Bull. Environ. Contam. Toxicol. (2005) 75:997–1003

DOI: 10.1007/s00128-005-0848-z

Bulletin of Environmental Contamination and Toxicology

Assessment of the Concentrations and Emission Sources of Airborne Metals in Particulate Matter in Seven Districts of Baixada Fluminense, Rio de Janeiro, Brazil

S. L. Quiterio,[1] V. Escaleira,[2] C. R. S. Silva,[1] L. F. P. G. Maia,[3], G. Arbilla[1]

[1] Physical Chemistry Department, Federal University of Rio de Janeiro, CT, Building A, Room 408, 21949-900, Cidade Universitária, Rio de Janeiro, RJ, Brazil
[2] National Center of Soil Research, EMBRAPA, Jardim Botânico Street, 1024, 22460-000, Rio de Janeiro, RJ, Brazil
[3] Laboratory of Research on Atmospheric Pollution, Meteorological Department, Federal University of Rio de Janeiro, CCMN, Building H2, Room 004, 21949-900, Cidade Universitária, Rio de Janeiro, RJ, Brazil

Received: 4 January 2005/Accepted: 17 August 2005

The Baixada Fluminense (BF) is a region of approximately 2,512 km^2, located in the northern region (Basin III) of Rio de Janeiro Metropolitan Area (RJMA), Brazil. The region has a population of 2,423,141 people which represents 40 % of the total population of the RJMA. The land use in the BF is distributed in residential, industrial and commercial sectors. The main pollution problem in this region are the high levels of particulate matter, which in several areas exceed the WHO guidelines (Mage et al. 1996) and the Brazilian air quality standards (FEEMA 2003). A crude update of the emission inventory showed that 80% of total particulate emissions come from industry, 11% from garbage burning and 9% from vehicles (World Bank 1997). The climate is tropical, hot and humid type, with an annual average temperature of 24.5^{0}C, high daily averages in summer (between 30^{0}C and 35^{0}C) and annual rainfalls varying from 780 to 1100 mm.

Since the emissions and levels of trace metals and particulate matter are strongly related, the heavy metal concentrations were determined in order to characterize the air quality of the region.

MATERIALS AND METHODS

Samples were taken in the period February 2002 to July 2003, every six days, during 24h, using a high volume sampler (1,1–1,7 m^3.min^{-1}) from Energética and borosilicate glass microfiber filters (Energética, Rio de Janeiro, Brazil, 254 X 203 mm, thickness 0,22 mm).

Total suspended particulate matter (TSP) was determined gravimetrically, by drying and weighing the filters to constant weight. For analysis of trace metals, the filters were extracted by adding 5mL of nitric acid (Merck Suprapur 65%), 2 mL of hydrochloric acid (Merck Suprapur 36%) and 10 mL of ultrapure water (18MΩ.cm^{-1} of specific resistivity) in a pyrex tube and standing for two hours at 95^{0}C. The extracted solution was filtered, made to 50mL with ultrapure water and kept in pre-cleaned polyethylene bottles in the refrigerator until analysed (Serrano et al. 1996; Beceiro Gonzalez et al. 1997).
Trace metal analysis was performed by Inductively Coupled Plasma Atomic Emission, Optima 3000 Perkin Elmer, with an atomic absorption spectrophotometer (ICP–OES), following Method IO–3.4 (1999).

Correspondence to: G. Arbilla

Detection limits were calculated as 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 range of the reference material.

Experimental data were analysed by CA (cluster analysis) using the STATISTICA (Statsoft) programme.

RESULTS AND DISCUSSION

The geometrical means values observed for TSP are shown in Figure 1. Primary and secondary national standards are 80 μg m^{-3} and 60 μg m^{-3}, respectively (CONAMA 1990). The geometrical means for the seven districts were (in units of μg m^{-3}): Belford Roxo (BR), 144.2 $\pm$ 59.2; Japeri (JP), 190.7 $\pm$ 47.8; Magé (MG), 55.4 $\pm$ 15.9; Mesquita (MQ), 241.6 $\pm$ 40.0; Nova Iguaçu (NI), 184.3 $\pm$ 50.4; Queimados (QU), 112.6 $\pm$ 60.0 and São João de Meriti (SJ), 149.2 $\pm$ 33.9. These values are higher than mean annual concentrations reported for Tokyo (Japan), Montreal (Canada), Sydney (Australia) and some Latin American urban areas as Caracas (Venezuela), San Salvador (El Salvador) and Cordoba (Argentine). They are also higher than values reported for the Industrial District of Santa Cruz (87 μg m^{-3}) and Cinelandia (133 μg m^{-3}), both in the RJMA (Quiterio et al. 2004a, Quiterio et al. 2004b). Similar mean values were reported for Buenos Aires (Argentine), São Paulo (Brazil), Guayaquil and Quito (Equador) and Lima (Peru) (Baldosano et al. 2002).

