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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 ecosystem health. Thus, control of watershed pollution is both necessary and essential in order to reduce and systematically eliminate the detrimental consequences that are evident in marine and estuarine ecosystems. The present study investigated the distribution of metals at the Guandu Watershed. Five sampling sites were selected for the soil analysis. Samples were collected from February 2013 to December 2014 and analysed for 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 of chemical industries. The data indicate the presence of metals at the research sites. While the levels of contamination are still slightly below the peak concentrations established by Brazilian legislation, they are approaching levels of concern, particularly with regard to As, Cd, Pb and Cr. The results indicate that the use of water from the Guandu Watershed for recreational purposes and fishing is harmful to both human health and the environment.

Keywords: environmental assessment, pollution, trace elements.

Distribuição e contaminação de metais no solo da bacia hidrográfica do Rio Guandu

RESUMO

As zonas costeiras proporcionam benefícios importantes para os seres humanos em termos de recursos alimentares e serviços ecossistêmicos. Ao mesmo tempo, as atividades humanas podem ter impactos negativos significativos sobre a saúde dos ecossistemas. Assim, o controle da poluição das bacias hidrográficas, além de necessária, é fundamental para reduzir e sistematicamente eliminar as atuais consequências impactantes que são evidentes nos ecossistemas marinhos e estuarinos. O presente estudo investigou a distribuição de metais na bacia hidrográfica do Rio Guandu. Cinco pontos de amostragem foram selecionados para as análises de solo. As amostras foram coletadas a partir de fevereiro a novembro de 2014, e analisadas para as concentrações de As, Cd, Zn, Cu, Pb, Cr, Ni e Co, utilizando ICP. Para o controle, algumas amostras foram utilizadas em áreas não-contaminadas, fora do efeito direto das indústrias químicas. Os dados indicam a presença dos metais pesquisados no solo dos

locais de pesquisa estão contaminados; ainda que levemente abaixo das concentrações máximas estabelecidas por referência brasileira, mas atingindo concentrações preocupantes, destacando As, Cd, Pb e Cr. No que diz respeito aos resultados, sinaliza que o uso da água da bacia hidrográfica do Guandu para fins recreativos e pesca é prejudicial para a saúde humana e ambiente.

Palavras-chave: avaliação ambiental, análise de solo, elementos-traço, poluição.

1. INTRODUCTION

The entry of contaminants into the environment due to human and natural activities is one of the most important issues facing today's communities. Due to industrial and economic growth and the production of a variety of compounds and chemicals well as increased consumption, man creates various unwanted pollutants, many of which cause serious problems and risks for the environment and for man himself (Shanbehzadeh et al., 2014).

Metals are among the most common environmental contaminants, and persist for long periods in the environment, mainly in soil. They therefore represent a potential threat to biodiversity and ecosystems. In addition, in aquatic ecosystems, these elements can undergo chemical transformations that make them even more harmful to the environment. High concentrations of Cd, Hg, Pb, Zn, Cu, Ni and semimetals such as As, for example, may have harmful effects on aquatic organisms or predators, since these are biomagnified in the food chain (Ferreira and Horta, 2010; Miranda Filho et al., 2011).

The ingress of municipal, industrial, and agricultural waste is another source of human environmental pollution. Water, including surface water such as rivers, is among the most critical of resources, and its importance in meeting the needs of humans, animals and industries indicates the essential need to protect it from contamination. As municipal, industrial, and agricultural wastes enter water, biological and chemical contaminants including metals enter as well. Although some of these metals are essential as micronutrients, their high concentration in the food chain can cause toxicity and environmental impacts and endanger aquatic ecosystems and their users (Sherman et al., 2015).

