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The contribution of heavy metal pollution derived from highway runoff to Guanabara Bay sediments – Rio de Janeiro/Brazil

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ABSTRACT

In this study, geochemical and particle size analyses of thirty-four street sediment samples collected from an urban environment around Guanabara Bay, shows highway run-off to be a potential source of heavy metals for the pollution of near-shore sedimentary deposits. Concentrations of Fe, Mn, Zn, Cu, Pb, Cr and Ni were found to be higher in these sediments when compared to concentrations found in samples from the natural environment, where an Enrichment Factor (EF) index was used to distinguish between natural and anthropogenic sources. Particle size analysis shows these sediments to be predominantly composed of sand and no distribution pattern was observed between the sand, silt and clay fractions. High levels of organic matter and heavy metals would indicate that these street run-off materials are a potential source of pollution for the near-shore sediments of Guanabara Bay.

Key words: heavy metals, urban runoff, Guanabara Bay.

INTRODUCTION

Established research has shown that sediments and dusts transported and stored in the urban environment have the potential to provide considerable loadings of heavy metals to receiving waters and water bodies, particularly with changing environmental conditions. Street sediments that accumulate along pavements in urban environments originate mainly from atmospheric deposition and human activities such as quarrying, cultivation and construction. These deposits have become an important medium for the study of anthropogenic pollutants and their possible sources (Ferguson and Kim 1991, Watts and Smith 1994, De Miquel et al. 1997, Naqerotte and Day 1998, Baptista Neto et al. 1999, McAllister et al.

2000, 2005). Natural elements such as Fe, Mn and Al originate mainly from local soil that undergo a process of resuspension or mobilization and finally become incorporated in the street sediments. These soils contain clay and associated minerals along with pollen, algae and fungi. Association of natural elements in these street sediments is coherent with the red-podzolic soil type typical of this area (McAllister et al. 1998). Other possible sources of particulate matter that may be incorporated into street sediments come from fossil fuel combustion, industrial processes, abrasion of vehicular components and their exhaust emissions, incinerators, power plants and foundry operations. Urban street sediments have limited residence times and therefore provide a record of recent accumulations. Heavy metal concentrations vary between the various size fractions within these sedi-

ments and limited research in this field makes direct comparisons difficult (Sutherland and Tolosa 2000, Pagotto et al. 2001, Sutherland 2003). Along with sewage, urban street runoff has been identified as one of the main sources of heavy metals to coastal and estuarine systems (e.g. Odun and Drifmeyer 1978, Ellis 1979, Pope 1980, Lacerda et al. 1987, Smith and Orford 1989, Watts and Smith 1994, Chon et al. 1995, Baptista Neto et al. 1999, McAllister et al. 2000, 2005).

Guanabara Bay, Rio de Janeiro, Southeast Brazil (Fig. 1), is considered to be one of the most polluted environments on the Brazilian coastline, where the main direct sources originate from domestic and industrial effluents (Rebello et al. 1986, Vandenberg and Rebello 1986, Leal and Wagener 1993, Baptista Neto et al. 2000). However, there is a lack of information concerning indirect sources of pollution such as the urban street sediments and to study this premise geochemical and particle size analyses was carried out on sediments collected from highways located in the littoral of Guanabara Bay.

BACKGROUND TO THE STUDY AREA

Guanabara Bay is one of the largest on the Brazilian coastline, located in Rio de Janeiro State (Fig. 1). The bay has an area of approximately 384 km² including its several islands and presents a coastline of 131 km long and a mean water volume of 1.87×10^9 m³ (Kjerfve et al. 1997, Amador 1980). It lies within the tropics of southeastern Brazil and due to its coastal location, a humid sub-tropical climate prevails between December and April with 2,500 mm (high altitudes) and 1,500 mm (low land) of rainfall with a mean annual temperature of 20-25°C (Nimer 1989). The drainage basin of Guanabara Bay has an area of 4080 km² and this consists of 32 separate sub-watersheds with 91 rivers and channels (Kjerfve et al. 1997). However, only six rivers are responsible for 85% of the total mean fresh water input, in the order of 100 m³ s⁻¹ (JICA 1994).