Mean values for the concentrations of trace metals are presented in Figure 2. Also, for comparison, results for typical urban and remotes regions as well as USA National Standards and the WHO guidelines are shown.

In all districts, excepting MG, mean values for Mn, were 2.9 – 8.3 higher than reported values for La Plata (Argentine) (Bilos et al. 2001) and 1.8 – 3.8 higher than reported values for Milan, Italy (Rizzio et al. 1998). In NI, Cd mean concentration was 2.2 and 2.8 higher than values recommended by US-EPA (ATSDR 2002) and WHO, respectively (WHO 2002). In all districts, excepting MG, mean values for Fe were 2.7 – 7.8 higher than reported values for Birmingham, UK (Harrinson et al., 1996) and 1.8 – 3.8 times higher than the mean value for Tito Scalo, Italy (Ragosta et al. 2002). Mean concentrations for Zn were higher than typical values in European and North American cities (Lantzy & Mackenzie 1979). Values were also 1.1 – 88 times higher than reported concentrations for industrial areas such as Southeast Chicago, USA (Sweet et al. 1993) and La Plata, Argentina (Bilos et al. 2001).
A similar situation was found for Cu, with mea values 2.7 – 18.0 times higher than the mean value for Southeast Chicago, USA (Sweet et al. 1993).
Al concentrations were extremely high in comparison with typical values for urban areas (TPAl 1999).

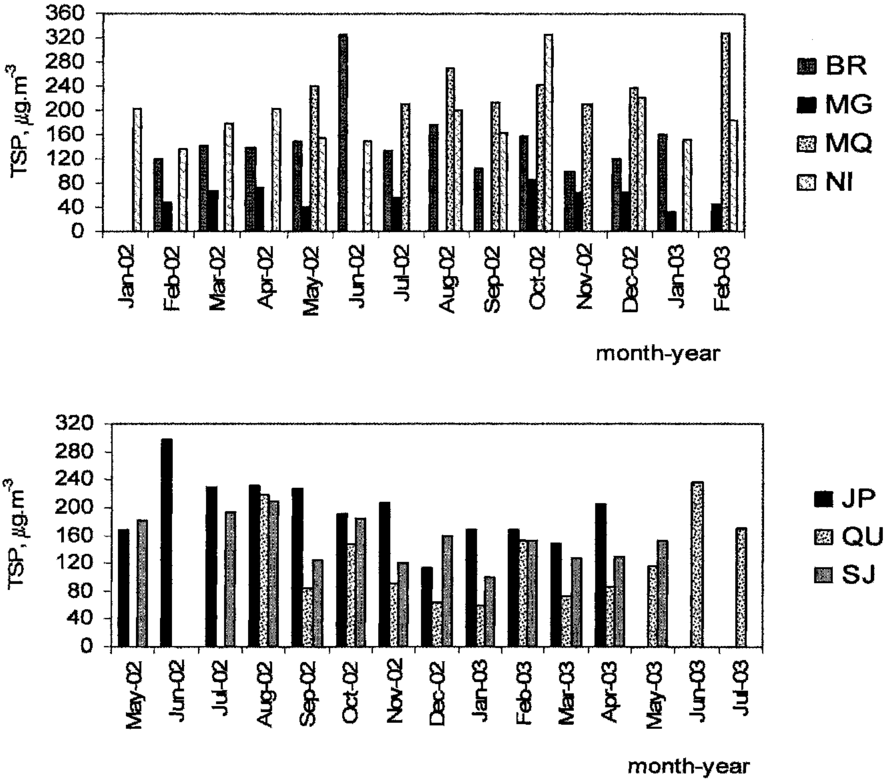

Figure 1. Geometrical means values of TSP (µg m^{-3}) for districts BF area in the period February 2002 to July 2003.

Excepting Queimados, mean concentrations for Ni were 1.2 – 2.4 higher than recommended values (ATSDR 2002). Pb levels were comparable or lower than remote area typical values (Veron et al. 1992) since in Brazil, it was banned as a gasoline additive and is not used since 1992. According to Brazilian legislation, Pb concentration should be lower than $0.005g.L^{-1}$, the detection limit of ASTM D-3237 Method (ANP 2004).

The mean value for Cr concentrations was lower than the US-EPA standard (ATSDR 2002). The large Na and K levels are probably due to the proximity of the Atlantic coast and the biomass burn.

