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Evolution of Particulate Matter and Associated Metal Levels in the Urban Area of Rio de Janeiro, Brazil

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Abstract The levels of total suspended particles and airborne particulate trace metals were determined in three locations. Two of these locations are in the metropolitan area of Rio de Janeiro, where the main source of pollution is vehicular traffic. The remaining location is in a suburban area characterized by industrial and vehicular emissions, as well as natural input. Enrichment factors found in the downtown area for Zn, Cu, Pb and Cd were in the interval 21-3237, indicating an important contribution of anthropogenic sources. In the suburban area, Zn levels were unusually high (596.8–5475.4 ng m^{-3}) and may be attributed to the proximity of a company that produces lubricants and lubricant additives.

Keywords Airborne particulate matter · Trace metals · Industrial sources · Vehicular emissions

Non-attainment of total suspended particulate matter (TSP) national air quality standards (CONAMA 1990) is a frequent problem encountered in the Rio de Janeiro metropolitan area (RJMA), mainly in the Basin III region, which includes Baixada Fluminense and the northern region of the city of Rio de Janeiro. Previous results obtained in seven districts of Baixada Fluminense (Quiterio et al. 2005), including Belford Roxo, during the period of 2002–2003 showed TSP geometric means between 55.4 ± 15.9 and 241.5 ± 40.0 μg m^{-3}. Enrichment factors (EF) showed that Zn, Cu, Cd and Pb were present due to anthropogenic emissions. Zn, Cu and Cd levels were high compared to other urban and industrial areas. The mean concentrations of Zn, Cu and Cd were 1–88, 3–61 and 3–130 times higher, respectively, than the reported values for other industrial areas. Data obtained downtown in 2001–2002 (Quiterio et al. 2004a) showed a TSP geometric mean of 133 ± 48 μg m^{-3}. The EF values for Pb, Cu, Cd and Zn suggest anthropogenic inputs of these metals, while the other main contributions are natural sources.

The purpose of this study was to determine the levels of total suspended particles (TSP) and airborne particulate trace metals in three locations, Belford Roxo, Maracanã and São Cristóvão, in order to assess the evolution of air quality in Basin III.

Materials and Methods

The RJMA and Basin III areas are shown in Fig. 1. RJMA is a region of approximately 5,645 km^2 formed by 20 districts. Basin III accounts for 8% of the total area. Because Basin III is the most worrisome area of the RJMA in terms of air quality and its health impact, a new study in collaboration with the local environmental protection agency (INEA) has been developed in this region. Baixada Fluminense is a suburban region characterized by urban and industrial sources of pollution, as well as an important contribution

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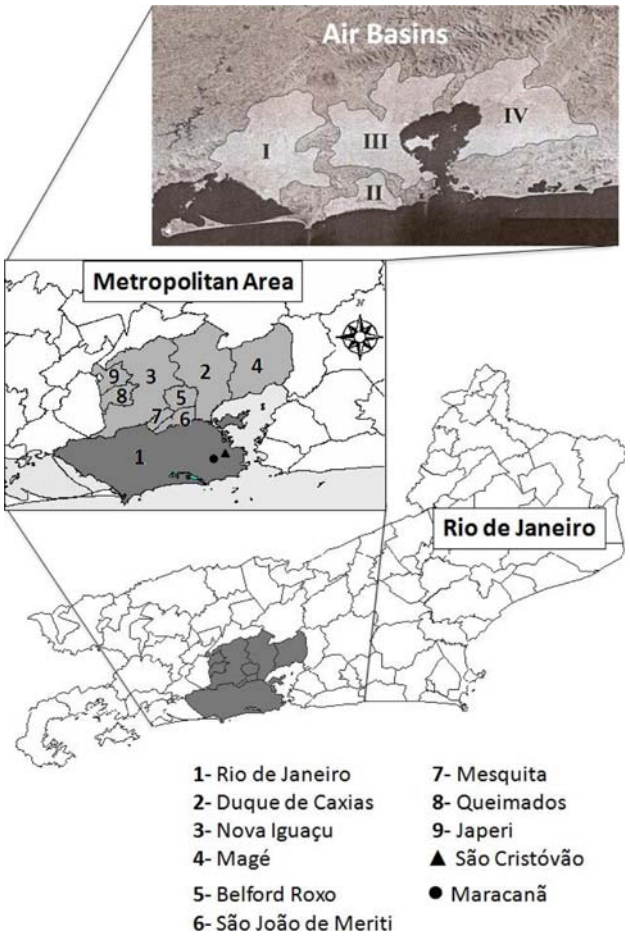