Approximately 11 million inhabitants live in the greater Rio de Janeiro metropolitan area and as a result of rapid urbanization and population growth; untreated sewage is discharged directly into the bay. This area is the second largest industrial region in Brazil and has over 12,000 industries operating along the Guanabara Bay drainage basin and these account for 25% of the

organic pollution released to the Bay (FEEMA 1990). Two oil refineries process 7% of the national oil and approximately 2,000 commercial ships dock in the port of Rio de Janeiro every year, making it the second largest harbor in Brazil. The bay is also the homeport to two naval bases, a shipyard, and a large number of ferries, fishing boats and yachts (Kjerfve et al. 1997).

Over the past 100 years catchments areas around Guanabara Bay have been greatly modified by deforestation and uncontrolled settlement. These activities have increased river flow velocities and transport of sediment load has increased by 1 to 2 cm year⁻¹ (Godoy et al. 1998).

MATERIALS AND METHODS

SAMPLE COLLECTION AND ANALYSES

Thirty-four samples were collected from the main highways that experience intense traffic conditions around Guanabara Bay using a clean plastic dustpan and brush from a 1 m² area which was measured using a quadrat (Charlesworth and Lees 1999) (Fig. 1). The samples were collected during the rainy season, three days after the rain, stored in sealed polythene bags and transported to the laboratory for analysis. They were then air dried at 30-35°C and separated into two sub-samples using a riffle box and one portion was used for chemical and the other for physical analyses. Samples for chemical analyses were oven dried at 105°C overnight and the < 63 µm fractions separated by passing them through a nylon mesh sieve (by dry sieving). Sub-samples (0.2 g) were digested in 5 ml of an aqua regia solution under pressure in PTFE digestion bombs, aqua regia is a partial digestion procedure used to determine potentially toxic metals in sediments and that those bound to silicate minerals are considered unimportant when studying metal mobility. Aqua regia digestion provides satisfactory recovery for most base metals as demonstrated by Kackstaetter and Heinrichs (1997). Elemental analyses (Pb, Zn, Ni, Cr, Cu, Mn and Fe) were carried out using a Perkin Elmer Analyst 200 atomic absorption spectrometer, the detection limits (ppm) for the metals are: Fe = 0.05, Mn = 0.03, Zn = 0.02, Cu = 0.03, Cr = 0.10, Pb = 0.15 and Ni = 0.05. In order to calculate the enrichment factors (EFs) for all the elements was used the formulae $EF = (metal/Fe)_{sample} / (Metal/Fe)_{std. Shale}$ (Salomons and