In order to get some insight about the sources of metals and the main correlation among them, cluster analysis (Ward`s method; Euclidean distances) and principal component analysis (PCA) were applied. Since results for both methods were similar, only the dendograms are shown in Figure 3.

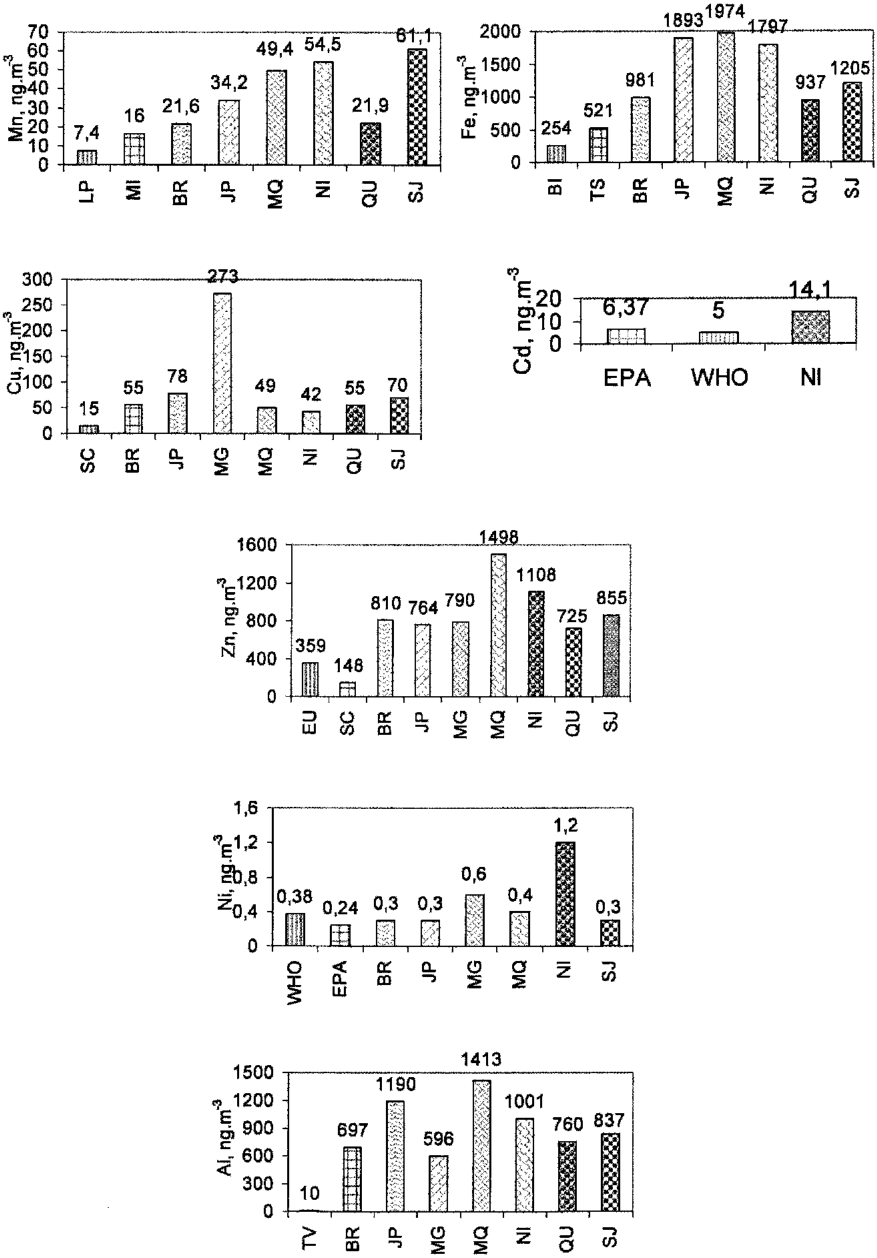

Figure 2. Mean values for the concentrations of trace metals in seven districts of BF. Typical values for industrial and urban areas and quality of regulatory agencies are shown for comparison (La Plata – LP; Milan, Italy – MI;Birmingham, UK –BI; Tito Scalo, Italy – TS; European and North American cities – UE; Southeast Chicago, USA – SC; typical values –TV)).