Contaminated sediments do not always remain at the bottom of a water body. Anything that stirs up the water, such as dredging, can re-suspend sediments (Binning and Baird, 2001). Re-suspension may mean that all of the animals in the water, and not just the bottom dwelling organisms, will be directly exposed to toxic contaminants (Temmerman et al., 2013). Different aquatic organisms often respond to external contamination in different ways, and the quantity and form of the element in the water, sediment, or food will determine the degree of accumulation (Casado-Martínez et al., 2006). Many dangerous chemical elements, if released into the environment, accumulate in soil and water bodies. Under certain conditions, chemical elements accumulated in the silt and bottom sediments of water bodies can migrate back into the water. Silt can become a secondary source of metal pollution (Frignani and Bellucci, 2004; Li et al., 2013a). Sediments are likewise a significant repository for metal pollutants that enter the sea. Sediments provide habitats for many aquatic organisms and are also a major repository for many of the more persistent chemicals that are introduced into surface waters. 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 (US-EPA, 1999; Bertolotto et al., 2005; Wang et al., 2007; Ferreira, 2011).

Industrial development and population growth in recent decades, and in particular growth in sectors linked to the production of energy, are related to a large number of human actions that endanger the environment (Slatin, 2011). Energy is often the foundational issue upon which the developmental plans of nations rest; however, governments, society, research institutions and companies themselves must be responsible for generating responsible and sustainable management of natural resources (Cahen, 2006).

Management of water resources is difficult. Two extremes must be considered in determining the effluent load that may be sustainably adsorbed by a water body. First, the cost of the effluent treatment facilities, which increases with the degree of treatment required; and second, the capacity of the receiving water body to absorb this surplus pollution. Domestic and industrial wastewater effluents into rivers, the use of fertilizers and pesticides, soil degradation caused by deforestation, landfills and mining are the major drivers impacting on the country's water resources (Leal Neto et al., 2006). The environmental impacts arising from various pollution sources make clear that there is urgency for concrete actions to prevent, control, preserve and restore water quality (Freitas et al., 2001). In this context, scientific research guides actions to mitigate impacts on water resources, thereby increasing their effectiveness (Ferreira, 2010).

Metals are favourably transferred from the dissolved to the particulate phase and this is reflected in their concentration in marine soil. Consequently, concentrations of metals frequently exceed those in overlying water by several orders of magnitude (Wang et al., 2013). When soil stores metals, concentrations can become elevated and potentially toxic. Exposure and uptake of even a small fraction of soil-bound metal by organisms could have a significant toxicological effect, particularly where circumstances favour bioavailability. In addition, increased metal concentrations in pore water may further enhance soil toxicity (Gray and Shadbegian, 2004).

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

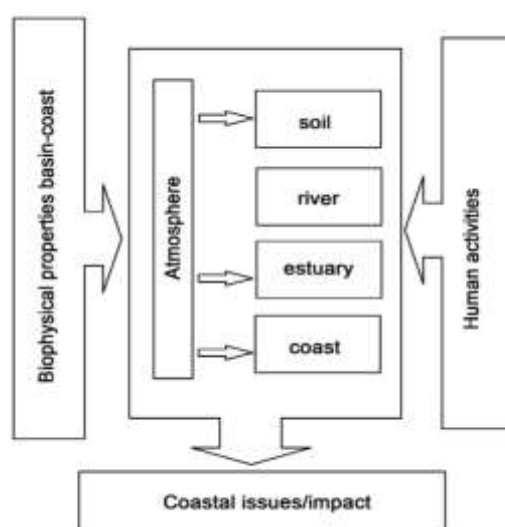


Figure 1. Framework of impact on coastal zone system: environmental pressures. Source: Meybeck et al. (2006).

Apart from direct inputs into 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 show abnormal concentrations. Accelerated land-use changes in coastal basins also contribute to the remobilization of deposited pollutants on soil (Landrot et al., 2012).

There is a lack of information in Brazil regarding pollutant emissions by industrial activities (Costa et al., 2011). Moreover, there is no national inventory of potentially polluting industries, with data on the amount of pollutants and their location. Monitoring systems at emission sources are poor and / or absent. These systems require specialized personnel and should be performed continuously during the procedure. In this context, where data are scarce and pollution emission monitoring is not performed, methodologies which estimate pollutant emissions are extremely important tools. These methodologies make it possible to define critical areas of pollution and rank the most polluting industrial typologies where the government can focus its efforts on pollution mitigation.