Fig. 1 Location of the sampling sites

from dust suspension due to mineral extraction activities and the lack of basic infrastructure such as paved roads. The northern region of the city includes downtown and some commercial and residential neighborhoods, such as Maracanã and São Cristóvão. There, the main source of pollution is vehicular traffic fueled by gasohol (gasoline with 24% ethanol), neat ethanol, compressed natural gas and diesel. A total of 55 samples were taken from March to November of 2007. Sampling was performed using high volume samplers (Energética) and borosilicate glass microfiber filters (Energética, 254 × 203 mm, thickness 0.22 mm). An aspiration flow rate of 1.1–1.7 m^3 min^{-1} and 24 h sampling periods were used.

TSP levels were determined gravimetrically by drying and weighing the filters to constant weight. For the trace metals analysis, the same procedure as previous studies was used (Quiterio et al. 2004a, b; Loyola et al. 2006). Filters were extracted by adding 5 mL of nitric acid (Merck Suprapur 65%), 2 mL of hydrochloric acid (Merck Suprapur 36%) and 10 mL of ultrapure water (18 MΩ cm^{-1} of specific resistivity) to a Pyrex tube on a heating plate that was left to stand for 2 h at 95°C (Fernández et al. 2000; Method IO-3.4 1999).

The extracted solutions were filtered using Whatman no. 41 (WH1441-110) filters, completed to 50 mL with ultrapure water and kept in refrigerated pre-cleaned polyethylene bottles until the analyses (Serrano et al. 1996; Beceiro-González et al. 1997). The same procedure was followed for filter and reagent blanks. The metal content of the blanks for Ca, Mg, Mn, Fe, Zn, Cu, Co, Ni, Al, Cd and Pb was less than 5% of sample average content. For Cr, it represented less than 8%.

Metals were determined by ICP-OES (inductively coupled plasma optical emission spectroscopy) according to method IO-3.4. The detection limits and method accuracy were determined following Method IO-3.4. Detection limits were computed as three times the standard deviation of the distribution of outputs for ten repeated standard measurements that contained no metals (Boss and Fredeen 1999). These limits were calculated as 80 ng m^{-3} for Al and Cr, 10 ng m^{-3} for Zn, 8 ng m^{-3} for Fe, Co and Cu, 4 ng m^{-3} for Mn, 2 ng m^{-3} for Ni, 0.2 ng m^{-3} for Cd and 0.1 ng m^{-3} for Pb.

Method accuracy was evaluated using a standard reference material (SRM, 2783 Air particulate on Filter Media-NIST). Three samples of the reference material were evaluated in triplicate and the results were compared to the concentration reported in the certificate of analysis. The obtained concentrations differed by less than 8%. The concentrations of all of the samples, as well as that of SRM, were in the range of the reference material (3–8%). All samples and the SRM were analyzed in triplicate, and differences of less than 1% were considered acceptable.

Results and Discussion

The measured TSP levels are shown in Fig. 2. The mean values were calculated as 211.2 ± 40.4, 64.2 ± 21.3 and 102.6 ± 30.7 μg m^{-3} in Belford Roxo, Maracanã and São Cristóvão, respectively. The primary and secondary national standards (annual geometric mean) are 80 and 60 μg m^{-3}, respectively. For 24 h sampling, the primary and secondary national standards are 240 μg m^{-3} and 150 μg m^{-3}, respectively (CONAMA 1990).

