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Metals in Airborne Particulate Matter in Downtown Rio de Janeiro, Brazil

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Anthropogenic emissions are the main source of toxic trace metals in urban areas where several sources, as vehicle exhausts and energy production, release large quantities of pollutants into the atmosphere (Bilos et al. 2001). To our knowledge, there are no reports of metals in airborne particulate matter for the city of Rio de Janeiro. The metropolitan area of Rio de Janeiro, located on the Atlantic coast of Brazil, has about six million inhabitants distributed over an area of 1255 km^2. The climate is tropical, hot and humid type, with an annual average temperature of 22^0C, high daily averages in summer (between 30^0C and 32^0C) and annual rainfalls varying from 800 to 1000 mm. The main pollution problem in this city 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; SMAC 2003).

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

The study area, Cinelândia, is located in the center of the city of Rio de Janeiro. The area is representative of downtown vehicle fleet, including light duty and diesel fueled heavy duty vehicles.

Samples were taken period September 2001 to August 2002, 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) masses were determined by gravimetry, 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 ($18M\Omega.cm^{-1}$ of specific resistivity) in a pyrex tube and stilling for two hours at 95^0C. The extracted solution was filtered, completed to 50mL with ultrapure water

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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 – AES), following Method IO – 3.4 (1999).

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.

Detection and quantification limits were calculated as 0.003 mg L^{-1} for Mn, Zn, Cr and Fe, 0.015 mg L^{-1} for Al and Cd, 0.006 mg L^{-1} for Cu, 0.012 mg L^{-1} for Ni and 0.018 mg L^{-1} for Pb.

RESULTS AND DISCUSSION

The monthly mean values observed for TSP are shown in Figure 1. Primary and secondary standards for Brazil are shown for comparison (CONAMA 1990). The geometric mean for the period (September 2001 – August 2002) was 133 ± 48 μg m^{-3}, which is 1.66 times the primary national standard and 2.2 secondary national standard. This value is 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). Similar mean values were reported for Buenos Aires (Argentine), São Paulo (Brazil), Guayaquil (Equador) and Lima (Peru) (Baldosano et al. 2002).

Mean values and amplitudes for the concentrations of trace metals are presented in Table 1 (54 samples). Results for typical urban and remotes regions as well as USA National Standards and the WHO guidelines are shown for comparison.

The concentrations of Mn, Fe, Cu, Cr, Ni, Cd and Pb were 1.6 – 53 times lower than those reported for USA and European cities (Lantzy and Mackenzie 1979). The values of Cr and Pb were also lower than those reported for the downtown area in La Plata (Argentine). Mn, Fe, Zn, Cu and Cd levels are comparable to the values registered in downtown area in La Plata (Argentine) (Bilos et al. 2001). Al levels were 47 – 1186 higher than typical values for urban areas and Ni mean concentration was 645 times higher than EPA standard.

The concentrations of airborne metals were relatively low in comparison to values reported for not highly polluted cities. This fact reflects the main activities developed in the area (administrative and commercial) and suggest that the main emission sources are vehicle exhausts.

The higher levels of TSP may be attributed to diesel vehicle emissions which represent about 15 % of the total fleet.

Table 1. Concentrations of trace metals in particulate matter for Cinelândia (n=54) compared with other urban and remote areas around the world and regulatory agencies guidelines.

Local	Concentration ($ng.m^{-3}$)														
	Ca	**Mg**	**K**	**Na**	**Mn**	**Fe**	**Zn**	**Cu**	**Cr**	**Co**	**Ni**	**Al**	**Cd**	**Pb**	**Ref**
mean value	2203.6	512.5	610.3	2546.0	24.1	1212.8	628.3	70.7	2.1	0.4	3.1	474.6	0.3	14.9	1
range	40.9 - 5668.2	115.6 - 1301.4	0 - 4472.4	0 - 4370.6	1.9 - 55.1	169.8 - 3322.2	10.2 - 4299.0	20.9 - 145.2	0 – 4.6	0 - 2.2	0 – 10.3	38.4 - 2619.6	0 - 3.1	1.5 - 41	1
Regulatory Agencies															
EPA	-	-	-	-	500	-	-	-	100	-	0.24	-	6.37	1500	2
WHO	-	-	-	-	150	-	-	-	10^3	-	0.38	-	5	500	3
Urban area															
Typical value	-	-	-	-	-	-	$<10^3$	20-200	10-30	-	-	0.4-10	40	-	4
GAV	-	-	-	-	149	3710	359	110	32	-	-	-	-	-	5
Remote area															
Atlantic Ocean (30^0N-43^0N)	-	-	-	-	0.05-9.7	3.4-240	0.3-154	0.12-56	0.07-1.1	-	8-12	-	0.003-0.62	0.10-64	6
Antarctica	-	-	-	-	0.004-0.99	0.22-46.8	0.018-24.8	0.025-1.17	0.0025-0.10	-	0.03-0.06	-	0.005-0.5	0.07-5.41	7

