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Traffic and catalytic converter – Related atmospheric contamination in the metropolitan region of the city of Rio de Janeiro, Brazil

Lílian Irene Dias da Silva [a], Jorge Eduardo de Souza Sarkis [b], Fátima Maria Zanon Zotin [c], Manuel Castro Carneiro [a], Arnaldo Alcover Neto [a], Alzira dos Santos Amaral Gomes da Silva [d], Mauri José Baldini Cardoso [e], Maria Inês Couto Monteiro [a,*]

[a] *Coordenação de Análises Minerais, Centro de Tecnologia Mineral – CETEM, Av. Pedro Calmon 900, Cidade Universitária, CEP 21941-908 Rio de Janeiro, R.J., Brazil*
[b] *Centro de Lasers e Aplicações, Instituto de Pesquisas Energéticas e Nucleares – IPEN, Av. Lineu Prestes 2242, Cidade Universitária, CEP 05508-000 São Paulo, S.P., Brazil*
[c] *Instituto de Química, Universidade do Estado do Rio de Janeiro, Rua São Francisco 524, Maracanã, CEP 20550-900 Rio de Janeiro, R.J., Brazil*
[d] *Departamento de Planejamento, Fundação Estadual de Engenharia do Meio Ambiente – FEEMA, Rua Fonseca Teles 121, São Cristóvão, CEP 20940-200 Rio de Janeiro, R.J, Brazil*
[e] *CENPES/PETROBRAS S.A., Av. Horácio de Macedo 950, Cidade Universitária, CEP 21941-915 Rio de Janeiro, R.J., Brazil*

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Abstract

In this work, 24-h PM_{10} samples were collected in Rio de Janeiro, Brazil, and analysed for trace elements (Cd, Ce, Cu, La, Mo, Ni, Pb, Pd, Rh, Sb and Sn). The sampling was carried out at five locations (Bonsucesso; Centro, downtown city; Copacabana; Nova Iguaçu and Sumaré) with different traffic densities and anthropogenic activities. An analytical method based on the EPA method for the determination of trace elements in airborne particulate matter (PM), using ultrasonic-assisted extraction and inductively coupled plasma mass spectrometry (ICP-MS) was applied. Our results suggest that vehicular traffic is the most important source of environmental pollution at the studied sites. The presence of Mo, Pd and Rh in the analysed filters reflects an additional source of pollution caused by the erosion and deterioration of automotive catalytic converters.

Keywords: PM_{10}; Airborne particulate matter; Automotive catalytic converter; Trace elements

1. Introduction

Air pollution has been a major concern in modern urban and industrial areas (Park and Kim, 2005; Valavanidis et al., 2006; Srivastava and Jain, 2007). The problem concerning atmospheric contamination by airborne particulate matter (PM) has notably worsened in the last years due to the increase of motor vehicles, urban constructions, industries (Fernández et al., 2000) and waste incineration (Gómez et al., 2005). The release of these elements to the atmosphere can eventually affect the human health, since they can be deposited in lung tissues and other areas of the respiratory system during the breathing (Bilos et al., 2001; Yoo et al., 2002).

Elements such as Cd, Sb (Gómez et al., 2005), Pb (Gómez et al., 2001, 2005; Salma and Maenhaut, 2006), Cu (Gómez et al., 2001; Birmili et al., 2006), Ni (Park and Kim, 2005; Zotin et al., 2005), Sn (Viana et al., 2006), Ce (Morcelli et al., 2005), La (Gandhi et al., 2003), Mo (Baldanza et al., 2000; Gandhi et al., 2003),

* Corresponding author. Tel.: +55 21 3865 7338; fax: +55 21 2290 4286.
E-mail address: mmonteiro@cetem.gov.br (M.I.C. Monteiro).

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Pd, Pt and Rh (Baldanza et al., 2000; Gómez et al., 2001; Rauch et al., 2001; Lambrou et al., 2004; Morcelli et al., 2005; Bocca et al., 2006; Zotin et al., 2005) are traffic-related elements (TRE), which can be found in the atmosphere of the cities.

Cu (Birmili et al., 2006) and Sb (Gómez et al., 2005) are used as components in the brake pad material, and represent a public health concern, since the brake wear dust is partially inhalable (1–10 μm) (Birmili et al., 2006). Ni is associated to vehicular emissions, since it is used as a fuel additive (Park and Kim, 2005) and in automotive catalytic converters to minimize H_2S emissions (Zotin et al., 2005). Pb can be emitted to the atmosphere either from leaded-gasoline combustion (Zheng et al., 2004; Gómez et al., 2005), mechanical attrition (Salma and Maenhaut, 2006) or incineration of vehicle tires (Gieré et al., 2006). In 1989, Brazil was one of the first countries to remove Pb from automotive-gasoline.

The platinum-group elements (PGEs), primarily Pd, Pt and Rh are currently used in modern automotive catalytic converters for transformation of some pollutants, namely, C_xH_y, CO and NO_x, into less toxic substances (Gómez et al., 2001; Petrucci et al., 2004; Zereini et al., 2004; Morcelli et al., 2005; Bocca et al., 2006). Other elements such as Ce, La, Mo and Ni are also employed in the catalytic converter formulations (Gandhi et al., 2003; Baldanza et al., 2000; Morcelli et al., 2005; Zotin et al., 2005). In Brazil, catalytic converters based on Pd/Rh are used for gasoline vehicles (Morcelli et al., 2005), whereas Pd/Mo are used for alcohol vehicles (Baldanza et al., 2000).