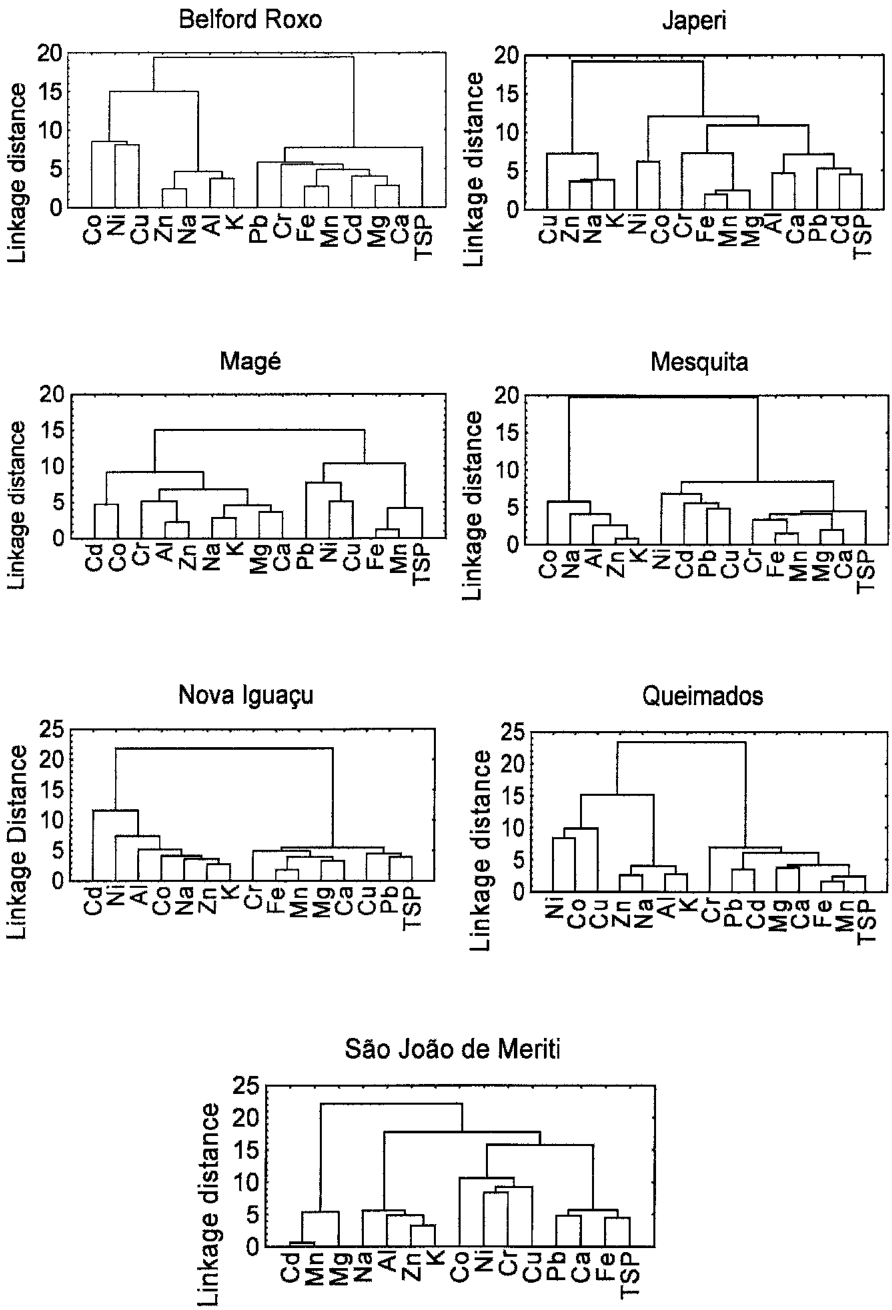

Figure 3. Dendograms of the cluster analysis of metals and TSP.

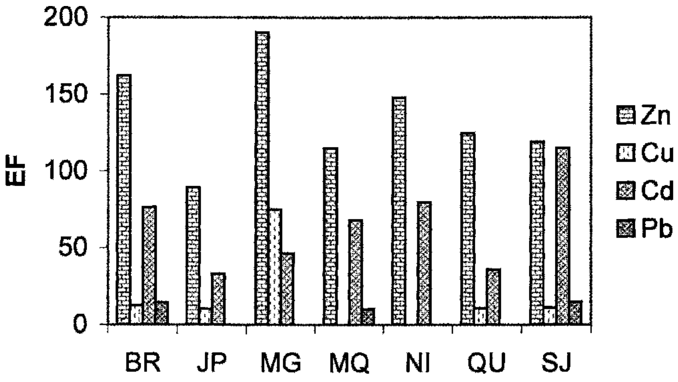

Figure 4. Enrichment factors for the mean concentrations.

The statistical analysis fails to show a geographical distribution of emission sources and a clear distribution between natural and anthropic sources. For each metal a different distribution of metals in the dendogram is found. This fact may be attributed to the presence of many sources for each pollutant and transport processes within Basin III and shows that this region has common characteristics regarding air pollution.