GAV - General average values – USA and European cities

Air quality standards (EPA = Environmental Protection Agency, USA; WHO = World Health Organization)

TP = Toxicological Profile Atlanta, Geórgia: U.S. Departament of Health and Human Services. Public Health Services. Agency for Toxic Substances and Disease Registry.[s.v : s.n] (TPAl, 1999; TPCd, 1999; TPCo, 1992; TPCr, 2000; TPCu, 1990; TPMn, 2000; TPNi, 1997; TPPb, 1999; TPZn)

Ref.: 1) This study; 2)www.epa.gov.br; 3) WHO; 4) TP; 5) Lantzy & Mackenzie,1979; 6) Duce et al., 1975; Veron et al., 1992; 7) Zoller et al., 1974; Loureiro et al., 1992; Rädlein and Heumann, 1992; Khandekar et al., 1992

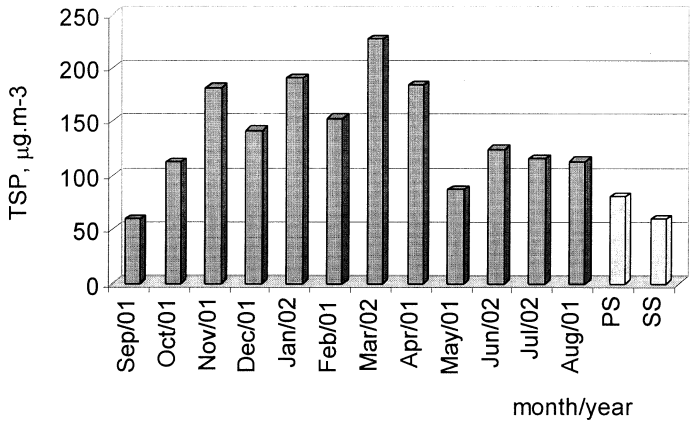

Figure 1. Monthly mean values of TSP (µg m^{-3}) for Cinelândia area in the period September 2001 to August 2002. Primary (PS) and secondary (SS) national standards are also shown.

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.

Initially, the metals and TSP levels were taken into account for the analysis. The correlation matrix [54 x 16] gave three clusters and three significant principal components (PCs), which explain 79% of the data variance. The dendogram is presented in Figure 2 and the PCA results in Table 2. Three main groups may be identified.

If TSP concentrations are not considered in the construction of the correlation matrix [43 x 15], similar results are obtained.

The main PC1 components (Ca, Mg, Mn and Fe) are probably attributed to natural inputs, mainly soil-derived dust. Pb and Cu are probably due to anthropogenic emissions. Pb can not be ascribable to motor vehicle emissions since it has been banned, in Brazil, since 1995.

Enrichment factors (EFs) relative to continental crustal abundances were also calculated to help the identification of anthropic and natural sources (Bilos et al. 2001, Taylor et al. 1995, Webelements 2003). Average values are 77 and 42 for Pb and Cu, respectively, confirming the importance of anthropogenic inputs.

Ni has been identified as one of the main pollutants in the industrial and suburban areas of Rio de Janeiro. However, the calculated EF is 1.7 which is compatible to prevailing natural source.