In the State of Rio de Janeiro, PM_{10} glass-fiber filters are used by FEEMA, the environmental regulatory agency of the State, to monitor airborne particles up to 10 μm in aerodynamic diameter. High-volume samplers with glass fiber filters have been widely used for suspended PM collection in a number of contaminated areas because of their high collection efficiency for particulates and low flow resistance, even when they may contain relatively high levels of some trace elements as impurities (Smichowski et al., 2005).

Atmospheric concentration of trace metals in Brazil has been determined in some cities, such as Rio de Janeiro (Quiterio et al., 2004a,b), Niterói (Sella et al., 2004), Rio de Janeiro metropolitan area (Quiterio et al., 2005, 2006), Campinas (Miranda and Tomaz, 2007) and Salvador (Pereira et al., 2007). However, 24-h PM_{10} samples were collected only for Campinas and Salvador. Moreover, no report about atmospheric contamination by traffic-related elements (Ce, La, Pd, Rh and Sb) in Brazil was found.

This study presents the concentrations of trace elements collected on PM_{10} filters at five sites in the metropolitan area of City of Rio de Janeiro, Rio de Janeiro State, Brazil, from January to December 2005. Correlations between elements (Cd, Ce, Cu, La, Mo, Ni, Pb, Pd, Rh, Sb, Sn) and PM_{10} concentrations were determined by Pearson's correlation analysis. Clusters analysis was applied to the PM_{10} levels.

2. Experimental

2.1. Equipment

A sector field ICP-MS instrument (Element; Finnigan MAT), running in the low-resolution mode, was used for the elemental analysis. Indium at final concentration of 1 ng g^{-1} was used as internal standard. The extraction of the elements from the filters was performed by using a heated ultrasonic bath (Thornton) or a microwave oven (CEM Model Mars 5), a vortex mixer (FANEM Model 251) and a centrifuge (FANEM Model Excelsa 3 plus 280).

2.2. Reagents and standards

All reagents used were of the highest purity available or at least of analytical reagent grade. Water was distilled and deionized (Milli-Q, Millipore Corp., Millford, MA, USA), and nitric acid was purified by sub-boiling double distillation in a quartz apparatus. Ultra-pure HCl solution (Merck, Darmstadt, Germany) was used to prepare an acid mixture containing 5.55% w/w of HNO_3 and 16.75% w/w of HCl. All calibration solutions and the internal standard solution were daily prepared by diluting the 1000 mg l^{-1} stock solutions of the elements (Spex Industries Inc., Edison, NJ, USA). All intermediate solutions were stored in polyethylene bottles. Glassware was cleaned by soaking in 10% v/v HNO_3 for 24 h and rinsing at least three times with Milli-Q water. Then, the material was dried and stored in a class 100 laminar flow hood.

2.3. Sample collection

The climate of the metropolitan area of Rio de Janeiro City is Atlantic tropical with summer rains and warm summers. In 2005, there were about nine million inhabitants and two million registered vehicles. It experienced an average maximum temperature of 27.6 °C in March and an average minimum temperature of 22.0 °C in June. Annual average relative humidity was 73%. The rainfall varied in the range of 6 mm in August to 183 mm in December. Winds were predominantly southwest with monthly average speed varying in the range of 3.1–3.6 m s^{-1} (Meteorological National Institute of Brazil).

The sampling was conducted in five permanent sampling stations of FEEMA in the metropolitan area of Rio de Janeiro City (Fig. 1): Sumaré station (22° 55′ S and 43° 13′ W), considered as an altitude background site by FEEMA, is located in a sub-tropical forest, about 700 m above the sea level and close to a poor residential area (slum); Centro station (22° 54′ S and 43° 10′ W) is located in downtown Rio de Janeiro, on the margins of Guanabara Bay, with intensive car and bus traffic; Copacabana station (22° 57′ S and 43° 11′ W) is located inside an electrical substation, near Copacabana beach, and it is a residential and commercial area with intense car and bus traffic; Nova Iguaçu station (22° 45′ S and 43° 26′ W) is placed in an

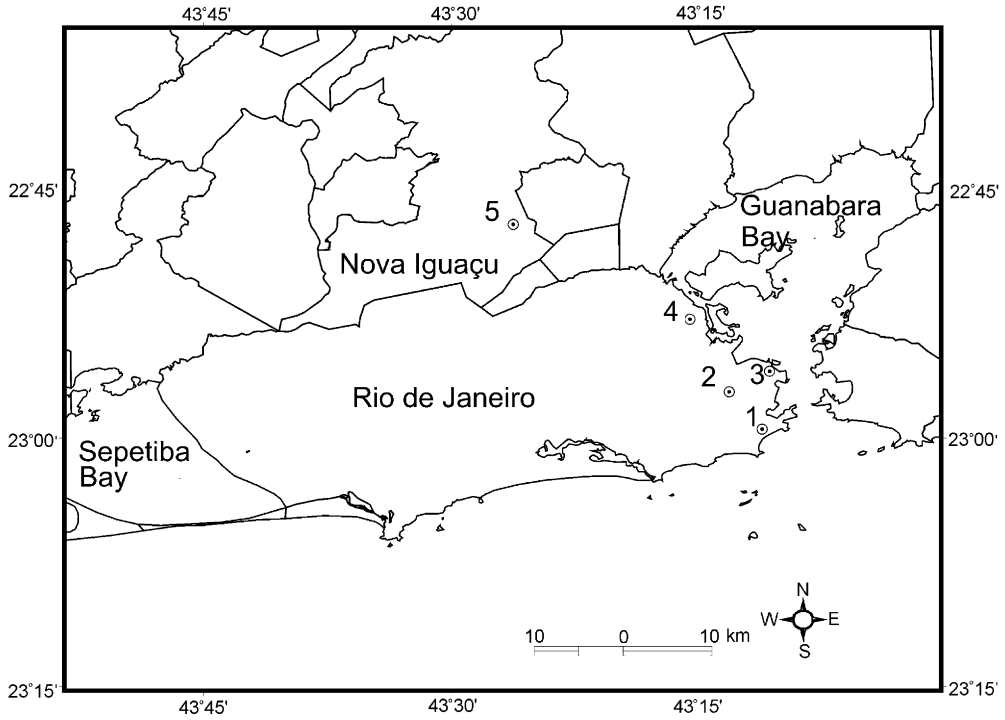

Fig. 1. Location of sampling sites: 1 - Copacabana; 2 - Sumaré; 3 - Centro; 4 - Bonsucesso; 5 - Nova Iguaçu.