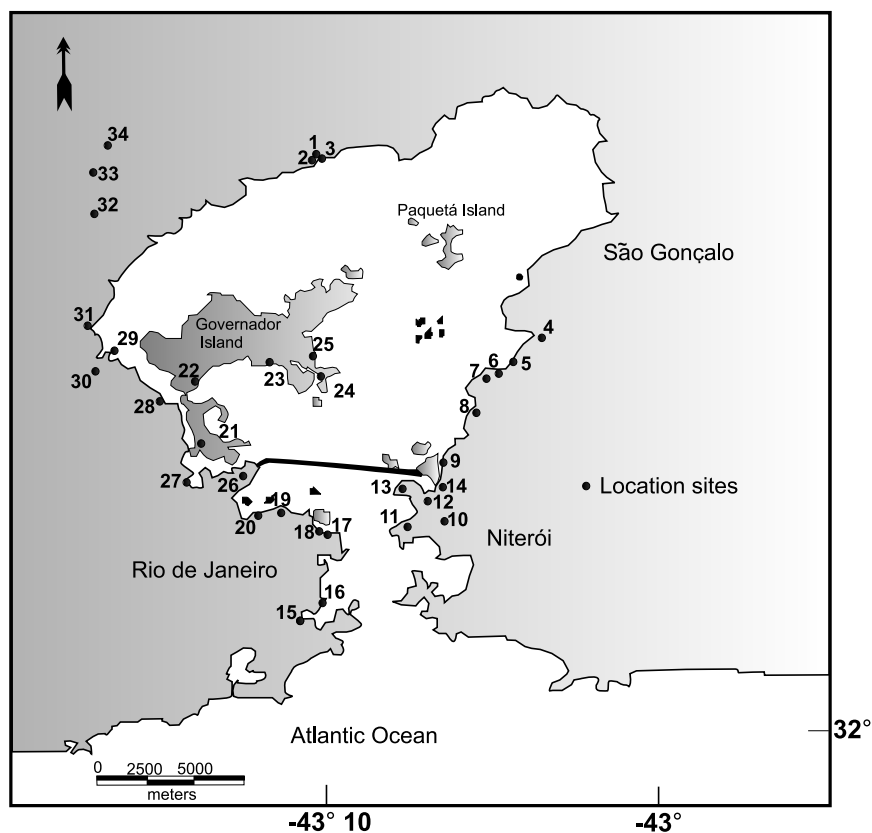


Fig. 1 – Location map of study area.

Forstner 1984, Turekian and Wedepohl 1961). Grain size analysis was carried out using a standard sieve technique (for 2 mm-63 μm) Wentworth scale and pipette ($< 63 \mu\text{m}$) after removal of organic matter by digesting in 30% H_2O_2 . Oxidizable organic carbon was determined using the Walkley and Black (1934) technique.

RESULTS AND DISCUSSION

PARTICLE SIZE

Results presented in Figure 2 shows the amount of coarse sand, fine sand, silt and clay in the samples. It must be emphasized that the particle size distribution for urban street sediments does not obey the laws of the hydrodynamics like materials found in natural environments such as beaches and rivers. For example, in urban environments particulate matter can be deposited in different ways and these include moving parts of vehicles, loads

spilling from trucks, accidents, erosion of gardens and atmospheric deposition.

Results show the different particle size pattern, with sand being the predominant fraction (0.17, 0.5 and 2.00 mm). Similar research on heavy metals and particle size distribution was carried out on urban runoff sediments from an area close to London (Ellis and Revitt 1982) where a particle size range between 0.5 to 2.00 mm was recorded. This size range was also recorded in other research (Shaheen 1975, Sartor and Boyd 1972, Cordery 1976), and they concluded that this was due to intense traffic conditions. Similar research carried out on urban runoff sediments from Niterói City found the predominant size fractions to range from 0.125 to 1.00 mm (Baptista Neto et al. 1999). Samples collected in Niterói, for this study (Samples 10-14) indicate a predominance of size fractions between 0.88 to 0.25 mm, except for station 13 where the 2.00 mm fraction was highest.