Brazilian soil guidance values are established by CONAMA (2009), which includes guiding quality values for the presence of chemical substances and establishing guidelines for environmental management of areas contaminated by these substances as a result of human activities. These values indicate 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, considering a generic exposure scenario. Toxic components and / or substances included in the list of Guiding Values for soil are presented in Table 1.

Table 1. Toxic elements and / or substances of Guiding Values for Soil (mg.kg⁻¹ dry weight).

Element	Quality reference value	Intervention	
		Residential	Industrial
As	3.5	55	150
Cd	<0.5	8	20
Zn	60	1000	2000
Cu	35	400	600
Pb	17	300	900
Cr	40	40	75
Ni	13	100	130
Co	13	65	90

Source: CONAMA (2009).

In economic terms, Sepetiba Bay is strategically located. It has a radius of 500 km and generates about 70% of gross national product - GDP (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 and its connections to main federal highways, as well as investments in petrochemical programs, local housing and sanitation. Therefore, the goal of this study was to compare soil contaminated by metals to pristine soil (control areas) within the industrial zone of the Guandu Watershed, Rio de Janeiro, Brazil.

2. MATERIALS AND METHODS

2.1. Study site: Guandu watershed

The Guandu watershed is located in the State of Rio de Janeiro, Brazil, (coordinates UTM 7420000/6400000 extreme NW and 7483500/6880000 extreme SE), with a 1921 km² drainage area. Its contributions to Sepetiba Bay have 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 Sepetiba Bay and its respective average flow are the Guandu River, also known as the Channel of San Francisco (89 m³ s⁻¹); the Guarda River (6.8 m³ s⁻¹); Ita channel (3.3 m³ s⁻¹); the Piraquê River (2.5 m³ s⁻¹); the Portinho River (8.8 m³ s⁻¹); the Mazomba River (0.5 m³ s⁻¹) and the Cação River (1.1 m³ s⁻¹). The other rivers are water bodies of smaller basins, with very low flows. The 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 water for Rio de Janeiro city (Cunha et al., 2006).

The water that supplies the Rio de Janeiro metropolitan region and some Baixada Fluminense municipalities comes from Guandu Watershed, and its treatment is done by the State Company for Water and Sewage (CEDAE), responsible for a flow rate of approximately 40 m³/s. In Rio de Janeiro, it has great importance for the population, as the only source of water supply for over 12 million people, including 80% of metropolitan area inhabitants (Castro and Ferreirinha, 2012).

2.2. Reagents and materials

All glassware was washed with extran (5% v/v), with HNO₃ solution 1:1 (v/v) and finally with deionised water. All solutions were prepared with "analytical grade" reagents (Merck or Sigma) and deionised water purified through the Milli-Q system (Millipore). The reference solutions to obtain the analytical curves for the determination of metals in soil 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 HNO₃ 1.0 mol L⁻¹.

2.3. Sampling

There are 261 industrial occupants of the study area according to data obtained from the Federation of Industries of Rio de Janeiro (FIRJAN). However, for this study only enrolled representatives of metallurgical (16), chemical (40) and rubber and plastic (19) sectors were included, encompassing a total of 75 industries, including the sources of most pollutants. The five sampling stations represent the sectors occupied by these industries in the area investigated (Figure 2). Their coordinates were recorded with the aid of a GPS device: P1 (22°36'03''S / 43°32'21''W), P2 (22°36'12''S / 43°49'24''W), P3 (22°38'22''S / 43°43'20''W), P4 (22°40'48''S / 43°33'11''W) and P5 (22°54'20''S / 43°43'23''W).

From February 2013 to December 2014, five (5) soil samples were collected at each of the sampling stations in the Guandu watershed. For control, a few samples were used in presumably uncontaminated areas outside of 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 a 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 metals in soil 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 (Haiyan and Stuanes, 2003; Iwegbue et al., 2006). Generally content of toxic metals is significantly higher in top soil 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 the study site, which showed no evidence of human disturbance. In the laboratory, the samples were dried at 40-50°C 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.