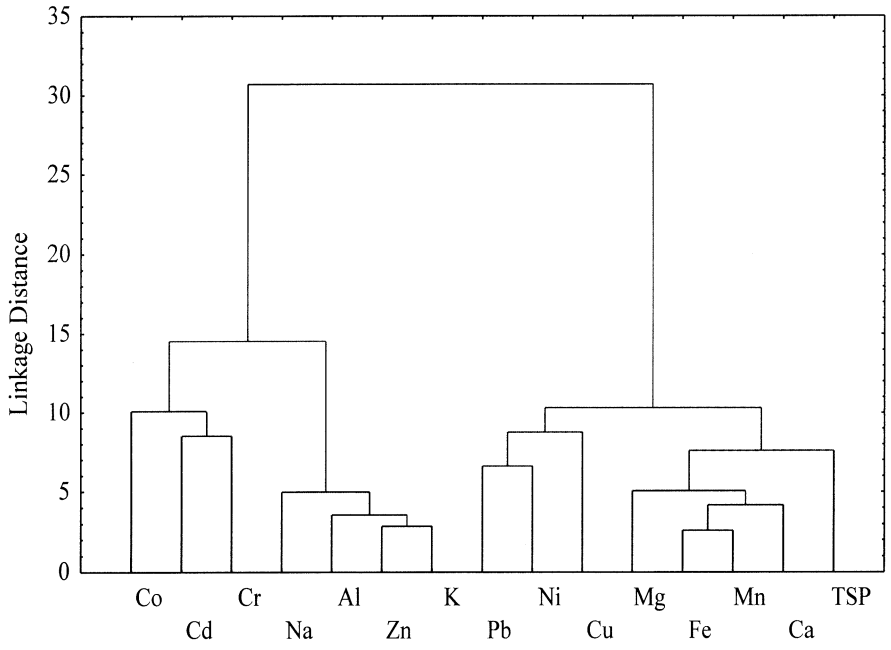

Figure 2. Dendogram of the cluster analysis of metals and TSP levels.

PC2 components may be associated to vegetation burning (K), marine aerosol (Na) and dust resuspension (Al). The high Al concentrations may be related to the composition of soils in the Metropolitan area of Rio de Janeiro (gnaisse rocks). The average EF for Zn was calculated as 324 reflecting an anthropogenic input.

Regression analysis shows a correlation between, Mn and Ca (R = 0.88), Ca and Mg (R= 0.77), Mn and Mg (R = 0.81) and, also, between Fe and Mn (R = 0.94) and Ca (R = 0.85) and Mg (R = 0.84) and between K and Na (R=0.81), Na and Al (R = 0.72); K and Al (R=0.90), confirming that they probably have the same origin.

EFs for Cr and Co were lower than 1.0 and for Cd an average value of 126 was obtained.

The EFs for Pb, Cu, Zn and Cd suggest anthropogenic inputs while for the other metals the main contributions are natural processes.

Similar results were obtained by Bilos et al. (2001) for La Plata (Argentine). These data are, to our knowledge, the first report on airborne particulate metals for a Brazilian city and can be considered an index of air quality in the urban area of Rio de Janeiro.

Table 2 - Results of PCA for the correlation matrix [54 x 16]. All metals and TSP were considered for the construction of the matrix.

PC	1	2	3
Eigenvalues	5.4	4.1	1.4
% total variance	36.1	27.4	9.1
MP	**0.70**	-0.06	-0.36
Ca	**0.92**	0.24	0.04
Mg	**0.85**	-0.07	-0.33
K	-0.10	**0.96**	0.12
Na	-0.04	**0.85**	0.35
Mn	**0.94**	-0.13	0.01
Fe	**0.93**	-0.14	-0.02
Zn	0.03	**0.95**	0.22
Cu	0.58	0.05	-0.45
Cr	0.27	0.22	**0.75**
Co	0.37	0.21	0.19
Ni	0.63	0.12	0.12
Al	0.14	**0.95**	-0.06
Cd	-0.13	0.20	**0.69**
Pb	**0.77**	-0.03	0.26

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REFERENCES

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

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

Duce RA, Homan GL, Zoller WH (1975) Atmospheric trace metals at remote northern and southern hemisphere sites: pollution or natural? Science 187:59-61

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

Khandekar RN, Tripathi RM, Raghunath R, Sathe AP, Nambi KSV (1992) Heavy metal concentrations in air, water and rock samples at Antarctica during 1989-1990. Curr Sci 63:201-204

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

Loureiro ALM, Vasconcellos MBA, Pereira EB (1992) Trace elements determination in aerosols from the Antarctic Peninsula by neutron activation analysis. J Radioanal Nucl Chem 159:21-28

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

Raédlein N, Heumann KG (1992) Trace analysis of heavy metals in aerosol over the Atlantic Ocean from Antarctic to Europe. Int J Environ Anal Chem 48:127-150

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

SMAC (2003) Secretaria de Meio Ambiente Prefeitura da Cidade do Rio de Janeiro. http://www.rio.rj.gov.br/smac/

Taylor SR, McLennan SM (1995) The Continental crust: its comparison and evolution. Rev Geophys 33:241-265

Veron A, Church TM, Patterson CC, Erel Y, Merril JT (1992) Continental origin and industrial sources of trace metals in the Northwest Atlantic troposphere. J Atmos Chem 14:339-351

Webelements (2003) Abundance in Earth's crust. http://www.webelements.com/ /webelements/properties/text/definitions/abund-crust.html

WHO (2000) World Health Organization Guidelines for Air Quality. Geneva. http://www.medwebplus.com/subject/Guidelines/Public_Health

Zoller WH, Gladney ES, Duce RA (1974) Atmospheric concentrations and sources of trace metals at the South Pole. Science 183:198-200