

## Geochemical distribution and bioavailability of heavy metals and oxalate in street sediments from Rio de Janeiro, Brazil: a preliminary investigation

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### Abstract

As urbanisation accelerates within less-economically developed countries, populations in cities such as Rio de Janeiro are subject to numerous health risks relating to “heavy metal”, sewage and vehicle pollution. These risks apply especially to children, through inhalation and dermal contact with pollutant-rich street sediments that reflect contamination from atmospheric deposition and act as effective sinks for heavy metals and oxalates. To assess the nature and extent of these risks street sediments were collected from industrial, commercial, residential and recreational areas with varying traffic densities within Rio de Janeiro. A modified selective extraction procedure was used to study the geochemical partitioning and bioavailability of Fe, Mn, Zn, Cu, Cr, Ni, Pb and  $C_2O_4^-$ . Oxalate partitioning has not been studied by traditional sequential methods and results from this procedure highlight the potential bioavailability of both oxalates and “heavy metals”, especially Pb and  $C_2O_4^-$  in industrial and recreational areas.

### Introduction

Street sediments that accumulate along the edges of paved streets in urban areas reflect local geological and environmental conditions. They can originate from sources such as atmospheric deposition, quarrying, cultivation and construction activities (Neto *et al.* 1999), and are known to be effective sinks for “heavy metals” (Forstner & Wittmann 1983; Watts & Smith 1994; Abrahams 2002; Charlesworth *et al.* 2003; Sezgin *et al.* 2003).

Soil erosion can create airborne clay-sized particles and if these contain adsorbed  $H_2SO_4$  or  $HNO_3$  acids, serious lung damage may result (Abrahams 2002). Epidemiological studies in the USA have suggested that a greater number of deaths occur from inhalation of fine clay, also referred to as “fugitive dust”, than from highway

accidents (Brady & Weil 1999). In addition to heavy metals, research carried out in Niteroi, Brazil, has also shown street sediments to be very effective sinks for organic matter and high concentrations of a toxic by-product, calcium oxalate dihydrate (Weddellite). Oxalate was found to concentrate mainly in the fine fractions and is a result of sewage overflow mixing with street sediments to produce a highly organic matrix that contains “heavy metals” and acts as a sink for this anion (McAlister *et al.* 2000).

Small amounts of essential “heavy metals” necessary for human health are common in our environment and diet. However, there is a narrow boundary between toxicity and sufficiency that can be crossed as metals bio-accumulate in organisms over time. Ingestion is a common route for metal adsorption and could be expected to be significant

in cities such as Rio de Janeiro where large numbers of children inhabit the streets without, for example, access to washing facilities and hand-to-mouth activity is common. In addition to "heavy metal" contamination, urbanisation, high population densities and fewer controls over fuel composition, vehicle emissions and sewage management in developing cities are likely to raise levels of organic pollutants such as calcium oxalate above those found in the developed world. Exposure to even low levels of oxalate can cause kidney and nervous system damage. Eye contact may cause corneal and retinal damage (Hodgson *et al.* 1998). To study elemental and oxalate concentrations related to environmental conditions, street sediments were collected in Rio de Janeiro from an industrial area with intense traffic conditions, three recreational beach areas, a commercial/residential site, an established commercial area that experiences heavy traffic conditions and a commercial city centre area with very intense traffic conditions. Selected elements and oxalate concentrations were analysed using a modified selective extraction procedure to identify the particular phase(s) with which they were associated. This is indicative of both their geochemical distribution and mobility within the samples. Extracts from water-soluble, exchangeable/carbonate, amorphous Mn, amorphous Fe/Mn, crystalline Fe/Mn, and from organic and residual (lithogenic) phases, were analysed for Fe, Mn, Zn, Cu, Pb, Cr and Ni.

This research goes further than traditional selective extraction procedures (e.g. Tessier *et al.* 1979; Ure *et al.* 1993; Quevauviller *et al.* 1994) by measuring oxalate concentrations bound to the water-soluble, exchangeable/carbonate, amorphous Mn, amorphous Fe/Mn, crystalline Fe/Mn and organic phases. Metals and oxalate extracted from each phase are expressed as percentages of their total concentrations. This shows an overall extraction pattern and makes comparisons between the different elements and samples more efficient.

### Background to the study area

The metropolitan area of Rio de Janeiro extends over 6500 km<sup>2</sup> and has a population of approximately 10.8 million (Demographia 2001). Rapid industrialisation and metropolitan growth have contributed to urban pollution and environmental

conditions have deteriorated due to the lack of integrated land-use policies and urban settlement controls. Rio de Janeiro experiences a sub-tropical, humid climate with an annual rainfall of 1100–1800 mm and summer temperatures that range from 30 to 32 °C. Humidity, especially near coastal areas remains high throughout the year, along with high levels of marine aerosols. By-products from fuel combustion influence the formation of smog components. For example, the photochemical reaction between NO<sub>x</sub> and O<sub>3</sub> produces nitrate that reacts with acetaldehyde to form nitric acid and a peroxy-free radical (Nguyen *et al.* 2001; Martins & Arbilla 2003). This has led to a significant decline in air quality and it is very common to observe a photochemical smog over the whole metropolitan area (Daisey *et al.* 1987; Miguel 1991; Azevedo *et al.* 1999; Smith *et al.* 2004). This highly acidic atmosphere occurs mainly during the summer season and precipitation pH values between 3.8 and 5.4 have been recorded within the city (de Mello 2001).