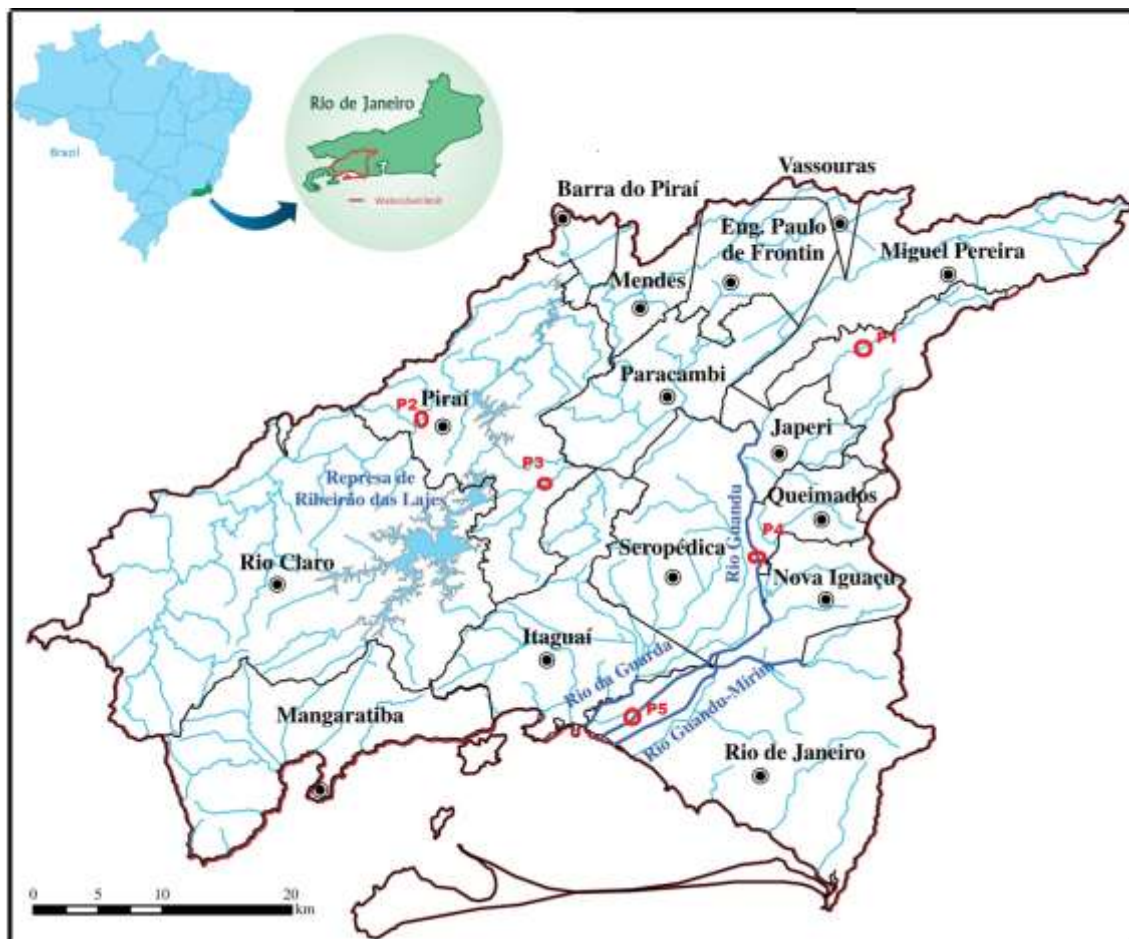


Figure 2. Study site: Guandu Watershed. P indicates sampling stations, 2013-2014.

Source: Comitê Guandu (2012).

2.4. Soil parameters

The values of pH and organic matter content in the soil samples were also determined. Fifteen grams of sample soil were dissolved in 15 ml of deionised water, and after mixing for 24h 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 600°C and weight loss was assessed.