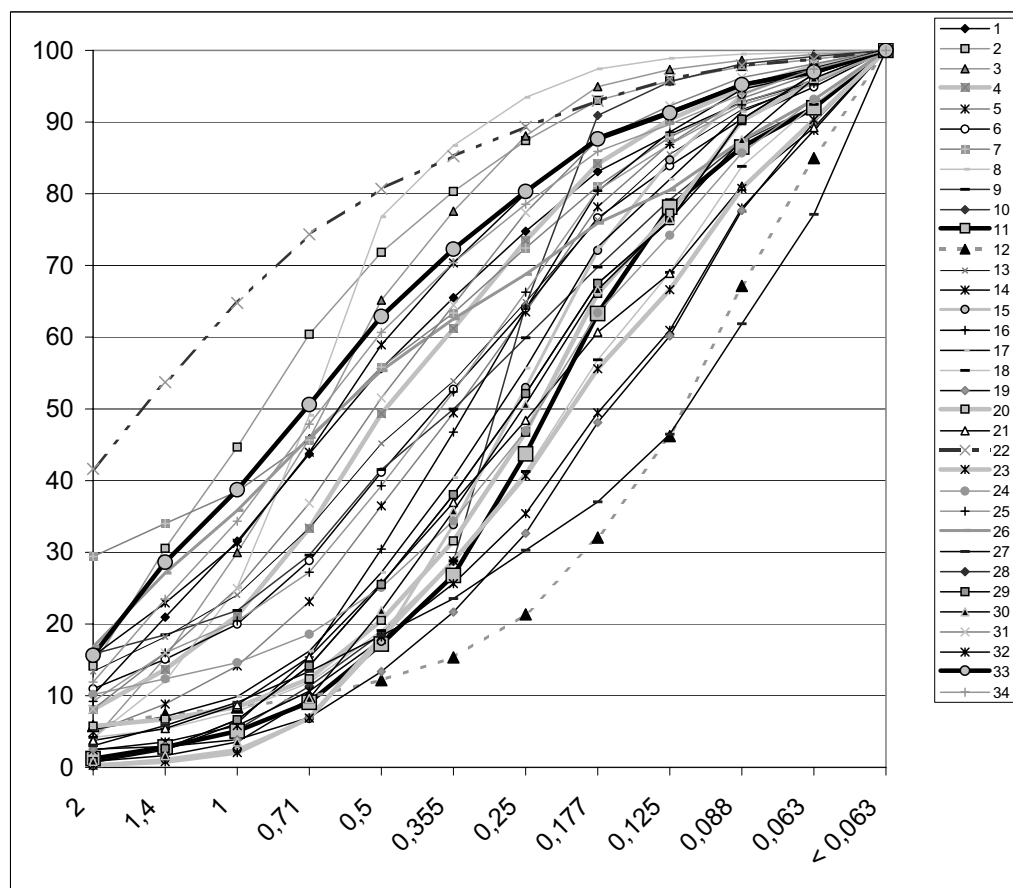


Fig. 2 – Particle size of the urban street sediments around Guanabara Bay.

Particle size analysis of urban runoff sediments in this study and in the study carried out by Baptista Neto et al. (1999) showed finer size fractions when compared to the other studies mentioned and this may be due to the different weathering processes that take place in temperate and tropical regions.

In urbanized areas, mechanical methods of highway cleaning collect larger size fractions and this results in the finer fractions being concentrated along highway surfaces (Ellis and Revitt 1982, Gromaire et al. 2000). Silt and clay fractions (mud) in the sediments tend to be low with an average of 5.3%, with the lower value of 0.29% being found at station 8 (Niterói-Manilha highway). These values have also been reported in other studies (Ellis and Revitt 1982, Roberts et al. 1988, Baptista Neto et al. 1999).

Organic matter concentrations (Fig. 3) show a similar pattern to the particle size, with a number of samples having an average value of 6.5%. However, a minimum value of 0.6% was found at station 3 and a maximum value of 18.22% was found at station 33.

GEOCHEMISTRY

Trace elements are bound to street sediments by various mechanisms. Exchange reactions hold ions electrostatically using surface charges and attachment is sufficiently weak to enable them to be replaced by other ions. Secondary oxides of iron and manganese present as coatings on fine surface particles scavenge trace elements by mechanisms such as, co-precipitation, adsorption, surface complex formation, ion exchange and penetration of the lattice (Jenne 1968, Ellis 1979, 1985).