### Selective extraction

Most studies of street sediments as indicators of elemental pollution have relied on strong acid extraction procedures and others that completely dissolve samples (Davies *et al.* 1987; de Miguel *et al.* 1997; Sezgin *et al.* 2003). These methods are very important when examining acid extractable and total concentrations, but selective extraction procedures allow identification and quantification of those elements present in different operationally defined phases within samples. From this their bioavailability can be examined in greater detail.

Operationally defined phases or fractions responsible for elemental distribution within geological materials may be water-soluble, exchangeable, carbonate, amorphous Fe and Mn, crystalline Fe and Mn, organic, and residual. Mobile (labile) elements are found in the more soluble phases of a sample matrix, such as water and ion exchange sites, whereas the least mobile (non-labile) are held in the acid soluble and residual (lithogenic) silica phase. Selective extraction exposes these phases to a sequence of solutions of increasing concentrations using a stepwise procedure under specific conditions (Chao 1972; Agemain & Chau 1977; Hoffman & Fletcher 1979; Skei & Paus 1979; Tessier *et al.* 1979; Ure *et al.* 1993; Quevauviller *et al.* 1994; Hall *et al.*

1996; McAlister & Smith 1999; Charlesworth *et al.* 2003; McAlister *et al.* 2003).

As is the case with all analytical techniques, selective extraction procedures have some operational problems (Pickering 1981; Van Valin & Morse 1982). Selectivity of elements for a specific phase is thermodynamic and differences in specificity between the various methods means that selectivity cannot be fully achieved. A general agreement as to which solutions should be used to extract elements from the various phases does not exist since matrix effects are involved in heterogeneous processes. Therefore, the choice of extracting solution will depend on the study aim, sample type and the elements of interest. Analyte contamination, burner and plasma clogging plus insoluble residue formation may also cause problems during analysis. These problems may be overcome by choosing an extracting solution of high purity and by using the correct sample/solution ratio and methods of extraction (Rauret *et al.* 1989; Hall *et al.* 1996; McAlister & Smith 1999; McAlister *et al.* 2003; Van Elteren & Budic 2004). Selective extraction constitutes a differential approach between “operationally” defined phases and identifies the phase(s) responsible for element adsorption.

## Sampling and analysis

### *Sample collection*

Samples representative of each site were collected by sweeping a large area of road from the pavements towards the centre of the road, away from major junctions and traffic lights. Bulk samples were thoroughly mixed and sub-sampled into polythene bags for analysis. A map of the study area and sample site locations is presented in Figure 1.

Samples 1–4 were collected from an industrial area situated next to busy main roads. Samples 5–7 represent residential and recreational areas where sediments were collected from roads along the front of Copacabana, Botafoga and Flamengo Beaches, and 8 and 9 were collected from a commercial/residential area. Samples 10–12 were collected from a traditional commercial part of Rio that experiences intense traffic conditions and samples 13–18 were collected from the city centre where very intense traffic conditions are experienced on a daily basis.

### *Sample preparation and analysis*

The <63  $\mu\text{m}$  fractions were analysed since they are undiluted by coarser sizes and allowed a more accurate prediction of the threat to an ecosystem by “heavy metals” (Forstner & Wittmann 1983) and oxalate pollution (McAlister *et al.* 2000). Samples were air dried at 30–35 °C since extractable ions were being analysed (Hesse 1971) and passed through a nylon mesh sieve to collect the <63  $\mu\text{m}$  fractions. Iron, Mn, Zn, Cu, Pb, Cr and Ni were analysed using a Perkin Elmer AAnalyst 200 atomic absorption spectrometer and oxalate analysis employed a Dionex Model DX 500 ion chromatograph. Oxidisable organic carbon was analysed using the Walkley and Black (1934) method and pH was determined in deionised water extracts (Hesse 1971) using an Orion Model 410A meter. XRD analysis was carried out on the <63  $\mu\text{m}$  powdered fractions and on the <2  $\mu\text{m}$  fractions by a membrane-mounting technique (McAlister & Smith 1995a, b) using a Siemens 5000 Diffractometer. Acid digestion of the residual phase was carried out using a Perkin Elmer microwave digestion system. Water-soluble ions were extracted using a modification of the Buurman *et al.* (1996) technique. A smaller sample weight (0.5 g) was extracted with a lower volume of deionised water (2.5 ml), diluted to 10 ml after extraction and membrane-filtered (0.2  $\mu\text{m}$ ) prior to analysis (McAlister *et al.* 2003). Selective extraction employed both shaking and heating techniques (McAlister *et al.* 2003). The extraction protocol was modified to include the organic phase which was extracted by heating the sample residues in a 1 M  $\text{HNO}_3$ /1 M HCl mixed solution at 85 °C for 2 h on a sand bath, transferring them to an oven and heating at 85 °C overnight. A reduction in oxalate concentration in acid solution can occur within a few days of initial preparation. One possible mechanism is photo-decomposition of the iron–oxalato complex to form carbon dioxide and formate. It is very important to store sample extracts in the dark at 4 °C after all stages of extraction and analyse for oxalate as soon as possible or within 12 h after acidification (Zuo & Holgne 1992). Samples contained weathering products such as iron oxyhydroxides as shown in the amorphous iron phase and kaolinite by XRD analysis. Soils from this area are classified as weathered red/podzolics (McAlister *et al.* 1998).

