operating procedures, climatic and economic factors. The Table 3 express the results obtained in laboratorial analyses performed for metal distribution at Sepetiba bay Watershed sediment, 2013-2014.

Table 3. Reports the results obtained in laboratorial analyses performed for the soil levels of metals at Sepetiba bay Watershed sediment, 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

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.

The metals may have their levels of occurrence in soils related to its source material and therefore are considered naturally occurring ("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. (1979) and Kabata-Pendias et al. (1986), 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.

Exposure to chemicals is often connected with probabilities of causing negative health effects. The character and harshness of these effects depend on the inherent properties of the substances and the exposure situation (Hämäläinen et al. 2009). 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 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 poses 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.

REFERENCES

Agency for Toxic Substances and Disease Registry, 2007. CERCLA **Priority List of Hazardous Substances**.

Banuelos GS and Ajwa HA. 1999. Trace elements in soils and plants: An overview. **J. Environ. Sci. Health A.** 4:951-974.

Cahen B. 2006. Implementation of new legislative measures on industrial risks prevention and control in urban areas. **J Hazard Mater.** 130(3):293-9.

CETESB. 2005. **Decisão de Diretoria No. 195-2005-E, de 23 de novembro de 2005**. Dispõe sobre a aprovação dos Valores Orientadores para Solos e Águas Subterrâneas no Estado de São Paulo, em substituição aos Valores Orientadores de 2001.

Cunha CLN, Rosman PCC, Ferreira AP and Monteiro TCN. 2006. Hydrodynamics and water quality models applied to Sepetiba Bay. **Continental Shelf Research** 26:1940-1953.

Chang AC, Warneke JE, Page AL and Lund LJ. 1984. Accumulation of heavy metals in sewage sludge treated soils. **J. Environ. Qual.** 13:87-91.

Ferreira AP. 2011. Assessment of heavy metals in *Egretta thula*. Case study: Coroa Grande mangrove, Sepetiba Bay, Rio de Janeiro, Brazil. **Brazilian J. Biol.** 71:77-82.

FIRJAN. 2005. Federação das Indústrias do Estado do Rio de Janeiro. **Índice FIRJAN de Desenvolvimento Municipal – IFDM.** Rio de Janeiro.

Freitas MB, Brilhante OM and Almeida LM. 2001. Importância da análise de água para a saúde pública em duas regiões do Estado do Rio de Janeiro: Enfoque para coliformes fecais, nitrato e alumínio. **Cadernos de Saúde Pública** 17(3):651-660.

Gray WB and Shadbegian RJ. 2004. Optimal pollution abatement-whose benefits matter, and how much? J. Environ. **Economics and Management** 47(3), 510−534.

HAIYAN W AND STUANES AO. 2003. Heavy metal pollution in air-water-soil-plant system of Zhuzhou city, Hunan province, China. **Water, Air, Soil Pollut**. 147:79-107.

Hämäläinen P, Saarela KL and Takala J. 2009. Global trend according to estimated number of occupational accidents and fatal work-related diseases at region and country level. **J Safety Research** 40:125-139.

Iwegbue CMA, Isirimah NO, Igwe C and Williams ES. 2006. Characteristic levels of heavy metals in soil profiles of automobile mechanic waste dumps in Nigeria. **Environmentalist** 26:123-128.

Landrot G, Tappero R, Webb SM and Sparks DL. 2012. Arsenic and chromium speciation in an urban contaminated soil. **Chemosphere** 88(10):1196-201.

Leal Neto AC, Legey LF, González-Araya MC and Jablonski S. 2006. A system dynamics model for the environmental management of the Sepetiba Bay Watershed, Brazil. **Environ Manage.** 38(5):879-88.

LI J, LI F, LIU Q And ZHANG Y. 2013. Trace metal in surface water and groundwater and its transfer in a Yellow River alluvial fan: Evidence from isotopes and hydrochemistry. **Sci Total Environ**. 472C:979-988. (a)

Li H, Qian X and Wang Q. 2013. Heavy metals in atmospheric particulate matter: a comprehensive understanding is needed for monitoring and risk mitigation. **Environ Sci Technol.** 47(23):13210-1. (b)

Slatin C. 2011. Environmental and occupational health and human rights. **New Solut.** 21(2):177-95.

Souza PSA, Marques MRC, Soares MLG and Pérez DV. 2012. Trace Metals Concentrations in Mangrove Sediments of Sepetiba Bay (Rio de Janeiro, Brazil): Microwave Assisted Digestion with Nitric Acid and Aqua Regia. **Rev. Virtual Quim.** 4(4):464-473.

Sterckeman T, Douay F, Priox N and Fourrier H. 2000. Vertical distribution of Cd, Pb and Zn in soils near smelters in the North of France. **Environ. Pollut,** 107:377-389.

Temmerman S, Meire P, Bouma TJ, Herman PM, Ysebaert T and De Vriend HJ. 2013. Ecosystem-based coastal defence in the face of global change. **Nature** 504(7478):79-83.

Wang Y, Liu D, Richard P and Li X. 2013. A geochemical record of environmental changes in sediments from Sishili Bay, northern Yellow Sea, China: Anthropogenic influence on organic matter sources and composition over the last 100 years. **Mar Pollut Bull,** 77 (1-2):227-36.