Because data in this study were taken during a limited period of seven months and were not collected every 6 days, these results are not directly comparable with the standards. The results obtained in Maracanã and São Cristóvão were not substantially different from those previously determined for downtown, but many values were higher than the air quality national standards. The results for the area of Belford Roxo showed a clear deterioration

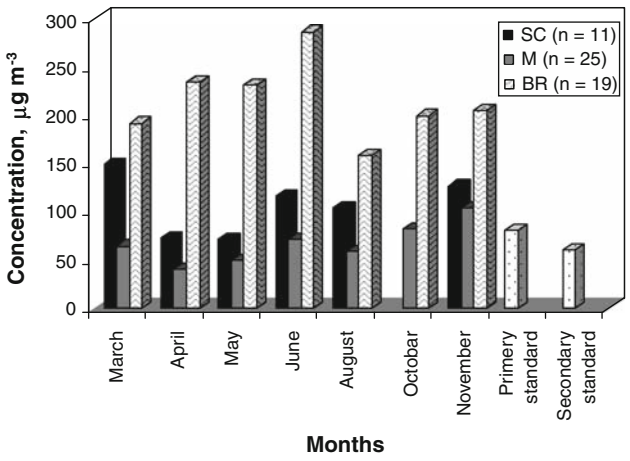

Fig. 2 TSP levels determined in Belford Roxo (BR), Maracanã (M) and São Cristóvão (SC) during the period of March to November, 2007. The total number of samples is indicated in the *parentheses*

of the atmospheric conditions, with TSP levels 2.0–3.6 times higher than the primary national standard.

The mean values of the TSP metal concentrations are presented in Table 1. For comparison, results for other areas of the RJMA, as well as typical urban values, USA national standards and WHO guidelines are included. The levels of individual metals in Maracanã and São Cristóvão were similar to those previously determined in downtown. In Belford Roxo, concentrations were higher than those previously reported for the 2002–2003 period. This could be due to many reasons, but is probably because a different sampling location was used. In the previous study, samples were collected in a residential area, while in this work the sampling location was in a region of industrial suppliers, including one of the more important Brazilian pharmaceutical companies, a manufacturer of lubricant additives for engine oils, gasoline and diesel fuels, and a company

Table 1 Mean values of the TSP metal concentrations in Belford Roxo (BR), Maracanã (M) and São Cristóvão (SC), RJMA, Brazil, for the period of March–November, 2007

Location	Concentrations (ng m^{-3})												References
	Ca	Mg	Mn	Fe	Zn	Cu	Cr	Co	Ni	Al	Cd	Pb	
BR (N = 19)	1700.1	611.2	35.6	1767.4	3511.0	87.2	1.2	2.7	4.1	1678.7	0.0	12.0	This study
BR – Min	0.0	119.7	4.2	239.7	596.8	29.6	0.7	0.0	0.0	0.0	0.0	0.0	
BR – Max	4591.3	993.9	43.9	2335.4	5475.4	87.3	4.5	16.1	4.3	2959.4	0.5	24.0	
M (N = 25)	1719.6	413.5	21.0	942.8	3351.5	149.5	0.7	3.8	3.0	1837.5	0.0	7.9	This study
M – Min	0.0	165.0	6.5	235.9	0.0	23.7	0.0	0.0	0.0	329.2	0.0	0.0	
M – Max	9233.9	905.7	66.5	3702.0	9050.9	1356.7	8.8	25.3	7.2	7432.2	0.0	25.9	
SC (N = 11)	1233.6	457.8	23.5	1162.7	2991.9	96.7	88.5	3.4	3.1	1161.5	0.0	13.0	This study
SC – Min	0.0	211.9	7.5	384.8	69.0	33.5	0.4	0.0	0.0	0.0	0.0	0.0	
SC – Max	5061.2	1375.9	25.8	2821.2	10787.7	227.0	5.9	16.6	8.0	6091.0	0.0	72.4	
BR (N = 40)	1109.5	228.4	21.6	980.7	810.4	55.0	1.7	0.5	0.3	697.3	0.5	12.2	Quiterio et al. (2005)
JP (N = 39)	1108.6	452.5	34.2	1892.6	763.6	77.7	2.0	0.4	0.3	1189.5	0.3	7.1	Quiterio et al. (2005)
MQ (N = 23)	3123.2	569.8	49.4	1974.3	1498.1	49.3	3.8	1.0	0.4	1412.9	1.1	21.7	Quiterio et al. (2005)
NI (N = 35)	1862.6	414.1	54.5	1796.9	1107.9	42.0	3.1	1.2	1.2	1001.0	14.1	11.9	Quiterio et al. (2005)
QU (N = 48)	802.3	199.4	21.9	936.9	725.4	55.1	1.2	0.2	0.1	760.3	0.3	6.4	Quiterio et al. (2005)
SJ (N = 49)	1488.8	328.6	61.1	1204.9	854.6	70.4	2.7	0.2	0.3	837.1	1.0	17.6	Quiterio et al. (2005)
Regulatory agencies													
EPA	nda	nda	500	nda	nda	nda	100	nda	0.24	nda	6.37	$1.5.10^3$	ATSDR[a] (2002)
WHO[b]	nda	nda	150	nda	nda	nda	10^3	nda	0.38	nda	5	500	WHO (2002)
Urban area													
GAV	nda	nda	149	3710	359	110	32	nda	30	nda	2	790	Lantzy and Mackenzie (1979)
Downtown, Brazil	2204	513	24	1213	628	71	2.1	0.4	3.1	475	0.3	15	Quiterio et al. (2004a)