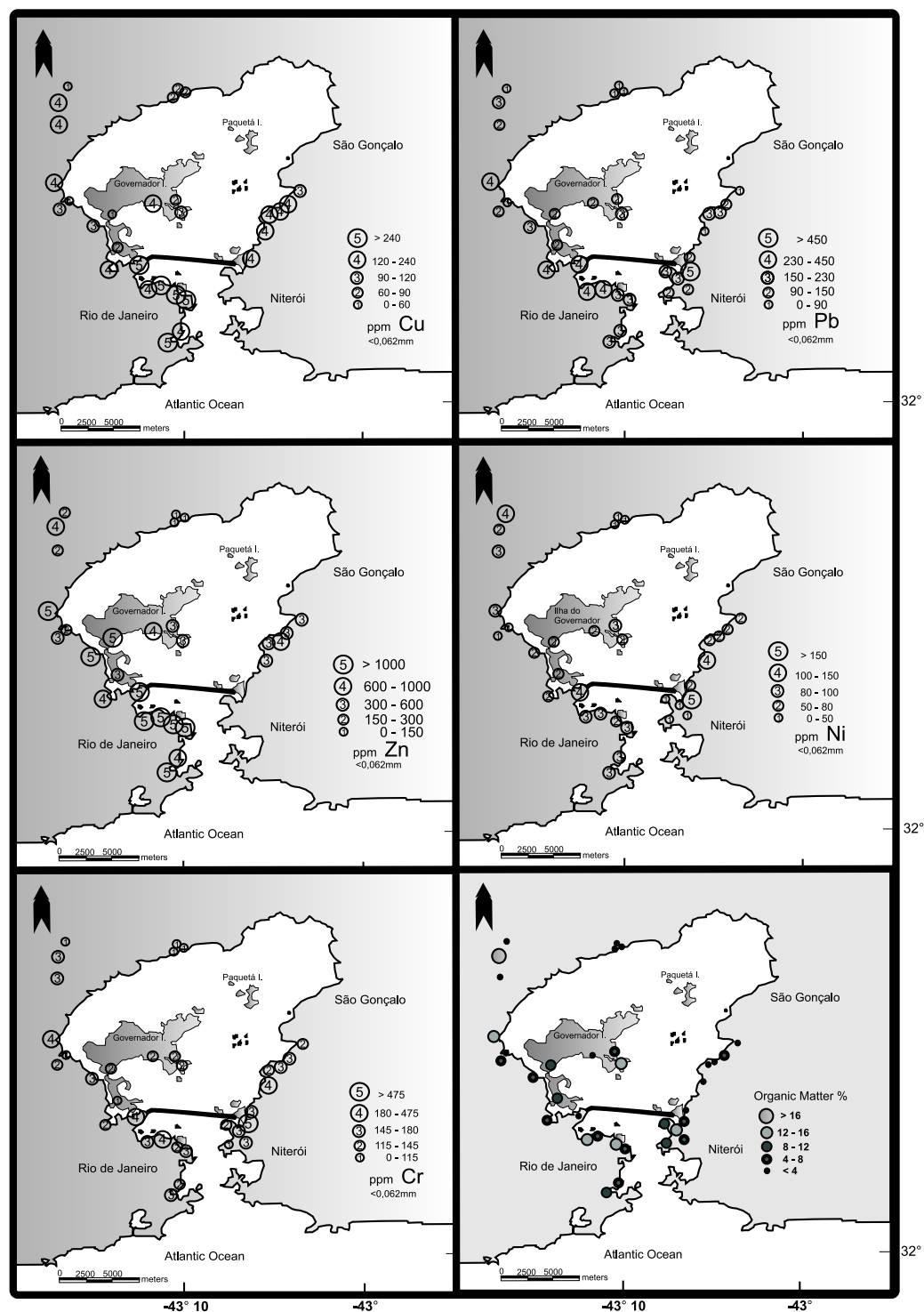


Fig. 3 – Distribution of Zn, Cu, Ni, Pb and Cr concentration in the urban street sediments around Guanabara Bay.

Mineral dissolution, precipitation and complex reactions are controlled by hydrogen ion activity (pH) and redox potential (Eh). Metal cations are more soluble under acidic conditions (Richards et al. 2000). Mobility can also increase at high pH values when organo-metallic complexes are formed, since organic matter becomes more soluble as pH increases (McBride 1998).

Research has indicated that the metals in street sediments are predominantly associated with the fine particulate phase (Ellis 1988, Weeks 1981, Wilkinson 1956, Cordery 1976). This is a crucial point, considering the environmental mobility of the sediments and the bio-availability of the metals, which depends of their concentration in solution plus pH and Eh conditions.

Elements are divided into two groups (a) those that occur naturally (e.g. Fe and Mn), in modest abundances in most environments, and (b) those that occur in nature but are also products of anthropogenic activities (Zn, Cu, Ni, Pb and Cr) (Bricker 1993). Concentration enrichment of elements such as Zn, Cr, Cu, Pb and Ni in street sediments is generally an indication of urban and industrial pollution and their presence in these samples provides evidence to demonstrate the importance of urban street sediments as a medium for transport of pollution to the coastal environment, and for metal accumulation in the urban environment.