Enrichment factors (EF) for the mean concentrations (Caroli et al. 1996) were calculated using K as reference. For Ca, Mg, K, Na, Mn, Fe, Cr, Co, Ni and Al, the values are in the range 0.0 – 2.0, suggesting a natural input. Zn, Cu, Cd and Pb values are in the range 10.2 - 190.4 confirming that for these elements anthropic sources prevail over natural inputs (Figure 4). A similar result was obtained in a previous work for downtown Rio de Janeiro (Quiterio et al. 2004b). These metals, are probably due to local industrial activities (metallurgical and structural steel manufacture, solvent and paint production) and to diesel and high duty vehicles emissions. The high concentrations of Al may be attributed to mineral extraction activities and to dust suspension in areas without paved streets and parklands. For this reason, EF fails to identify this metal as being of anthropic origin.

Acknowledgments. We thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for financial support.

REFERENCES

ANP (2004) ASTM D-3237 Method. Agência Nacional do Petróleo. www.anp.gov.br.

ATSDR (2002) Agency for Toxic Substances and Disease Registry. www.atsdr.cdc.gov/toxprofiles/tp11-c8.pdf.

Baldasano JM, Valera E, Jimenez P (2002) Air quality data from large cities. Sci Tot Environ 307:141-165

Beceiro-González E, Andrade-Garda JM, Serrano-Velasco E, Lópes-Mahía P (1997) Metals in airborne particulate matter in La Coruña (NW Spain). Sci Tot Environ 196:131-139

Bilos C, Colombo JC, Skorupka CN, Rodrigues Presa MJ (2001) Sources, distribution and variability if airborne trace metals in La Plata City area, Argentina. Environ Pollut 111:149-158

Caroli, S, La Torre, F, Petrucci, F, Violante, N. (1996). Element speciation in bioinorganic chemistry. New York. Wiley-Interscience Publication

CONAMA (1990) Padrões Nacionais de Qualidade do Ar (06-28-1990). http://www.lei.adv.br/conama.htm

FEEMA (2003) Fundação Estadual de Engenharia do Meio Ambiente. http:// www.feema.rj.gov.br

Harrinson, RM, Smith, DJT, Luhana, L. (1996). Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. Environ Sci Technol 30: 825-832

Lantzy RJ, Mackenzie FT (1979) Atmospheric trace metals: Global cycles and assessment of man's impact. Geochim Cosmochim Acta 43:511-525

Mage D, Ozolins G, Peterson P, Webster A, Orthofer R, Vanderweerd V, Gwynne M (1996) Urban air pollution in megacities of the world. Atmos Environ 30:681-686

Method IO-3.4 (1999) Determination of metals in ambient particulate matter using inductively coupled plasma (ICP) spectroscopy. http://www.epa.gov/ttn/amtic /inorg.html

Quiterio, SL, Arbilla, G, Silva, CRS, Escaleira, V (2004a). Metals in airborne particulate matter in the Industrial District of Santa Cruz, Rio de Janeiro, in an annual period. Atmos Environ 38: 321-331.

Quiterio, SL, Arbilla, G, Escaleira, V, Silva, CRS, Maia, LFPG (2004b). Metals in airborne particulate matter in downtown Rio de Janeiro (Brazil). Bull of Environ Contam Toxicol 72: 916-922

Ragosta, M, Caggiano, R, Démilio, M, Macchiato, M (2002). Source origin and parameters influencing levels of heavy metals in TSP, in an industrial background area of Southern Italy. Atmos Environ 36: 3071-3087.

Serrano E, Beceiro E, López P, Prada D (1996) Heavy metals determination in atmospheric particulate matter of La Coruña. Quimica Anal 15:38-44

Sweet, CW, Vermette, SJ, Landsberg, S (1993). Sources of toxic trace elements in urban air in Illinois. Environ Sci Technol 27: 2502-2510.

TPAl (1999) Toxicological profile for aluminum. Atlanta, Geórgia: U.S. Departament of Health and Human Services. Public Health Services. Agency for Toxic Substances and Disease Registry.[s.v : s.n], July 1999. 393p

Ure, AM, Davidson, CM (1995). Chemical speciation in the environment. London, Blackie Academic & Professional. 408p.

WHO (2002) World Health Organization Guidelines for air quality. Geneva. http://www.medwebplus.com/subject/Guidelines/Public_Health

World Bank (1997). Brazil: Managing environmental pollution in the State of Rio de Janeiro. www.worldbank.org/la1er/rio-e.htm