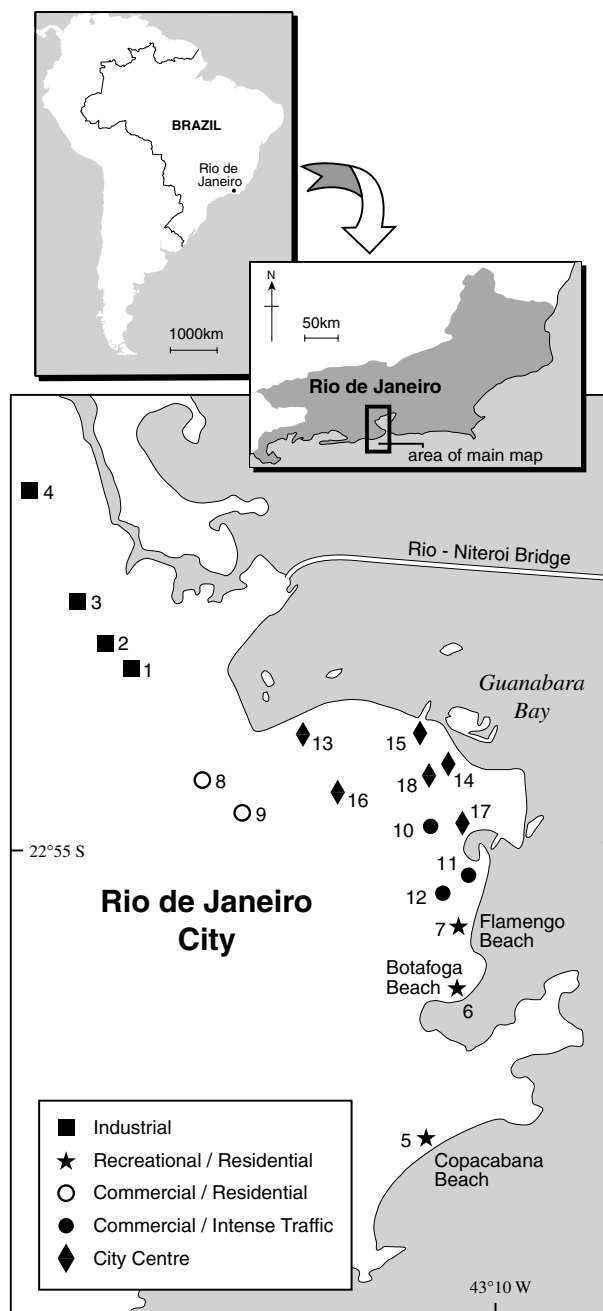


Fig. 1. Map showing the study area and sampling sites.

and therefore contain high concentrations of both Fe and Al. Hydrogen peroxide is commonly used with nitric acid to extract the organic fraction of soils and sediments (Quevauviller 1998), however, in this study it was omitted since  $H_2O_2$  can react to form oxalato-aluminate or oxalato-ferrate com-

plexes (Farmer & Mitchell 1963). This could lead to erroneous results since oxalate concentrations could increase as a result of these reactions. A 1 M HCl/1 M  $HNO_3$  solution was chosen as 1 M HCl was used to extract total oxalates from soils and street sediments (Liliehalm *et al.* 1992; McAlister

*et al.* 2000) and 1 M HNO<sub>3</sub> was included to oxidise organic matter. Samples (0.5 g) were weighed into acid washed polypropylene centrifuge tubes and blanks were prepared by taking each extractant without the sample through all the preparation procedures prior to analysis. Analytical grade chemicals were used and all solutions were prepared using grade A glassware and deionised water.

## Results and discussion

Details of the selective extraction protocol are given in Table 1. Percentages of the total Fe, Mn, Zn, Cu, Pb, Cr and Ni bound to each phase are shown graphically in Figure 2a–g and percentages of the total C<sub>2</sub>O<sub>4</sub> for the water-soluble, exchangeable/carbonate, amorphous Mn, amorphous Fe/Mn, crystalline Fe/Mn and organic phases are presented in Figure 2h. Total element and oxidisable organic carbon concentrations plus pH values are shown in Table 2.

### Iron

Total Fe concentrations range from 3 to 4% at all the sites, apart from sample 18, which contained high concentrations of iron oxide and had a value

of 69,000 mg/kg or 6.9% (Table 2). One possible source for iron may be from weathered red/podzolic soils that have an Fe concentration of between 2 and 3% and are typical of this area (McAlister *et al.* 1998). The soils may be eroded and washed into streets from, for example, locations such as construction sites. Iron may also come from industrial sources and combustion particles. Iron was not bound in the water-soluble phase and low percentages of the total were retained by the carbonate and amorphous Mn phases at all the sites studied and may be classified as being non-labile or not bioavailable. An even distribution occurred between the remaining phases for all samples, except again in sample 18 where 33 and 36.6% (22,920 and 25,250 mg/kg) of the total was partitioned between the amorphous and crystalline Fe/Mn phases, respectively (Figure 2a). Higher concentrations of Fe present in the crystalline phase may indicate the presence of weathered rock from soils from the surrounding area. XRD analysis verified the presence of kaolinite and iron oxide, with peaks at 7.15 and 2.47 Å, respectively. The organic and residual phases were also efficient sinks for Fe and approximately 21–29% (6080–11,960 mg/kg) and 20–31% (6500–14,500 mg/kg) of the total was bound, respectively.