Distribution patterns showing the concentrations of Zn, Cu, Ni, Pb and Cr in the urban street sediments around Guanabara Bay is presented in Figure 3 and these show higher concentrations when compared to the average levels found in shale and sandstone materials (Turekian and Wedepohl 1961) (Table I), and also compared with other environments, impacted or not by anthropogenic activities (Table I). Highest concentrations of these elements are found in the areas that experience intense traffic conditions and especially in Rio de Janeiro and Niterói city centers. In general, the highest concentrations for all the metals were recorded at stations 14 (closed to one of the main shipyard in Niterói), 19 (one of the oldest site in Rio de Janeiro downtown) and 26 (Rio de Janeiro Harbor). Automobiles are very important sources of heavy metal contamination in urban environments (Ellis 1988, Baptista Neto et al. 1999), with lead being one of the most significant pollutants. Metals are mobilized in an urban environment as a result of

human activities, however, vehicular traffic accounts for a significant proportion of the pollution load. Metals are released from vehicles in numerous ways, for example, nickel is present in several moving parts and it is also added to gasoline, copper is a component of brake cable devices and zinc is present in lubricants, tiers and galvanized components. Sewers are another important source of metals to street sediment runoff, especially in these study areas where sewage overflow is very common, especially during the rainy season.

The degree of correlation between trace metals and other major constituents such as organic matter and size distribution is often used to study the origin of many metals (Windom et al. 1989). To verify this relationship correlations between all the metals and the parameters mentioned were carried out for (a) all the stations and (b) after dividing them into their various regions. Correlation coefficients for the metals, sand, silt and clay plus organic matter were low for all the stations (Table II).

These results were unexpected, since heavy metals have a high affinity for organic and silt and clay fractions (Bodur and Ergin 1994, Zonta et al. 1994). However, this low correlation can be indicative of distinctive sources for these metals in these urban areas. Despite this low correlation between the samples, Cr shows a high correlation with Fe and Ni. According to Feely et al. (1983) trace element enrichments have been linked to scavenging reactions involving hydrous oxides. Several studies carried out in aquatic or "natural" environments had linked the enrichment of heavy metals to scavenging by hydrous Mn and Fe oxides.

In an attempt to evaluate the influence of the source areas for the various metals, sample stations were divided into 6 areas, all with a similar type of land-use, but however, correlation coefficients were still very low. The most significant correlations were found between Fe/Mn, Fe/Zn, Fe/Cu, Fe/Pb, Fe/Cr, Mn/Zn, Mn/Pb, Mn/Cr, Zn/Cu, Zn/Pb, Zn/Cr, Cu/Pb, Cu/Cr and Pb/Cr (Table III), at stations 26-34.

According to Wong et al. (2006) one would expect that the ability of the urban terrestrial environment to fixate or immobilize metal pollutants is therefore severely limited in comparison with that of the natural environment. Furthermore, the urban environment is predominantly occupied by infrastructure, pavements, and build-

TABLE I
Heavy metal concentration (ppm) in the study area (average) (minimum value \pm maximum value) (average SD), compared with values from the literature.

Location	Pb (ppm)	Zn (ppm)	Cu (ppm)	Cr (ppm)	Ni (ppm)
This study	180.3	657.8	225.1	169.3	84.6
	(55-450)	(125-1750)	(55-900)	(72.5-222.5)	(47.5-137)
	91.6	428	233	70,5	24.3
Guanabara Bay ¹	100.5 (18.2-556)	237.5 (8.6-940)	60.8 (0-242)	64.8 (0.2-322)	
Sediments from Guapimirim mangrove ²	26	26.7	28.3		12.0
Sediments from Duque de Caxias mangrove ²	86.7	53.3	46.7		10.3
Sediments from the NE region of the Guanabara Bay ³	69	290	119		1
Jurujuba Sound, Niterói ⁴	61 (5-123)	158 (15-337)	51 (5-213)	89 (10-223)	48 (15-79)
São João de Meriti River and estuary Guanabara Bay ⁵	132 (11.6-212)	560 (169-1059)			
Average shale ⁶	20	95	45	90	68
Average sandstone ⁶	7	16	10	35	2