Values for other locations and quality standards of various regulatory agencies are also shown

BR Belford Roxo, *JP* Japeri, *MG* Magé, *MQ* Mesquita, *NI* Nova Iguaçu, *QU* Queimados, *SJ* São João de Meriti, *M* Maracanã, *SC* São Cristóvão, *GAV* general average values—USA and European cities; *nda* no data available, *nd* no detected; *Max* maximum, *Min* minimum

[a] Air quality standards, *EPA* Environmental Protection Agency, USA

[b] *WHO* World Health Organization

that manufactures clutch facings and railroad brake shoes and pads.

Enrichment factors (EF) were calculated using Mg as a reference (Caroli et al. 1996; Wedepohl 1995). In Belford Roxo, the EF factors were calculated as 2294, 120, 50 and 21 for Zn, Cu, Pb and Cd, respectively. In Maracanã, the values were 3237, 305 and 48 for Zn, Cu and Pb, respectively. In São Cristóvão, the values 2610, 178, 71 and 31 for Zn, Cu, Pb and Cd, respectively, were obtained. These values suggest a possibly significant role for anthropogenic processes at those sites. The concentrations of Zn were unusually high. Several tests were performed with blank samples in order to discard filter contamination and no other source was identified. Zn has been attributed to brake wear and oil additive emissions. The proximity of a company that produces lubricants and lubricant additives may be related to the increased Zn levels. It should be noted that this company accounts for 30% of the total production of Brazil. The manufacture of brake shoes and pads may also contribute to Zn emissions. In any event, an unknown source of contamination should not be discounted.

As previously obtained (Loyola et al. 2009) for a bus station with a high contribution of diesel exhausts, the data for Belford Roxo showed high correlations (0.71–0.95) for Ca, Mg, Fe and Al in all samples. Furthermore, Zn and Fe showed a high correlation (0.81), while the value for Zn and Cu was very low. The pattern observed may be attributed to the contribution of several sources, such as tail pipe emissions, brake wear, tire wear, resuspended dust and some industrial emissions.

In RJMA, the most important air pollution problems are related to the high level of particulate matter and associated compounds (metals and polycyclic aromatic hydrocarbons). Numerous scientific studies have provided evidence that particulate matter in ambient air is associated with adverse health effects and the increase of daily mortality, even at levels below air quality standards. Clearly, the size of particles is directly linked to their potential to cause health problems. In Brazil, both total particulate matter and inhalable particles (PM_{10}) are considered *criteria pollutants* and national quality standards have been set for them. In Rio de Janeiro, in spite of legislation, many monitoring stations are not provided with PM_{10} samplers and there is not enough information concerning the impact of air pollution on public health. The TSP levels observed in this study show the poor air quality of the studied areas. These results are probably due to anthropogenic input, mainly vehicular emissions. In Belford Roxo, the situation is worse due to industrial emissions and the lack of basic infrastructure. How the observed contamination problems affect the health of people living in this area still needs a closer and more detailed assessment. The levels of fine particles should be determined in order to assess the potential risks to public health.

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