### Manganese

Total Mn ranges from approximately 500–1200 mg/kg (0.05–0.1%) and showed higher concentrations when compared to soils from the area (145–620 mg/kg) (McAlister *et al.* 1998). A 1 M hydroxylamine hydrochloride solution at pH 4.86 was selective towards Mn and very low percentages of total Fe and Zn were the only other metals bound to the amorphous Mn phase. The water-soluble phase retained a very low percentage of the total and this element was precipitated as ferromanganous compounds with the highest percentages of the total being held in the amorphous Fe/Mn phase (Figure 2b). Organic complexation and crystalline formation were not prominent at any of the sites. Concentrations of this element were relatively distributed between the strong acid soluble amorphous Fe/Mn and residual phases; however, similar and at some sites higher percentages were also bound by the exchangeable/carbonate and amorphous Mn phases when

Table 1. Selective extraction procedure.

Phase/extractant	Ratio	Time	Conditions
<i>Water-soluble</i>			
Deionized water	1:5	2 h, overnight	Shaking
<i>Exchangeable/carbonate</i>			
1 M NH <sub>4</sub> OAc (pH 5)	1:50	6 h	Shaking
<i>Amorphous Mn</i>			
0.1 M NH <sub>2</sub> OH·HCl (pH 4.86)	1:50	1 h	Shaking
<i>Amorphous Fe/Mn</i>			
0.25 M NH <sub>2</sub> OH·HCl/ 0.25 M HCl	1:50	2 h	60 °C
<i>Crystalline Fe/Mn</i>			
1 M NH <sub>2</sub> OH·HCl/25% CH <sub>3</sub> COOH	1:50	3 h	90 °C
<i>Organic</i>			
1 M HNO <sub>3</sub> /1 M HCl, overnight at 85 °C	1:20	2 h	85 °C
<i>Residual</i>			
HNO <sub>3</sub> /HF/HCl Microwave (3)/(1)/(0.5)	0.1:25	35 min	Digestion

compared to the crystalline Fe/Mn and organic phases. This element may be regarded as being non-labile or not bioavailable except under extreme environmental conditions.

### Zinc

High total concentrations were recorded at all the sites (Table 2), with an average of 2612 mg/kg. This concentration shows high zinc excess when compared to soils of this area, which range between 30 and 50 mg/kg, (McAlister *et al.* 1998). US Environmental Protection Agency (USEPA) recommends soil remediation if the concentration exceeds 23,000 mg/kg (USEPA 1995), whereas in New Jersey 350 mg/kg is used as a target value (Beyer 1990). The analysis of vertical sediment cores to study environmental change and short-term variations in atmospheric deposition is still common practice (Farmer, 1991; Neto *et al.* 1999). Zinc concentrations for estuarine sediment cores (< 63 µm fractions) from Jurujuba Sound, Rio de Janeiro State, range between 25 mg/kg in pre-

urbanisation sediments at the base and 400 mg/kg in contemporary deposits at the top of the cores (Neto *et al.* 1999). Zinc could be regarded as being bioavailable under acid rain conditions since up to 38.3, 52.6, 51.6, 53.6 and 61.6% of the total concentrations (396, 546, 828, 474 and 690 mg/kg) were adsorbed in the exchangeable/carbonate phase in the industrial, beach, commercial/residential, commercial and city centre sites respectively, however, very low levels were retained in the water-soluble phase (Figure 2c). Amorphous manganese and crystalline Fe/Mn oxides did not retain high concentrations of Zn and quite high retention in the amorphous Fe/Mn phase was observed. Organic complexation was important in samples from the industrial site, especially sample 1, where 64.8% of the total (1720 mg/kg) was bound compared to the other study areas. Zinc resembles alkali metals (e.g. Na, K) and alkaline earths (e.g. Ca, Mg) with respect to surface adsorption and favours ion exchange as an adsorption mechanism, which may explain its higher affinity for the exchangeable/carbonate phase.

Table 2. Total element, oxalate and oxidisable organic carbon concentrations and pH values of the street sediments.

Sample	mg/kg <sup>-1</sup>								% O.O.C	pH
	Fe	Mn	Zn	Cu	Pb	Cr	Ni	C <sub>2</sub> O <sub>4</sub> <sup>-</sup>		
<i>Industrial</i>										
1	40288	1218	2656	247	704	212	75.2	379	3.8	8.9
2	40784	985	1227	246	478	116	78.5	800	3.6	8.0
3	29547	821	1115	151	329	54.0	62.6	449	3.2	8.1
4	40024	748	1034	262	245	111	75.0	56	2.6	8.2
<i>Beaches</i>										
5	34600	629	1408	366	474	110	82.6	576	5.0	7.4
6	46614	942	1039	241	303	100	78.6	1015	4.2	7.8
7	36612	633	820	234	257	98.3	65.9	1756	6.7	7.5
<i>Commercial/residential</i>										
8	36545	664	1361	256	399	91.1	75.3	1600	8.7	6.1
9	42275	861	1606	388	314	100	87.3	704	6.0	7.4
<i>Commercial/intense traffic</i>										
10	30884	508	884	232	287	57.8	67.6	1416	9.3	7.2
11	34867	792	1210	290	352	74.3	81.6	1770	5.1	7.6
12	35317	876	1525	372	295	80.1	80.7	1265	5.3	7.2
<i>City centre/commercial/very intense traffic</i>										
13	34423	709	1264	234	333	84.2	67.2	906	4.7	6.9
14	34053	667	1268	397	544	69.5	76.8	1217	6.4	7.5
15	26566	588	1120	279	228	81.0	60.2	2077	6.4	7.7
16	38430	615	1136	186	198	98.8	67.7	1160	4.4	7.4
17	32993	802	1533	359	346	75.4	72.2	1216	4.5	7.8
18	69030	603	907	491	554	139	71.6	245	1.9	7.4