2.5. Metals

Metals assessed in this study were selected based upon the degree of toxicity (ATSDR, 2007). For each sampling location, composite samples were collected approximately from 200 g of soil collected with stainless steel implements from 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, the samples were heated at 80°C in a stove for 8 h. After cooling, solutions were filtered and

filled up to 25 ml with deionised water. The determination of elements (As, Cd, Zn, Cu, Pb, Cr, Ni, and Co) was performed by the optical emission spectrometry method in inductive plasma (Inductively Coupled Plasma-Optical Emission Spectrometry, ICP) with a physical argon flame. In order to define wavelengths in the ICP, we initially tested all of the possibilities offered by the device, both in 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 (R^2) 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 (mg.kg⁻¹ dry weight).

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

3. 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. An analysis of soil fertility, based upon soil particulate size in the area studied, revealed a high proportion of sand with small percentages of silt and clay (Table 2).

Table 2. Mean data of soil fertility analysis from Guandu Watershed 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. Soil contamination can vary over time depending on the frequency of the release of contaminants in the environment. Industrial contaminants typically

tend to behave this way because their addition to the medium varies with the product manufactured, problems in operating procedures, climatic and economic factors.

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. Due to source strengths and pathways, the greatest effects tend to be in the coastal zone. Waters and soil in such regions bear the main blow of industrial and sewage discharges and are subject to spoil dumping. Table 3 shows that the concentrations found in all samples greatly exceeded the natural levels.

Table 3. Results obtained in laboratorial soil analyses performed for metal distribution at Guandu Watershed, 2013-2014.

Sampling stations	Elements (mg.kg ⁻¹ dry weight)							
	As	Cd	Zn	Cu	Pb	Cr	Ni	Co
P1	35.8	9.7	376.2	122.6	234.9	119.6	14.5	28.5
P2	74.9	13.6	862.7	251.4	416.3	245.4	39.3	53.4
P3	66.7	16.6	643.9	235.8	329.6	225.8	34.5	32.8
P4	47.1	6.9	247.8	233.6	238.3	122.5	22.4	17.3
P5	126.6	19.2	738.5	519.7	641.2	362.3	111.2	64.6
C1	3.5	0.5	12.8	14.9	31.2	11.4	2.3	4.5
C2	11.2	0.8	4.3	25.7	18.6	5.3	4.7	6.9

The levels of occurrence of metals in soil related to the soil's source material and therefore are considered naturally occurring both by the standard Dutch as CETESB (2005). There is a background value of Brazilian soil (CONAMA, 2009) which complicates the interpretation of data obtained from sampling campaigns for research, because many factors can influence the occurrence of metals in soil, making it difficult to quantify the levels found in anthropogenic areas.

Metal concentrations in soil are strongly determined by influences, which was the main source of contamination at the studied site. Industrial effluent is likely to be the major source of metal concentrations because of anthropogenic actions (Hämäläinen et al., 2009; Araújo, 2010). The data obtained from this research were higher than the results found by Araújo (2010) in the analysis of metals in soils of the Apodi-Mossoró/RN river basin in urban Mossoró-RN. Similarly, the levels obtained were higher than the values reported by Su and Yang (2008) for Asian soil in relation to Cr (55.8 mg. kg⁻¹), Zn (33.7 mg. kg⁻¹), Cu (5.1 mg. kg⁻¹), Ni (17. mg. kg⁻¹), Pb (15. mg. kg⁻¹), (5.2 mg. kg⁻¹) and Co (5.7 mg. kg⁻¹).

The metal levels in industrial areas (P2, P3, P5) were higher than those close to urban areas (P1, P4) and identified the critical points of contamination. The results indicate the potential paths of metals through the soil transport of industrial areas for the Guandu Watershed.

Most legislation regarding environmental conservation, management and the sustainable use of coastal natural resources fails to consider human activities in catchment basins. These activities are sometimes far from the coast. Also, 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.

4. CONCLUSION

The results demonstrated that metal concentrations are below the maximum limits established for soil by CONAMA. Indeed, given the magnitude of industrialization in the area evaluated, the current results suggest that chemical facilities located in the industrial complexes of Rio de Janeiro are 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. A monitoring program is therefore clearly desirable, while some efforts should be focused on decreasing environmental levels of polluting elements.

5. ACKNOWLEDGEMENT

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