Bull. Environ. Contam. Toxicol. (2006) 77:119–125

DOI: 10.1007/s00128-006-1040-9

Bulletin of Environmental Contamination and Toxicology

Characterization of Airborne Trace Metal Distribution in Baixada Fluminense, Rio de Janeiro, Brazil, by Operational Speciation

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Received: 24 February 2006/Accepted: 25 May 2006

Baixada Fluminense is located in the Rio de Janeiro Metropolitan Area (RJMA), being itself a large metropolitan area with several Counties and Districts. The region, denominates Aerial Basin III, presents severe air pollution problems due to high concentration of particulate matter (World Bank 1997; Quiterio et al 2005b). It is known that factors such as toxicity, bioavailability, mobility and biodegradability of trace metals depend not only on their concentration but, mainly, on the chemical and physical associations that they suffer in natural systems. In terms of physical form, different metals are strongly fractionated among particles with different sizes. As it is well known, in terms of human respiration, particle size determines in which part of the respiratory system a particle and its associated metals will be deposited. In terms of chemical form, it is the oxidation state and the chemical species associated with a particular metal that govern the availability or toxicity of that metal to the biota. In the present work, an attempt to determine the distribution of trace metals within different chemical forms was done, following an operational speciation method similar to that used by Fernández et al. (2000). As further detailed later, five fractions were considered in the present work. Each fraction presents certain chemical characteristics so that it can be associated with specific forms of the metals. In fraction (f) 1 (exchangeable fraction), soluble metals and species that are easily interchangeable with water by sorption-desorption processes are found. In general, free metal ions are biologically available and are very toxic to living organisms. In f2 (carbonate fraction), metals are present as carbonates (or other forms susceptible to pH changes) or bound to hydrated oxides (susceptible to be released under reducing conditions). Carbonate complexation of metals, in general, reduces the toxicity of heavy metals to the microbiota. F3 (oxidizable fraction) contains metals binded to organic matter that is found adsorbed in living organisms, detritus, coatings of proteins, fats, mineral particles, etc. (easily soluble under oxidizing conditions). F4 (reducible fraction) contains Fe in the form of oxides and other organomettalic compounds. Alkyl metal complexes are soluble in lipids and are very toxic because they can pass directly through biological membranes. F5 (residual fraction) contains residual metals found in elementary form and in crystalline structures of 1^a and 2^a minerals, silicates, cements, passivated oxides, etc., that have to be extracted under hard acid conditions. The remaining final residue is formed by silica and clay (Ure et al.1995; Caroli et al. 1996).

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MATERIALS AND METHODS

A total of 48 samples were collected, at a height of 2 m, during the months of August and October of 2002, in six Counties of the area, namely, Belford Roxo, Japeri, Mesquita, Nova Iguaçu, Queimados and São João de Meriti. Samplings were taken every six days using high volume samplers (Energética) and borosilicate glass microfiber filters (Energética, 254 X 203 mm, thickness 0.22 mm). Flow rates of aspiration of 1.1–1.7 $m^3.min^{-1}$ and 24 hours sampling periods of time were used.

As described in previous works (Quiterio et al. 2004a; 2004b, 2005a; 2005b), TSP masses were determined gravimetrically.

Before chemical treatment, each filter was divided in five equal parts and each part was cut in small pieces. The chemical procedure consisted of applying a sequential extraction scheme of five fractions, an adaptation of the Tessier´s scheme for sediments (Tessier et al. 1979; Obiols et al. 1986). Table 1 presents the sequential extraction scheme adopted in the present work. Filter and reagent blanks were processed for nine filters following the same procedure, that is, cutting the filters in five parts and performing the same chemical treatment in each part. The average value of the blanks was used to correct sample values. No matrix effect of filters and reagents was detected.

Metals (Mn, Zn, Cr, Fe, Cu, Al, Cd, Ni and Pb) were determined by ICP-OES (Inductively coupled plasma optical emission spectroscopy) following Method IO-3.4 (1999). Detection limits and accuracy of the method were determined following Method IO-3.4 (1999). Detection limits were computed as three times the standard deviation of the distribution of outputs of ten repeated measurements of the standard used, which contained no metals (Boss and Fredeen 1999). Calculated detection limits are as follows: 3 ng m^{-3} for Mn, Zn, Cr and Fe, 15 ng m^{-3} for Al and Cd, 6 ng m^{-3} for Cu, 12 ng m^{-3} for Ni and 18 ng m^{-3} for Pb. The accuracy of the method was evaluated using a standard reference material (SRM 11355 ICP Multi Element Standard IV, Nist, 2000 from the U. S. Department of Commerce, National of Standards and Technology, Washington, D.C.). The obtained results were in the acceptable range of 3 - 8%.