Copper

Total Cu shows an average value of 290.6 mg/kg and soils from this area have an average of 10 mg/kg (McAlister *et al.* 1998). USEPA target 1000 mg/kg as an upper limit of concentration for sewage sludge prior to land application, New Jersey, 170 mg/kg and Florida has a target of 105 mg/kg

(Krieger *et al.* 1987). Copper concentrations in local near-shore sediment cores (<63 μm fractions) range from 5 mg/kg in pre-settlement sediments at the base to 100 mg/kg in contemporary sediments at the top (Neto *et al.* 1999). The majority of Cu was bound in the amorphous Fe/Mn oxide phase, with the remainder being partitioned between the crystalline Fe/Mn oxide and exchangeable/carbonate

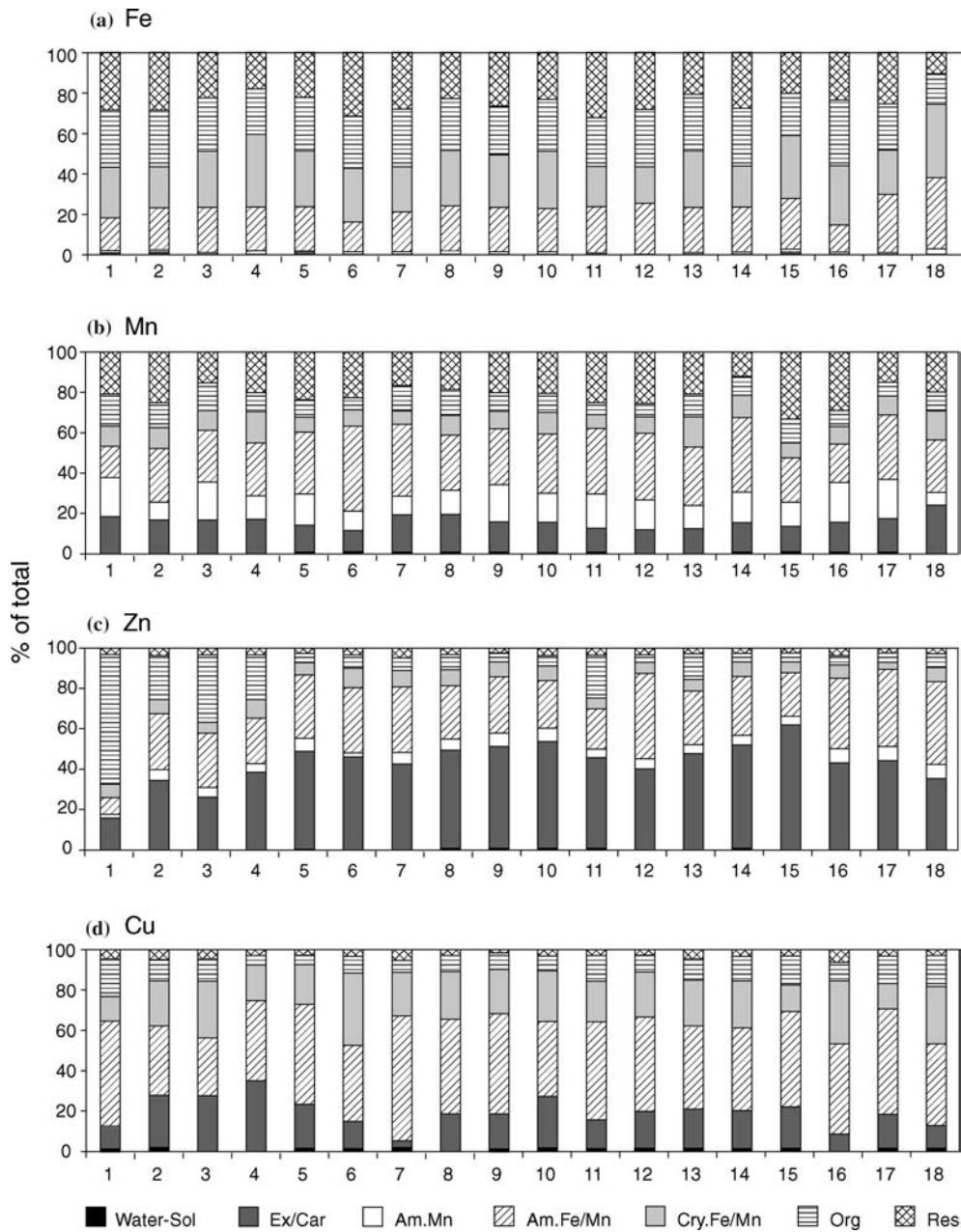


Fig. 2. (a-h) Histograms showing the percentage of the total elements and oxalate held in each phase.