¹Perin et al. (1997); ²Machado et al. (2002); ³Faria and Sanchez (2001); ⁴Baptista Neto et al. (1999);

⁵Barrocas et al. (1995); ⁶Turekian and Wedepohl (1961).

ings, and covered with artificial materials such as asphalt, concrete, metals, tiles, glass panels, and wood (with or without paint). Surfaces composed of these materials exhibit remarkably different metal sorption properties as compared to natural environment e.g. soil and plants. Even though artificial materials with a porous surface may display the capacity to retain metals, where their micro-structure can potentially serve as reservoir for metal pollutants, these materials may be inferior to soil in terms of their metal adsorption capacity and could even become a source of pollutants (Van der Sloot et al. 1996, Tossavainen and Forssberg 1999, Andersson et al. 2004). As a result, metal-enriched particulates and dust deposited in the urban environment often remain relatively mobile and tend to disperse, due to the urban environment often remain relatively mobile and tend to

disperse, due to the lack of means of physical entrapment and adhesion to substrates (Charlesworth and Lees 1999).

Several authors suggested that the dispersion and deposition of metal-enriched particulates and dust in the urban environment are governed by physical and micro-environmental factors, including topography, wind direction, and urban runoff (Cordery 1976, Charlesworth and Lees 1999, Andersson et al. 2004, Wong et al. 2006).

Urban runoff travels down gradients in accordance with the urban landscape, specifically topography and slope gradients. The fine sediments are swept and flushed along its path, whereby the runoff eventually becomes highly enriched with heavy metals. Since urban runoff is usually discharged with little or no treatment, this process can greatly affect the quality of the surrounding wa-

TABLE II
Pearson correlation coefficient matrix for heavy metals in the urban street sediments
(< 63 mm) from the road around Guanabara Bay.

	Fe	Mn	Zn	Cu	Pb	Ni	Cr	O.M.	Silt + clay
Fe	1	0.323	0.249	0.471	0.306	0.365	0.948	0.421	0.468
Mn		1	0.498	0.274	0.337	0.216	0.331	0.092	0.434
Zn			1	0.4	0.586	0.171	0.357	0.259	0.043
Cu				1	0.355	0.193	0.529	0.002	0.064
Pb					1	0.509	0.636	0.168	0.135
Ni						1	0.718	0	0.017
Cr							1	0.009	0.046
O.M.								1	0.044
Silt + clay								1	

ter bodies and biota (Check 1997, Mason et al. 1999, Turer et al. 2001, Duzgoren-Aydin et al. 2004).

ENRICHMENT FACTORS (EF)

According to Selvaraj et al. (2004) differentiation between metals originating from human activity and those from natural weathering is essential in this type of geochemical study. One such technique commonly applied is "normalization" of a textural or compositional characteristic, where for example conservative elements such as Al (Huang and Lin 2003), Li (Soto-Jiménez and Páez-Ozuna 2001), Cs (Ackeman 1980), Sc (Grousset et al. 1995) and Fe (Baptista Neto et al. 1999) have been used to indicate metal enrichment factors (EF). Iron has been used in several studies (Rule 1986, Ergin et al. 1991, Baptista Neto et al. 1999) and since it is a better proxy for the fine fraction and for its covariance with sewage signals in sediments (Bothner et al. 1998), this element and standard shale reference material are used in this study to calculate the enrichment factors (EFs). Enrichment factors of approximately 1.0 indicate that the element originated predominantly from lithogenous material, whereas EFs greater than 1.0 indicate an anthropogenic origin (Szefer et al. 1995).

Enrichment factors for elements analyzed show the majority to have values greater than 1, highlighting their anthropogenic origin (Table III). Stations 1-3 situated in an area with lower urbanization and less traffic also show high enrichment factors for all the elements, especially Zn and Pb.

Highest EF values were found at stations 15-20 (Table III), all located in Rio de Janeiro City. It was impossible to normalize the samples from Niterói, but a previous study carried out by Baptista Neto et al. (1999) in this area, indicated the importance of an anthropogenic contribution to the street sediments.