industrial and rural zone with heavy traffic; and Bonsucesso station (22° 51′ S and 43° 15′ W) is located near a residential, commercial and industrial area, near a major avenue, a road with high traffic of trucks and cars. Finally, Bonsucesso and Nova Iguaçu are located in flatlands regions surrounded by mountains whereas Sumaré, Centro and Copacabana are open areas with higher wind flow.

High-volume samplers, operating at about 1.2 m^3 min^{-1} with PM_{10} glass fiber filters (20.3 cm × 25.4 cm), were used to collect suspended matter, once a week, over a continuous 24-h period, from January to December 2005. Only for the Sumaré station, the samples from November to December could not be collected by FEEMA. One sample per month with the lowest rainfall was selected on the same date in all stations, to represent the worst air pollution situation, totaling 58 samples.

2.4. Sample treatment

A method based on the EPA method (EPA, 1999) for determination of trace elements in environmental PM was used. A strip of about 2.5 cm × 20.3 cm of each filter (exposed and blank filters) was cut on an acrylic plate, with the aid of an acrylic ruler and a surgical stainless steel blade. Each obtained strip was cut into 10 small fragments. The fragments were carefully piled up and placed in vertical position into a polyethylene centrifuge tube, which was weighed before and after adding the fragments. The masses of strips from blank and exposed filters were measured in order to calculate the PM_{10} mass. An aliquot of 10 g of acid mixture was added, such that the acid mixture covered all the fragments of the filter.

2.5. Optimization of extraction conditions

Two digesting procedures for the extraction of the elements from the filters were tested by using microwave oven or heated ultrasonic bath. The centrifuge tube containing the acid mixture and the PM_{10} was placed into a heated ultrasonic bath or into a polytetrafluoroethylene (PTFE) extraction bomb. Water was added to the ultrasonic bath or to the PTFE bomb, and the water level was maintained above the content of the tube. The microwave oven operating conditions were as follows: first and second stages: 300 W, a ramp time of 5 min and a hold of 3 min and third stage: 300 W, a ramp time of 23 min and a hold of 23 min. The temperature of the ultrasonic bath was maintained at 69 ± 3 °C for 3 h. After cooling to room temperature, the tube was weighed again to certify that no sample had been lost. About 10 g of water was added, the tube was tightly closed, and placed into a vortex mixer for 2–3 min to complete the extraction. The phases in the tube were separated by centrifugation for 20 min at 3000 rpm, and they were allowed to stand overnight at room temperature. Then, an aliquot of 6 g of supernatant was transferred to other centrifuge tube by using a pipette. An aliquot of 1 g of a 10 ng g^{-1} indium standard solution, used as internal standard, and 3 g of water were added.

2.6. Statistical analysis

Pearson's correlation analysis of the element and the PM_{10} concentrations and cluster analysis (CA) of PM_{10} concentrations using Ward's method and Euclidean distances were performed with the STATISTICA 5.1

(Statsoft) program. The correlation matrix [12 variables × 12 measurements] was applied to Bonsucesso, Centro, Copacabana and Nova Iguaçu stations and the correlation matrix [12 variables × 10 measurements] to Sumaré station.

3. Results and discussion

3.1. Interference study

The interference studies did not show any interference of molecular ions on the isotopes: ^{111}Cd, ^{140}Ce, ^{65}Cu, ^{139}La, ^{95}Mo, ^{62}Ni, ^{208}Pb, ^{105}Pd, ^{121}Sb and ^{118}Sn. In the case of ^{103}Rh, the influence of $^{63}Cu^{40}Ar^{+}$ was corrected by a mathematical equation.

3.2. Analytical performance

Similar results and precisions were obtained for the microwave oven and ultrasonic bath procedures. However, the ultrasound-assisted extraction was selected because of the possibility of placing a greater number of samples in the bath, and therefore, reducing the extraction procedure time.

Detection limits (LODs) for the ultrasound-assisted extraction method are: Cd (1.1 ng g^{-1}); Ce (0.51 ng g^{-1}); Cu (0.88 ng g^{-1}); La (0.61 ng g^{-1}); Mo (0.82 ng g^{-1}); Ni (4.1 ng g^{-1}); Pb (0.54 ng g^{-1}); Pd (0.92 ng g^{-1}); Rh (0.57 ng g^{-1}); Sb (0.71 ng g^{-1}) and Sn (0.81 ng g^{-1}). Platinum on the sampling filters was not detected (LOD = 0.12 ng g^{-1}).

To validate the ultrasound-assisted extraction method, a recovery test was carried out by adding multielemental standard to a loaded filter with particulate matter. The recoveries of the spiked sample were in the range of 88–115%.