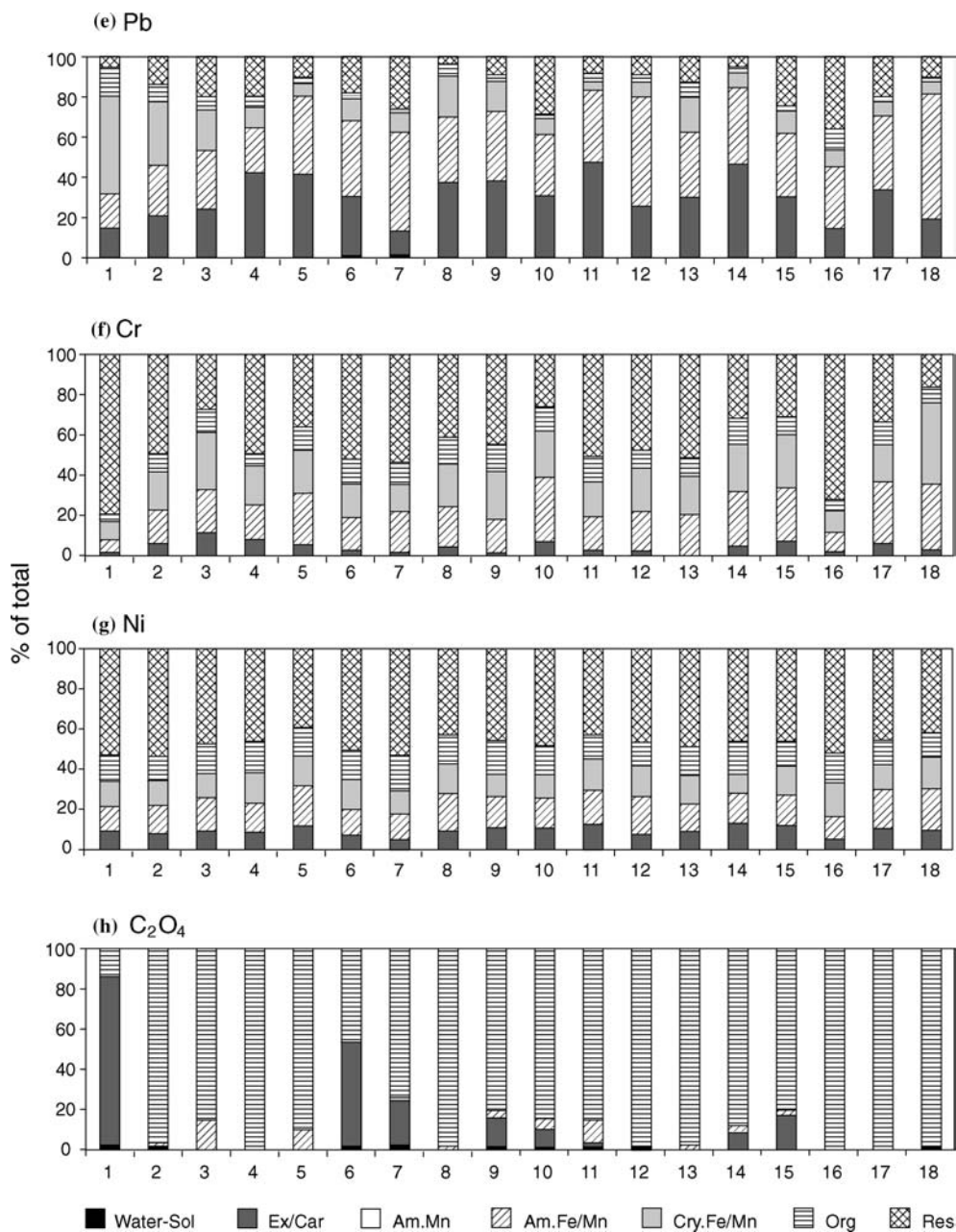


Fig. 2. Continued.

phases, where the latter was very variable, even for samples within some sites. Low percentages were bound in the water-soluble phase and the amorphous Mn phase retained no Cu at all. Retention by the organic and residual phases was not prominent, however, samples 1 and 18 showed higher organic complexation properties (Figure 2d). Results would indicate Cu to be mainly non-labile.

*Lead*

Total Pb ranges from 200 to 700 mg/kg and is 35 times higher than levels found in most soils (0.1–20 mg/kg) (Sezgin *et al.* 2003). Lead concentrations for local estuarine sediment cores (<63 μm fractions) range from 20 mg/kg in pre-urbanisation sediments at the base to 80 mg/kg in



contemporary samples at the top (Neto *et al.* 1999). Lead was bound mainly in the amorphous Fe/Mn and exchangeable/carbonate phases; however, values varied at and within the various sites (Figure 2e). Sample 18 was an exception in the amorphous Fe/Mn phase since it contained a much higher concentration of total iron than the other samples. Lead has a higher ionic radius than the other metals studied and this may explain the greater affinity of iron oxide surfaces for this element (Benjamin & Leckie, 1981; Coston *et al.* 1995). The crystalline Fe/Mn phase showed prominent retention in samples from the industrial area, which held up to 49% of the total (342 mg/kg). Selective extraction highlighted high retention in the exchangeable/carbonate phase at Copacabana beach, which is a recreational/residential area and at an industrial site, where 42% (198 mg/kg) and 46% (90 mg/kg) of the total was adsorbed, respectively. This could make Pb potentially bioavailable should a change in pH and redox conditions occur as a result of, for example, acid rain. Organic complexation did not play an important role in the retention of Pb and lithogenic/residual binding was very variable at and within all the study sites.