RESULTS AND DISCUSSION

Figures 1 and 2 show the fraction distribution of each metal in the six sampling stations, or Counties, one in each County, where measurements were made. The concentrations shown are mean values for each station. Number of samples (N) and sampling period for each station are indicated in the caption figures.

For the six stations, Fe, Ni, Al and Cr are mainly distributed between fractions f5 and f3, indicating that they are probably related to natural sources, such as suspended soils and crustal weathering. The only exception to this occurs in

Table 1. Sequential extraction scheme for chemical speciation of suspended particles used in this work.

Metallic Fractions	***Reagents and conditions – Sequential Extraction Method for 0.1g of TSP***
Fraction 1	10mL of CH_3COOH 2M and CH_3COONa 2M buffer solution (pH 4.7). Mechanical agitation during 16 hours at room temperature.
Fraction 2	10 mL of 0.1 M $NH_2OH.HCl$ in HNO_3 (pH 2). Mechanical agitation during 16 hours at room temperature.
Fraction 3	6 mL of 0.02 M HNO_3 (pH 2) + 10 mL 30% H_2O_2. Mechanical agitation during 15 hours at room temperature + 5 mL of 1.0 M CH_3COONH_4 , continuous agitation during 1 hour at room temperature.
Fraction 4	15 mL of NaOH 0,1M (pH 12). Mechanical agitation during 16 hours at room temperature.
Fraction 5	2 mL of conc. HNO_3 + 6 mL of conc. HCl + 10 mL H_2O Milli-Q, 90 min at 95°C, agitating occasionally.

Queimados where 100% of Ni is found in fraction f2 (carbonate fraction). This may be attributed to the high carbonate ($NiCO_3$) content of the soils of this region.

Mn is distributed over fractions f1, f2, f3 and f5, with a slight predominance of fraction f2 (30%), associated with oxides and carbonates of low toxicity. Less than 5% is found in fraction f4 (reducible fraction), which, for this metal, is the state more available, under a biological point of view (Ure et al.1995). Al, Fe and Mn are broadly considered as tracers characterizing soil erosion and dust in the absence of steel industries (Beceiro González et al. 1997; Morales et al. 1990).

Cu is found in all fractions. In Belford Roxo, Japeri, Queimados and São João de Meriti, about 55% is found in fractions f1 and f4, (exchangeable and reducible fractions, respectively). In Mesquita and Nova Iguaçu, about 20%, 30% and 20% are in fractions f2, f3 and f5, respectively.

For all stations, except Nova Iguaçu, about 60% of Zn is present is fractions f1 and f4. For Nova Iguaçu, about 75% of Zn is found in fraction f5. It should be noted that the monitoring station is installed next to a quarry, which may explain this result since fraction f5 usually contains residual metal found in elementary form and in the crystalline structure of primary and secondary minerals and silicates.

For Cd, 60% to 100% of the metal is found in fractions f1 and f4. In Belford Roxo, Mesquita and São João de Meriti about 60% of Cd is found in fractions f1 and f4 (exchangeable and reducible fractions, respectively). In Japeri, Nova Iguaçu and Queimados, 70%-100% is in fractions f2, f3 and f5, respectively. It should be noted that f4 (reducible fraction) is frequently lipid soluble and toxic.