3.3. Analytical results

The blank filter analyses ($n = 5$) indicated that the filters contain significant concentrations (ng m^{-3}) of all the evaluated elements, with exception of Cd (0.082 ± 0.002) and Rh (0.070 ± 0.002), as follows: Ce (4.67 ± 0.09), Cu (6.9 ± 0.2), La (2.67 ± 0.06), Mo (0.245 ± 0.007), Ni (8.9 ± 0.2), Pb (3.12 ± 0.08), Pd (0.142 ± 0.007), Sb (0.207 ± 0.003) and Sn (0.43 ± 0.01). All the blank values were subtracted from the measured concentrations.

Table 1 summarizes 24-h PM_{10} chemical data obtained in this work and in other cities: Campinas (urban area), located in a large industrial pole, situated 100 km northwest of the metropolitan area of São Paulo, Brazil (Miranda and Tomaz, 2007); Salvador downtown city, Bahia, Brazil, featured by heavy commercial and service activities and with car traffic (Pereira et al., 2007); Genoa, the most populated coastal town in the northwest of Italy (Ariola et al., 2006); Barcelona, located on the northeastern coast of Spain (Viana et al., 2006) and sites in Göteborg, Sweden, with heavy and low traffic (Rauch et al., 2001).

Comparison between PM_{10} average concentrations revealed that the values for Centro, Copacabana and Sumaré were 1.4–3.4 lower and for Bonsucesso and Nova Iguaçu were similar to that reported for Salvador (Pereira et al., 2007). Average concentrations of PM_{10} for Copacabana, Bonsucesso and Nova Iguaçu were 1.2–1.9 times higher, for Sumaré was 2.0 times lower and Centro was similar to that reported for Genoa (Ariola et al., 2006). Also, average concentrations of PM_{10} for Sumaré and Centro stations were 2.4 and 1.3 times lower than the European limit of 50 μg m^{-3} (Ariola et al., 2006), respectively. Sumaré, an altitude background station, presented the lowest value of PM_{10} (21.2 μg m^{-3}).

Average concentrations of Ni for all stations, except for Sumaré, were 3.2–12.6 times higher than that registered for Campinas (Miranda and Tomaz, 2007). On the other hand, average concentrations of Cd for all stations, except Nova Iguaçu (1.7 times higher), were 4.5–9.4 times lower than that observed for Campinas. Average concentrations of Cu for Centro, Nova Iguaçu and Sumaré were 5.2–22.9 higher than those reported for Campinas and Salvador (Pereira et al., 2007). Average concentrations of Cu for Bonsucesso, Copacabana and Sumaré stations were 2.6–4.3 times lower, for Centro was similar and for Nova Iguaçu was 1.5 times higher than that reported for Barcelona (Viana et al., 2006). Average concentrations of Pb found in this work were 1.2–38 times lower than the EPA standard of 1.5 μg m^{-3} (EPA, 1997) and that reported for Barcelona. However, they were 2.5–16.9 times higher than that published for Campinas. Furthermore, average concentrations of Pb for Bonsucesso, Copacabana and Nova Iguaçu were 1.4–5.1 times higher, for Centro was 1.3 times lower and for Sumaré was similar to that registered for Genoa (Ariola et al., 2006). The difference between Pb concentrations obtained for Rio de Janeiro and those reported for other sites needs a further investigation, since Pb concentrations for Rio de Janeiro do not reflect the long time use of lead-free fuels in Brazil. Average concentrations of Sb and Sn for all stations were 4.2–41 times lower than those published for Barcelona. Average concentrations of Pd for all stations were 24–607 times higher than that registered for Göteborg (Rauch et al., 2001). Also, average concentrations of Rh obtained for all stations were 1.6–300 times higher than those registered for Göteborg. Ranges of average concentrations of 0.65–8.3 ng m^{-3} La and 0.43–2.6 ng m^{-3} Mo were also found.

The lowest average concentrations of Cd, Ce, La, Mo, Ni, Pd, Rh and Sb were found for Sumaré, considered as an altitude background station. However, these lowest values are still high, especially for Cd, Mo and Ni. Average concentrations of Sn and Pb obtained for Sumaré were higher (2.9 times and 1.5 times) than those found for Centro, respectively. Also, the average concentration of Cu for Sumaré was higher (1.7 and 1.5 times) than those obtained for Bonsucesso and Copacabana, respectively. High Cu concentrations found for Sumaré are probably due to waste incineration (Pereira et al., 2007; Smichowski et al.,

Table 1
Comparison between 24-h PM_{10} chemical data at sites of Rio de Janeiro over the year 2005 and those reported for other sites

Element	This study										Other studies					
	Station															
	Bonsucesso		Centro		Copacabana		Nova Iguaçu		Sumaré		Campinas[a]	Salvador[b]	Genoa[c]	Barcelona[d]	Göteborg[e]	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Mean	Mean	Mean	Mean	Mean	Mean
															High traffic	Low traffic
Cd	0.44–1.8	1.1	0.14–1.03	0.56	0.33–2.1	0.74	2.30–28.8	8.7	0.16–0.84	0.53	5			4		
Ce	2.3–6.1	4.4	0.38–2.9	1.5	0.76–3.7	2.2	9.6–24.0	13.7	0.17–2.7	1.2						
Cu	40.0– 84.2	63.3	199–381	268	40.2–146	71.0	233–962	414	70.7–124	105	18.1	79.2[f]		275		
La	1.2.–2.9	2.3	0.24–1.7	0.89	0.39–1.6	1.1	5.5–11.9	8.3	0.20–1.2	0.65						
Mo	0.50–1.9	0.96	0.29–2.0	0.65	0.22–1.2	0.83	1.7–5.3	2.6	0.08–0.87	0.43						
Ni	12.7–21.2	19.2	10.4–16.0	13.9	13.9–20.8	16.9	39.0–83.2	54.3	2.6–9.0	5.2	4.3			42		
Pb	12.7–66.1	37.7	2.3–22.1	9.1	4.0–51.9	16.6	38.7–94.6	60.7	4.3–23.5	13.6	3.6		12	346		
Pd	0.13–0.69	0.33	0.10–0.47	0.16	0.17–0.28	0.22	0.55–2.1	0.85	0.06–0.33	0.12					0.0049	0.0014
Rh	<L.D.–0.06	0.05	<L.D.–0.05	0.04	<L.D.–0.06	0.03	0.12–0.25	0.15	<L.D.–0.07	0.02					0.0029	0.0005
Sb	1.0–11.6	4.8	0.46–4.3	1.9	1.2–19.1	4.0	7.3–30.4	13.6	0.27–2.8	1.4				57		
Sn	0.77–7.0	3.3	0.35–3.8	1.4	0.62–13.9	3.1	3.9–15.0	6.6	0.04–9.6	4.0				24		
PM_{10}	41.3–112	75.4	18.0–63.0	39.6	32.7–78.1	51.5	48.4–101	77.4	4.8–35.8	21.2		71.7	41.2			