#### Chromium

The average total concentration for all the sites is 202 mg/kg and the average found in local soils is 60 mg/kg (McAlister *et al.* 1998). USEPA targeted 1000 mg/kg as an upper limit for sewage sludge prior to land application, New Jersey, 100 mg/kg and Florida, 290 mg/kg (Krieger *et al.* 1987). Local near-shore sediment core concentrations range from 5 mg/kg in pre-urbanisation sediments to 100 mg/kg for contemporary samples (Neto *et al.* 1999). Chromium is retained in the residual phase in samples from all the sites, with 49–79% of the total (55–167.5 mg/kg) being bound in the industrial site samples and up to 71% (70 mg/kg) in samples from the city centre. The remainder was partitioned between the amorphous Fe/Mn and crystalline Fe/Mn oxide phases. The high Fe concentration in sample 18 makes these phases important sinks for this element. Adsorption by ion exchange mechanisms, by the amorphous Mn oxide and organic phases was not prominent and therefore this

element may be termed as non-labile or not bioavailable (Figure 2f).

#### Nickel

Total Ni averages 73.8 mg/kg and is evenly distributed between the sites. This is noticeably higher than the average found in local soils (22 mg/kg) (McAlister *et al.* 1998). Local near-shore sediment cores exhibit concentrations between 5 mg/kg for pre-urbanisation sediments and 30 mg/kg for post-urbanisation samples (Neto *et al.* 1999). Nickel is evenly partitioned between the amorphous Fe/Mn oxide, crystalline Fe/Mn oxide and organic phases, with the highest percentage of the total being bound in the residual phase at all sites (Figure 2g). Only a smaller percentage of the total is retained in the exchangeable/carbonate phase at all of the sites and this element may be termed as non-labile.

#### Oxalate

Information on oxalate concentrations in street sediments is very limited, except for a study carried out on trace metal and oxalate concentrations in street sediments from the city of Niteroi, across Guanabara Bay from Rio de Janeiro (McAlister *et al.* 2000). Total concentrations in the <63  $\mu\text{m}$  fractions of the samples showed higher values than the equivalent size fraction from Niteroi, except for one industrial and a city centre site (Table 2). However, no XRD peaks for Weddellite (calcium oxalate dihydrate) were found in the <2  $\mu\text{m}$  fractions, which is in contrast to the study of Niteroi where almost all of the Weddellite was bound to this fine fraction. This may be due to more regular and efficient street cleaning in Rio de Janeiro compared to Niteroi where sewage overflow appears to remain in the streets for much longer periods. This allows time for the formation of Weddellite (calcium oxalate dihydrate) and its adsorption to fine particulate and organic materials. Selective extraction provided more detailed information on oxalate partitioning within the various sample phases and on bioavailability (Figure 2h). Total concentrations vary from 56 to 2077 mg/kg (Table 2) and the organic phase was shown to be an important sink for this anion. Water-soluble oxalate con-

centrations are low compared to the total levels at all of the sites and this is probably due to efficient street cleaning practices. However, 84.4% (319.8 mg/kg), 53.3% (541.2 mg/kg) and 22.9% (401.4 mg/kg) of the total concentration are bound in the exchangeable/carbonate phase in the industrial area and at Copacabana and Botafoga Beach areas, respectively. High concentrations of oxalate in this phase, especially in recreational/residential areas, could easily lead to its release under acidic environmental conditions. The amorphous Mn and crystalline Fe/Mn phases do not retain oxalate at any of the sites (Figure 2h).

Elements that pose some risk to the environment within the short term as a result of their mobility/availability are termed bioavailable. Labile metals, are the sum of free metal ions and metals that can be easily dissociated from complexes or colloids. These metals respond readily to changes in physico-chemical conditions and are bound in the water-soluble and exchangeable/carbonate phases. The more concentrated reagents used in the selective extraction procedure release strongly bound metals and these are termed non-labile. Bioavailability of elements present in industrial and municipal wastes is a concern with respect to their potential toxicity and transport to ground or surface water systems. However, they must undergo release to the sediment solution before they can become available to the environment, and wastes that contain high levels of organic matter (e.g., sewage) may complex these metals and limit their availability. Organic matter contains humic and fulvic acids and attractive forces between ions and these substances range from weak to strong, whereby ions may be easily replaceable or may resemble chemical bonds that occur in metallic chelation reactions, respectively (Saxby 1969).