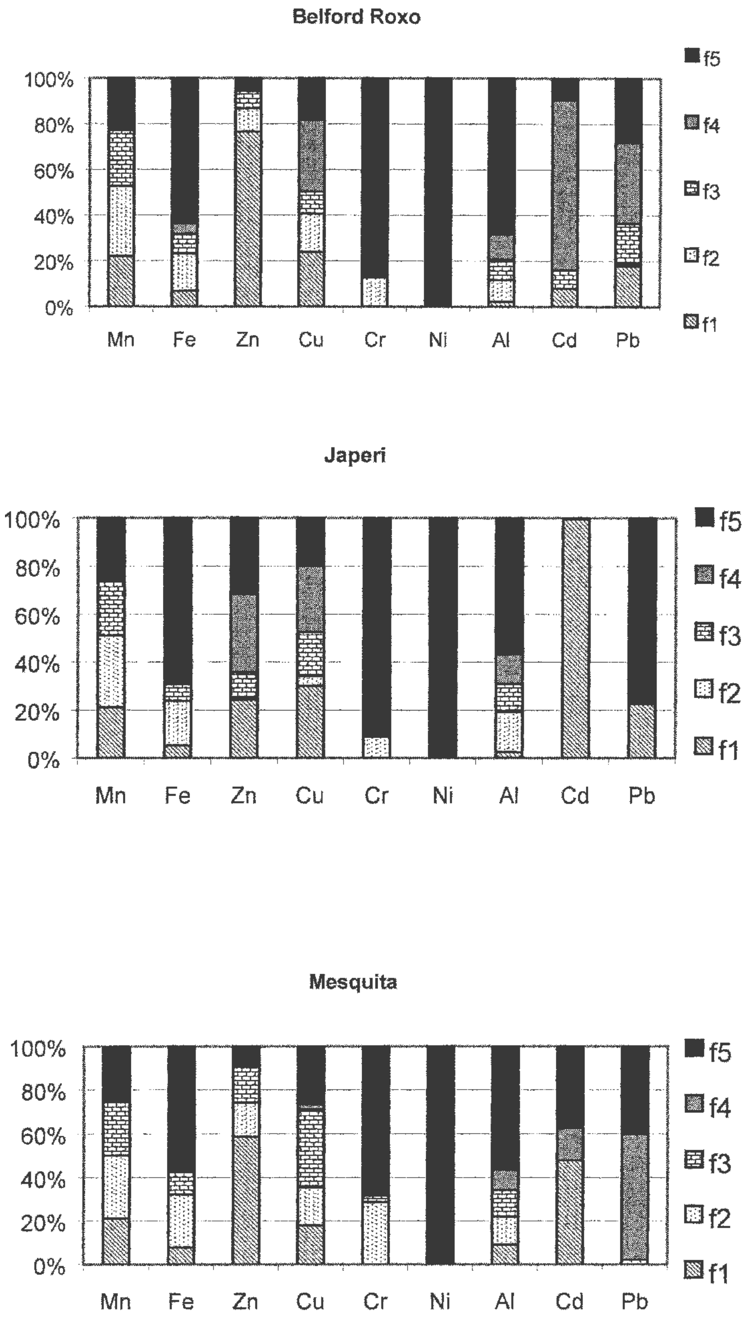

Figure 1. Metal distribution within fraction 1 to fraction 5 for samples collected in Belford Roxo (N=11), Japeri (N=7) and Mesquita (N=8) from August 2002 to October 2002.