CONCLUSION

This study shows the concentration of heavy metals in urban streets sediments in highways around Guanabara Bay to be very high and is therefore an important source of pollution to the receiving rivers and to Bay. Levels of heavy metals found, in practically all the stations are very high, especially when compared to other environments that experience anthropogenic activities.

Relationship between the levels of heavy metals, type of occupation and land-use, verified that the most polluted sites are located in the center of Rio de Janeiro and Niterói. These results were expected; since these areas experience intense traffic conditions and sewage overflows cause heavy metal pollution of the sediments.

Results would indicate that these types of sediments are potentially one of the main sources of heavy metal pollution since they are discarded directly into Guanabara Bay during precipitation, by pluvial water galleries and by the fluvial systems.

As well as heavy metals, which is the subject of this study, these sediments have larger concentrations of others pollutants such as hydrocarbons and pathogenic organisms and further research should be carried out, not

TABLE III
Enrichment factors for selected metals in the
urban street sediments (< 63 mm) from the road
around Guanabara Bay. Values normalized by iron
and using mean shale as reference (Turekian
and Wedepohl 1961).

Sample	Zn/Fe	Cu/Fe	Pb/Fe	Ni/Fe	Cr/Fe
1	2.45	8.17	5.22	1.20	3.39
2	5.26	5.16	8.33	2.19	5.61
3	3.81	5.14	7.95	2.13	6.4
4	12.14	4.65	5.83	1.26	5.49
5	9.38	4.64	5.84	0.99	5.53
6	11.96	4.23	10.44	1.31	5.44
7	10.26	4.27	9.46	1.51	4.68
8	9.0	2.85	4.52	1.66	5.82
9	6.85	4.39	6.03	1.10	5.10
15	19.72	8.76	15.11	1.79	6.29
16	15.03	9.28	16.19	1.74	5.07
17	15.46	10.15	12.08	1.87	6.34
18	24.56	18.52	12.00	1.47	5.52
19	16.20	21.99	17.86	1.62	5.97
20	16.98	4.94	25.03	1.35	5.72
21	8.85	2.14	8.87	1.42	4.09
22	17.30	2.19	8.22	1.55	4.88
23	15.00	4.37	8.67	1.64	5.17
24	7.07	4.00	14.67	1.25	5.65
25	8.01	2.28	10.09	1.80	4.82
26	6.33	8.98	7.05	0.76	5.10
27	12.28	4.54	15.23	1.33	5.37
28	14.53	4.31	12.0	1.35	5.63
29	4.05	2.09	5.13	1.19	4.52
30	8.79	4.19	8.50	0.86	5.12
31	11.52	3.77	10.52	1.45	5.46
32	5.42	2.81	6.55	1.13	4.94
33	11.22	3.52	10.66	1.04	5.31
34	4.06	1.87	5.44	2.99	4.41

only characterize these sediments, but also to quantify the amount of pollutant which is introduced to the bay, and compare this source in relation to others such as domestic sewers and the industrial pollution.

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RESUMO

Neste estudo, análises geoquímica e de granulometria de trinta e quatro amostras de sedimentos coletados ao longo de rodovias em um ambiente urbano ao redor da Baía de Guanabara, mostram que o escoamento superficial das rodovias pode ser fonte potencial de metais pesados para a poluição de depósitos sedimentares costeiros. Concentrações de Fe, Mn, Zn, Cu, Pb, Cr e Ni são bem altas quando comparadas com os valores encontrados em ambientes naturais, onde o Fator de Enriquecimento (FE), que é índice de normalização, foi utilizado para a distinção entre fontes naturais e antropogênicas de metais pesados. As análises granulométricas mostram que estes sedimentos são compostos predominantemente de areia e nenhum padrão de distribuição foi observado entre as frações areia, silte e argila. Os altos níveis de matéria orgânica e metais pesados indicam que estes materiais depositados sobre as rodovias são fontes potenciais de poluição para os sedimentos costeiros da Baía de Guanabara.

Palavras-chave: metais pesados, escoamento urbano, Baía de Guanabara.

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