Binding properties of Fe/Mn hydroxides and oxides, carbonates and organic matter are pH dependant. Metallic hydroxides have minimum solubility between pH 9 and 12 and at neutral pH, their solubilities are increased by several orders of magnitude (Jenne 1968). Sediments from the industrial site range between pH 8.1 and 8.9, those from the beach area shows values of 7.4, 7.8 and 7.5, the commercial/residential area shows pH values of 6.1 and 7.4 and the lower pH correlates

with a high oxidisable organic carbon concentration of 8.7% (17.4% organic matter). Sediments from the commercial site have pH values of 7.2, 7.6 and 7.2 and those from the city centre range from 6.9 to 7.8 (Table 2). At positive  $E_h$  values (free oxygen present) divalent metals are stable at pH values of 7–8 and as pH increases the carbonate and then the hydroxide phase becomes the most stable (Hem 1972). The pHs of these sediments are in the neutral to alkaline range and this may help to bind these heavy metals at some of the sites. Values for pH are compared on a logarithm scale and with respect to the Fe/Mn oxyhydroxide phase that remains stable between pH 9 and 12, levels in sediments from the industrial site were 10 times, those from the beach, commercial and city centre sites were 20 times and a sediment from the commercial/residential area was 30 times more acidic than these stable pH values. At these pH levels (see Table 2), elements from this phase may become bioavailable due to the varying environmental conditions experienced in this area and the production of acid rain (de Mello 2001). However, recent experiments carried out on the mobilisation of trace elements from sewage sludge (Qureshi *et al.* 2004) have shown that the presence of calcareous materials in the matrix of these types of sample reduces acidification and microbial activity (pH 6.6–8.0) and prevents their mobilisation.

In terms of possible sources, urban air pollution includes inorganic and organic particles such as soil, dust, fly ash, plant remains and pollen. However, another major pollution source is from the combustion of gasoline/ethanol mixed fuel, “gasohol” (which is unique to Brazil) and diesel, which are used to run light-duty and public transport vehicles, respectively. Diesel emissions are lower in carbon monoxide, hydrocarbon and carbon dioxide than gasoline but higher in oxides of nitrogen and particulate matter. Incomplete carbon and hydrocarbon combustion causes the formation of carbonaceous particles (soot) and volatile organic compounds (VOCs), respectively. Other by-products include, oxides of sulphur ( $SO_x$ ) plus aerosols of  $SO_3$  and Pb that react with the atmosphere to produce sulphuric acid, sulphates and ozone. Automobiles that use “gasohol” produce less carbon monoxide and volatile organic compound emissions compared to diesel (Howard *et al.* 1997; Schifter *et al.* 2001a, b). However, atmospheric  $NO_x$  and aldehyde concentrations are

increased and higher acetaldehyde : formaldehyde ratios have been recorded (Nguyen *et al.* 2001; Grosjean *et al.* 2002; Martins & Arbilla 2003). Acetaldehyde and formaldehyde concentrations influence the formation of other smog components such as nitric acid, which is a component of acid rain (de Andrade *et al.* 1998).

Human exposure to transport emissions is a function of population density and how close people live to transportation corridors, especially in densely populated developing cities like Rio de Janeiro. Another important pollution problem found in Rio, and in other developing cities, is the contamination of surface runoff by untreated sewage along with combined storm and foul water sewers. This results in both street sediments and estuarine/coastal sediments being contaminated with a much wider range of organic and inorganic pollutants than would normally be found in sediments from developed cities (Neto *et al.* 2000).

## Conclusions

Due to the diverse environmental conditions experienced in Rio de Janeiro, pH and  $E_h$  levels can be very variable. Since bioavailability depends on pH and bivalent elements are stable at pH 7–8, recorded precipitation pHs of 3.8–5.4 may cause short-term changes within street sediment matrices and increase the risk of heavy metal and oxalate pollution. Intense traffic conditions are experienced throughout Rio de Janeiro and this leads to an atmospheric environment high in diesel and “gasohol” emissions that can lead to acid rain conditions. Numerous studies on the binding properties of street sediments have employed single strong acid digestion procedures to extract elements and this has provided an overall classification of the metals present. However, when greater detail on bioavailability of elements and oxalate is required, selective extraction provides us with a much clearer view on ion mobility. The most soluble phases include, water-soluble and exchangeable/carbonate where the metal and oxalate ions are adsorbed by electrostatic and ion exchange mechanisms. This technique therefore emphasizes the possibility that high levels of Pb and oxalate may become bioavailable in industrial and especially in recreational/residential areas

that experience high levels of vehicle traffic. Iron retention in the water-soluble and exchangeable/carbonate phases is low, making this element non-labile. Water-soluble Mn concentrations are very low, although up to 19% of the total was bound by the exchangeable/carbonate phase at some of the sites (Figure 2b). Zinc is bound in the exchangeable/carbonate phase and this may increase its bioavailability at all the study sites under acid rain conditions. Copper is partitioned mainly between the amorphous Fe/Mn and crystalline Fe/Mn phases, however, up to 36.7% of the total was bound in the exchangeable/carbonate phase in an industrial area and may cause bioavailability at this site. Chromium and nickel are bound mainly in the residual phase and are therefore considered to be very immobile. Relatively efficient street cleaning practices in Rio de Janeiro compared to the nearby city of Niteroi may lead to the removal of street sediments containing sewage. This detailed study of oxalate partitioning showed this anion to be bound mainly in the organic phase in the <63  $\mu\text{m}$  fractions and not in the fine <2  $\mu\text{m}$  fractions found in street sediments from Niteroi (McAlister *et al.* 2000).

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