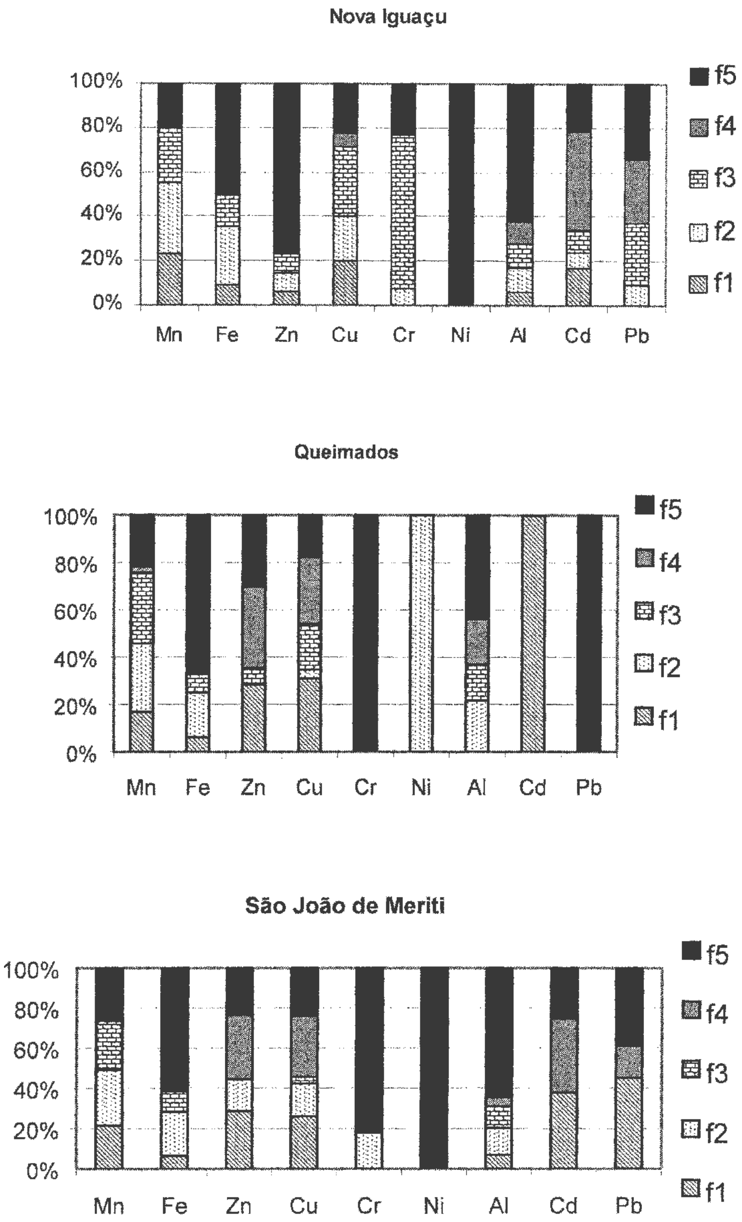

Figure 2. Metal distribution within fraction 1 to fraction 5 for samples collected in Nova Iguaçu (N=8), Queimados (N=7) and São João de Meriti (N=7) from August 2002 to October 2002.

Enrichment factors for all metals (Ure et al. 1995; Caroli et al. 1996) were calculated using mean concentrations values and with the element K as reference. As related in our previous work (Quiterio et al. 2005), enrichment factors for Ca, Mg, K, Na, Mn, Fe, Cr, Co, Ni and Al, in a general form, lie in the range of 0.0 to 2.0, suggesting a natural input. On the other hand, Zn, Cu, Cd and Pb values lie in the range of 10.2 to 190.4, confirming that, for these elements, anthropic sources prevail over natural inputs.

In particular, results not presented in our previous publication show that, for Cu, the enrichment factors are 12.4, 10.4, 10.9 and 11.2 for Belford Roxo, Japeri, Queimados and São João de Meriti, respectively. It is generally accepted that factors $\geq$ 10 are an indication of anthropic origin. This result, along with the fraction distribution of Cu shown in Figures 1 and 2, that indicate that about 30% of Cu is found in fraction f4, suggest that Cu emissions, in these places, have an anthropic contribution. For Mesquita and Nova Iguaçu enrichment factors were 4.3 and 6.4, respectively, with fraction f4 representing less than 5% of the total, as expected.

For Zn, enrichment factors are found to lie between 89.2 and 190.4 for all stations. These values are consistent with the predominance of fractions f1 and f4, as found in the sequential extraction. As stated above, in Nova Iguaçu, Zn is found in fraction f5 as a consequence of mineral extraction activities, which are, in fact, an anthropic activity.

For Cd all enrichment factors are higher than 30, with values up to 115 in São João de Meriti. Again, these values are consistent with the sequential extraction results.

For Pb the enrichment factors are 14.6, 10.2 and 15.0 for Belford Roxo, Mesquita and São João de Meriti, respectively. These are, coincidently, the places where a predominance of fractions f1 and f4 was found. For the other stations, enrichment factors are less than 10.

Results from the sequential extraction and the calculated enrichment factors are in good agreement, showing that Zn, Cu, Cd and Pb are due to anthropic emissions, mainly local industrial activities (metallurgical and structural steel manufacture, solvent and paint production), diesel and fuel combustion and biomass burning. For Nova Iguaçu, Zn is associated with fraction f5 and for Nova Iguaçu, Japeri and Queimados, Pb is found in fractions f2, f3 and f5, with a predominance of fraction f5. This is a clear consequence of mineral extraction activities in the region as well as crustal weathering and soil suspension, associated with the lack of paved roads and parks. For the other stations, these metals are found in fractions f1 and f4. Fraction f1 is water-soluble and bioavailable, while fraction f4 is frequently lipid soluble and toxic.

Further monitoring campaigns are highly recommended focusing on the determination and speciation of metals found in inhalable particles. These are known to have higher concentrations of Zn, Cu, Cd and Pb, which are considered of major health concern.

Acknowledgments. We thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for financial support and the kindly collaboration of DSc. Glauco Favilla Bauerfeldt and DSc. Maria Cristina Rodrigues.

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