Element concentrations in ng m^{-3}; PM_{10} concentrations in μg m^{-3}; L.D. - Limit of detection.

[a] (Miranda and Tomaz (2007)).

[b] (Pereira et al. (2007)).

[c] Ariola et al. (2006).

[d] Viana et al. (2006).

[e] Rauch et al. (2001).

[f] The highest value.

2005), which is carried out by the poor people who live near the station. On the other hand, Nova Iguaçu station showed the highest concentrations of the studied elements, reflecting a very polluted site.

Similar Pd/Rh average concentration ratios (mean = 5.9 ± 1.2) were found for all stations, indicating that these elements are probably associated to catalytic converters erosion and deterioration, since a Pd/Rh concentration ratio range of 5–9 in the commercial catalytic converters has been reported (Granados et al., 2006; Lambrou et al., 2004; Lassi, 2003). Also, these results are in agreement with those (Pd/Rh = 6.9 ± 1.8) obtained for 22 soil samples collected near a highway in São Paulo, Brazil (Morcelli et al., 2005), emphasizing the fact that PGEs are emitted to the atmosphere from catalytic converters. Similar Mo/Ni average concentration ratios (mean = 0.055 ± 0.015) were found for all stations. These atmospheric emissions are probably associated to catalytic converter erosion and deterioration, since both elements are employed in their formulations (Gandhi et al., 2003; Zotin et al., 2005). Also, Mo and Ni emissions can be associated to steel material detrition, since they are used in the steel composition (Querol et al., 2007). Similar Ce/La average concentration ratios (mean = 1.8 ± 0.1) were found for all stations. Although these elements can be related to catalytic converters, in this case, these elements were probably originated from natural source (soil particle resuspension), since a Ce/La average concentration ratio range of 5–7 in commercial catalytic converters has been reported (Zotin et al., 2005). Moreover, Ce/La average concentration ratio ranges for soil samples of 1.4–1.7 (Figueiredo et al., 2007) and 1.25–2.5 (Kitto et al., 1992) have been registered. Similar Pb/Sb average concentration ratios (mean = 6.2 ± 2.5) were found for all stations, whereas a mean of 4.5 ± 0.3 was found for Copacabana, Centro and Nova Iguaçu. This fact indicates that these elements are probably associated to traffic, particularly break wear (Sternbeck et al., 2002).

3.4. Statistical analysis

The dendogram of the cluster analysis of PM_{10} concentrations (Fig. 2) gave two main clusters (Nova Iguaçu/Bonsucesso and Sumaré/Centro/Copacabana). These results are in agreement with the different topographical features of the sites (item 2.3). Bonsucesso and Nova Iguaçu have lower transport of particulate matter by the winds than Sumaré, Centro and Copacabana.

Table 2 shows Pearson's correlations ($-0.60 \geqslant r \geqslant 0.60$, $p \leqslant 0.03$) between elements and PM_{10} concentrations. All stations showed positive correlations ($r \geqslant 0.60$, $p \leqslant 0.04$) between PM_{10} and elements (La and Mo for Centro, Mo for Copacabana, Mo for Sumaré and La, Ce and Mo for Bonsucesso and Nova Iguaçu). These results indicate that Mo is an important constituent of the particulate matter for all stations. Similar significant positive correlations ($\geqslant 0.72$, $p \leqslant 0.01$) between PM_{10} and elements (La, Ce, Mo, Pb and Sn) for Bonsucesso and Nova Iguaçu were found. This similarity is in agreement with cluster analysis of PM_{10} concentrations (Fig. 2). The same fact is not observed in Centro and Copacabana, probably due to high contribution of marine elements to the particulate matter in Copacabana. High positive associations ($r \geqslant 0.80$, $p \leqslant 0.003$) between pairs of elements were found for all sites: La/Ce and Mo/Pd for Bonsucesso; Mo/La, Mo/Pd and La/Ce for Centro; La/Ce for Copacabana and Sumaré and Mo/La and La/Ce for Nova Iguaçu. The high positive correlations between La/Ce are in agreement with the results of Ce/La concentration ratios (item 3.3). High positive associations between Mo/Pd found for Bonsucesso and Centro indicate that Mo was probably emitted from catalytic converter erosion and deterioration.

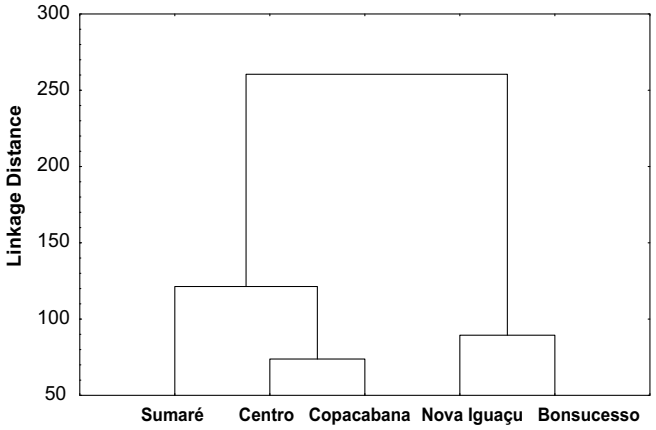

Fig. 2. Dendogram of the cluster analysis of PM_{10} concentrations.

High positive correlations ($r \geqslant 0.80$, $p \leqslant 0.003$) between Sn/Sb for Bonsucesso; Sn/Pb, Sb/Pb, Sb/PM_{10}, Sn/Sb and Pb/PM_{10} for Centro; Cd/Cu, Sn/Sb, Cd/Sb, Cd/Sn, Sb/Cu, Sb/Pb, Sn/Pb, Cd/Pb and Sn/Cu for Copacabana; Sb/Pb and Pb/PM_{10} for Nova Iguaçu and Cd/PM_{10}, Sb/Pb, Cd/Sn, Sn/PM_{10}, Sn/Pb, La/Pb, Mo/Sb, Cd/Sb, Cd/Pb, Sn/Sb, Sb/La, Sb/PM_{10} and Pb/PM_{10} for Sumaré may also indicate pollution from automotive sources.

High positive correlations ($r \geqslant 0.83$, $p \leqslant 0.001$) between Cu and other elements (Cd, Sn and Sb) were found for Copacabana, indicating that Cu may be associated to automotive emissions, since in Copacabana there are no industrial activities. On the other hand, no correlation ($r \geqslant 0.60$, $p \leqslant 0.04$) with Cu was found for other sites, except a low one for Bonsucesso (Sb/Cu, $r = 0.65$, $p = 0.02$), reflecting a different emission source. Also, significant negative correlations between Cu/Pd ($r = -0.77$, $p = 0.01$) and Cu/Ce ($r = -0.66$, $p = 0.02$) were found for Sumaré. The unexpected high levels of Cu may be explained by waste incineration that occurs in the slum located near this station.

Significant positive correlations between Ni and Mo with catalytic converter elements (Ni/Pd, $r = 0.78$, $p = 0.003$; Mo/Ni, $r = 0.72$, $p = 0.01$; Ni/Rh, $r = 0.60$, $p = 0.04$) were found only for Copacabana, indicating that these elements may be associated to traffic, particularly

Table 2
Pearson's correlation coefficients between elements and PM_{10} ($-0.60 \geqslant r \geqslant 0.60$, $p \leqslant 0.03$)

Bonsucesso		Centro		Copacabana		Nova Iguaçu		Sumaré	
La/PM_{10}	0.93	Sn/Pb	0.99	Cd/Cu	0.94	La/PM_{10}	0.90	Cd/PM_{10}	0.98
La/Ce	0.93	Sb/Pb	0.91	Sn/Sb	0.94	Mo/PM_{10}	0.89	Sb/Pb	0.96
Sn/Sb	0.86	Sb/PM_{10}	0.91	La/Ce	0.94	Sb/Pb	0.89	La/Ce	0.95
Mo/Pd	0.84	Mo/La	0.90	Cd/Sb	0.92	Ce/PM_{10}	0.88	Cd/Sn	0.94
Ce/PM_{10}	0.79	Sn/Sb	0.88	Cd/Sn	0.90	La/Ce	0.86	Sn/PM_{10}	0.92
Mo/La	0.77	Mo/Pd	0.84	Sb/Cu	0.90	Pb/PM_{10}	0.84	Sn/Pb	0.91
Cd/Sb	0.75	La/Ce	0.83	Sb/Pb	0.88	Mo/La	0.81	La/Pb	0.88
Sn/Pb	0.75	Pb/PM_{10}	0.81	Sn/Pb	0.87	Mo/Sn	0.78	Mo/Sb	0.85
Cd/Sn	0.74	La/PM_{10}	0.79	Cd/Pb	0.84	Sn/Pb	0.78	Cd/Sb	0.85
Sn/Pd	0.73	Cd/Pb	0.78	Sn/Cu	0.83	Mo/Ni	−0.78	Cd/Pb	0.85
Mo/PM_{10}	0.72	Cd/Sb	0.76	Ni/Pd	0.78	Mo/Pb	0.76	Sn/Sb	0.85
Sb/PM_{10}	0.68	Sn/PM_{10}	0.74	Pb/Cu	0.74	Mo/Ce	0.75	Sb/La	0.84
Sb/Cu	0.65	Cd/Sn	0.73	Mo/Ni	0.72	Sn/PM_{10}	0.75	Sb/PM_{10}	0.84
Sb/Pd	0.64	Mo/Sb	0.71	Mo/La	0.68	Sn/Ce	0.72	Pb/PM_{10}	0.82
Pb/PM_{10}	0.64	La/Pd	0.71	Rh/Pd	0.64	Pb/Ni	−0.71	Cu/Pd	−0.77
La/Pb	0.61	Sb/La	0.71	Ni/Rh	0.60	La/Pb	0.70	Ce/Pb	0.75
Sn/PM_{10}	0.61	Mo/PM_{10}	0.70	Mo/Pb	0.60	Sn/Sb	0.70	Mo/Pb	0.73
Mo/Ni	−0.61	Cd/PM_{10}	0.70	Mo/PM_{10}	0.60	Ce/Pb	0.68	Rh/Pd	0.72
Sb/La	0.60					Sn/La	0.68	Mo/PM_{10}	0.70
						Ni/PM_{10}	−0.68	Sb/Ce	0.69
						La/Ni	−0.67	Mo/Cd	0.66
						Rh/Pd	0.60	Ce/Cu	−0.66
								Mo/Sn	0.65
								Sn/La	0.64
								Cd/La	0.62

with erosion and deterioration of catalytic converters. Although similar Mo/Ni concentration ratios were found for all stations (item 3.3), significant negative correlations between Mo/Ni ($r = -0.61$, $p = 0.03$ and $r = -0.78$, $p = 0.003$) were found for Bonsucesso and Nova Iguaçu, respectively, suggesting that, in these sites, Ni and Mo were emitted from different sources.

4. Conclusions

Samples collected at different sites in Rio de Janeiro indicated the presence of particulate matter containing elements (Mo, Pd and Rh) that can be associated to the automotive traffic, particularly to the catalytic converter erosion and deterioration. Also, the elements Pb and Sb were found, and they are probably associated to vehicle engine, tire rubber and brake lining abrasion. Pt was not detected, indicating that the element was not used or was used in very low concentration in the catalytic converter formulations. The atmospheric contamination by Ce and La are probably associated to the soil resuspension. Although the Pb concentrations obtained in this work were lower than EPA standard, the difference between Pb concentrations obtained for Rio de Janeiro and those reported for other sites needs a further investigation, since Pb concentrations for Rio de Janeiro do not reflect the long time use of lead-free fuels in Brazil. Sumaré, an altitude background station, was contaminated by the traffic and waste incineration. Nova Iguaçu was the most polluted site.

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References

Ariola, V., D'Alessandro, A., Lucarelli, F., Marcazzan, G., Mazzei, F., Nava, S., Garcia-Orellana, I., Prati, P., Valli, G., Vecchi, R., Zucchiatti, A., 2006. Elemental characterization of PM_{10}, $PM_{2.5}$ and PM_1 in the town of Genoa (Italy). Chemosphere 62, 226–232.

Baldanza, M.A.S., Mello, L.F., Vannice, A., Noronha, F.B., Schmal, M., 2000. Adsorptive and calalytic properties of alumina-supported Pd-Mo catalysts. J. Catal. 192, 64–76.

Bilos, C., Colombo, J.C., Skorupka, C.N., Rodriguez Presa, M.J., 2001. Sources, distribution and variability of airborne trace metals in La Plata City area, Argentina. Environ. Pollut. 111, 149–158.

Birmili, W., Allen, A.G., Bary, F., Harrison, R.M., 2006. Trace metal concentrations and water solubility in size-fractionated atmospheric particles and influence of road traffic. Environ. Sci. Technol. 40, 1144–1153.

Bocca, B., Caimi, S., Smichowski, P., Gómez, D., Caroli, S., 2006. Monitoring Pt and Rh in urban aerosols from Buenos Aires, Argentina. Sci. Total Environ. 358, 255–264.

EPA – 454/R-92-009, 1997. Guidance for siting ambient air monitors around stationary lead sources.

EPA, Method IO-3.1, 1999. Selection, preparation and extraction of filter material.

Fernández, A.J., Ternero, M., Barragán, F.J., Jiménez, J.C., 2000. An approach to characterization of sources of urban airborne particles through heavy metal speciation. Chemosphere – Global Change Sci. 2, 123–136.

Figueiredo, A.M.G., Nogueira, C.A., Saiki, M., Milian, F.M., Domingos, M., 2007. Assessment of atmospheric metallic pollution in the metropolitan region of São Paulo, Brazil, employing Tillandsia usneoides L. as biomonitor. Environ. Pollut. 145, 279–292.

Gandhi, H.S., Graham, G.W., McCabe, R.W., 2003. Automotive exhaust catalysis. J. Catal. 216, 433–442.

Gieré, R., Blackford, M., Smith, K., 2006. TEM Study of $PM_{2.5}$ emitted from coal and tire combustion in a thermal power station. Environ. Sci. Technol. 40, 6235–6240.

Gómez, B., Gómez, M., Sanchez, J.L., Fernández, R., Palácios, M.A., 2001. Platinum and rhodium distribution in airborne particulate matter and road dust. Sci. Total Environ. 269, 131–144.

Gómez, D.R., Giné, M.F., Bellato, A.C.S., Smichowski, P., 2005. Antimony: a traffic-related element in the atmosphere of Buenos Aires, Argentina. J. Environ. Monitor. 7, 1162–1168.

Granados, M.L., Galisteo, F.C., Mariscal, R., Alifanti, M., Gurbani, A., Fierro, J.L.G., Fernández-Rúiz, R., 2006. Modification of a three-way catalyst washcoat by aging: A study along the longitudinal axis. Appl. Surf. Sci. 252, 8442–8450.

Kitto, M.E., Anderson, D.L., Gordon, G.E., Olmez, I., 1992. Rare earth distributions in catalysts and airborne particles. Environ. Sci. Technol. 26, 1368–1375.

Lambrou, P.S., Costa, C.N., Christou, S.Y., Efstathiou, A.M., 2004. Dynamics of oxygen storage and release on commercial aged Pd-Rh three-way catalysts and their characterization by transient experiments. Appl. Catal. B-Environ. 54, 237–250.

Lassi, U., 2003. Deactivation correlations of Pd/Rh three-way catalysts designed for Euro IV emission limits. Effect of ageing atmosphere, temperature and time department of process and environmental engineering, doctoral thesis. Department of Process and Environmental Engineering, University of Oulu, Finland.

Miranda, R., Tomaz, E., 2007. Characterization of urban aerosol in Campinas, São Paulo, Brazil. Atmos. Res.. doi:10.1016/j.atmosres.2007.08.002.

Morcelli, C.P.R., Figueiredo, A.M.G., Sarkis, J.E.S., Enzweiler, J., Kakazu, M., Sigolo, J.B., 2005. PGEs and other traffic-related elements in roadside soils from São Paulo, Brazil. Sci. Total Environ. 345, 81–91.

Park, S.S., Kim, Y.J., 2005. Source contributions to fine particulate matter in an urban atmosphere. Chemosphere 59, 217–226.

Pereira, P.A.P., Lopes, W.A., Carvalho, L.S., Rocha, G.O., Bahia, N.C., Loyola, J., Quiterio, S.L., Escaleira, V., Arbilla, G., Andrade, J.B., 2007. Atmospheric concentrations and dry deposition fluxes of particulate trace metals in Salvador, Bahia, Brazil. Atmos. Environ. doi:10.1016/j.atmosenv.2007.06.013.

Petrucci, F., Violante, N., Senofonte, O., de Gregorio, M., Alimonti, A., Caroli, S., Forte, G., Cristaudo, A., 2004. Development of an analytical method for monitoring worker populations exposed to platinum-group elements. Microchem. J. 76, 131–140.

Querol, X., Viana,M., Alastuey, A., Amato, F., Moreno, T., Castillo, S., Pey, J., de la Rosa, J., Sánchez de la Campa, A., Artíñano, B., Salvador, P., García dos Santos, S., Fernández-Patier, R., Moreno-Grau, S., Negral, L., Minguillón, M.C., Monfort, E., Gil, J.I., Inza, A., Ortega, L.A., Santamaría, J.M., Zabalza, J., 2007. Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. Atmos. Environ. 41, 7219–7231.

Quiterio, S.L., Arbilla, G., Escaleira, V., Silvs, C.R.S., Wasserman, M.A., 2006. Characterization of airborne trace metal distribution in Baixada Fluminense, Rio de Janeiro, Brazil, by operacional speciation. Bull. Environ. Contam. Toxicol. 77, 119–125.

Quiterio, S.L., Da Silva, C.R.S., Arbilla, G., 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, S.L., Escaleira, V., Souza, C.R.S., Maia, L.F.P.G., Arbilla, G., 2004b. Metals in airborne particulate matter in downtown Rio de Janeiro, Brazil. Bull. Environ. Contam. Toxicol. 72, 916–922.

Quiterio, S.L., Souza, C.R., Arbilla, G., Escaleira, V., 2005. Evaluation of levels, sources and distribution of airborne trace metals in seven districts of the Baixada Fluminense, Rio de Janeiro, Brazil. Atmos. Environ. 39, 3503–3512.

Rauch, S., Lu, M., Morrison, G.M., 2001. Heterogeneity of platinum group metals in airborne particles. Environ. Sci. Technol. 35, 595–599.

Salma, I., Maenhaut, W., 2006. Changes in elemental composition and mass of atmospheric aerosol pollution between 1996 and 2002 in a Central European city. Environ. Pollut. 143, 479–488.

Sella, S.M., Netto, A.D.P., Filho, E.V.S., Araújo, M.T., 2004. Short-term and spatial variation of selected metals in the atmosphere of Niterói City, Brazil. Microchem. J. 78, 85–90.

Smichowski, P., Marrero, J., Gómez, D., 2005. Inductively coupled plasma optical emission spectrometric determination of trace element in PM_{10} airborne particulate matter collected in an industrial area of Argentina. Microchem. J. 80, 9–17.

Srivastava, A., Jain, V.K., 2007. Size distribution and source identification of total suspended particulate matter and associated heavy metals in the urban atmosphere of Delhi. Chemosphere 68, 579–589.

Sternbeck, J., Sjödin, A., Andréasson, K., 2002. Metal emissions from road traffic and the influence of resuspension - results from two tunnel studies. Atmos. Environ. 36, 4735–4744.

Valavanidis, A., Fiotakis, K., Vlahogianni, T., Bakeas, E.B., Triantafillaki, S., Paraskevopoulou, V., Dassenakis, M., 2006. Characterization of atmospheric particulates, particle – bound transition metals and polycyclic aromatic hydrocarbons of urban air in the center of Athens (Greece). Chemosphere 65, 760–768.

Viana, M., Querol, X., Alastuey, A., 2006. Chemical characterisation of PM episodes in NE Spain. Chemosphere 62, 947–956.

Yoo, J., Kim, K., Jang, H., Seo, Y., Seok, K., Hong, J., Jang, M., 2002. Emission characteristics of particulate matter and heavy metals from small incinerators and boilers. Atmos. Environ. 36, 5057–5066.

Zereini, F., Alt, F., Messerschmidt, J., Bohlen, A.V., Liebl, K., Püttmann, W., 2004. Concentration and distribution of platinum group elements (Pt, Pd, Rh) in airborne particulate matter in Frankfurt am Main, Germany. Environ. Sci. Technol. 38, 1686–1692.

Zheng, J., Tan, M., Shibata, Y., Tanaka, A., Li, Y., Zhang, G., Zhang, Y., Shan, Z., 2004. Characteristics of lead isotope ratios and elemental concentrations in PM_{10} fraction of airborne particulate matter in Shanghai after the phase-out of leaded gasoline. Atmos. Environ. 38, 1191–1200.

Zotin, F.M.Z., Gomez, O.F.M., Oliveira, C.H., Alcover, N.A., Cardoso, M.J.B., 2005. Automotive catalyst deactivation: Case studies. Catal. Today (107/108), 157–167.