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Article

Trace Metals in the Urban Aerosols of Rio de Janeiro City

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De janeiro a abril de 2009, amostras de partículas suspensas (TSP) e de materiais particulados (PM_{10} e $PM_{2.5}$) foram coletadas de uma área urbana característica altamente impactada pelo tráfego de veículos. As concentrações de metais nestas amostras foram determinadas por ICP-OES (espectroscopia de emissão por plasma indutivamente acoplado). Ca, Mg, Fe e Al foram os metais mais abundantes presentes em TSP e PM_{10}, com concentrações maiores que 427 ng m^{-3}. Em $PM_{2,5}$, os metais mais abundantes foram Fe e Ca (307 e 60 ng m^{-3}, respectivamente), enquanto que as concentrações de Mg, Zn e Cu foram aproximadamente 20 ng m^{-3}. Para PM_{10} e $PM_{2,5}$, correlações elevadas foram obtidas para Ca, Mg e Al, enquanto a correlação de Ca e Mg com Fe mostrou-se pobre, indicando assim que Ca, Mg e Al provavelmente se originam principalmente da resuspensão de poeira, enquanto Fe pode ser também proveniente de uma fonte adicional, como o desgaste de freio. Elementos antropogênicos (Zn e Cu) tiveram fatores de correlação baixos, sugerindo fontes de emissões diferentes. A presença de Cu pode estar relacionada com o desgaste dos freios e a de Zn pode ser atribuída ao desgaste do pneu. Em partículas finas, Ca, Mn, Fe, Zn e Cu estavam presentes em razões mais elevadas do que em material da crosta. Uma vez que estas partículas são observadas principalmente devido aos processos de combustão, elas podem estar presentes na gasolina, óleo e lubrificantes. Fe foi correlacionado com Mn, enquanto fatores de correlação entre Ca e Mg foram relativamente baixos.

From January to April 2009, samples of suspended particles (TSP) and particulate matters (PM_{10} and $PM_{2.5}$) were collected from a well-characterized urban area that is highly impacted by vehicular traffic. The metal concentrations in these samples were determined using ICP-OES (inductively coupled plasma-optical emission spectroscopy). Ca, Mg, Fe and Al were the most abundant metals present in TSP and PM_{10}, with concentrations higher than 427 ng m^{-3}. In $PM_{2.5}$, the most abundant metals were Fe and Ca (307 and 60 ng m^{-3}, respectively), while the concentrations of Mg, Zn and Cu were approximately 20 ng m^{-3}. For PM_{10} and $PM_{2.5}$, high correlations were obtained for Ca, Mg and Al, while the correlation of Ca and Mg with Fe was poor, thereby indicating that Ca, Mg and Al probably originate mainly from the resuspension of dust, while Fe may also be originated from an additional source, such as brake wear. Anthropogenic elements (Zn and Cu) had low correlation factors, suggesting different emission sources. The presence of Cu may be linked to the abrasion of brakes, and Zn may be attributed to tire wear. In fine particles, Ca, Mn, Fe, Zn and Cu were present in higher ratios than in crustal material. Because these particles are mainly observed due to the combustion processes, they may be present in gasoline, oil and lubricants. Fe was correlated with Mn, while correlation factors between Ca and Mg were relatively lower.

Keywords: total particulate matter, PM_{10}, $PM_{2.5}$, trace metals, vehicle emissions

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Introduction

The most commercialized automotive fuels in Brazil are gasohol, ethanol, diesel and compressed natural gas (CNG). Recently, the first national vehicular emission inventory was published with data that was current up to 2009.[1] According to these data, the national fleet consists of *ca.* 36 million vehicles with 59% light-duty vehicles, 27% motorcycles, 10% commercial light vehicles and 4% heavy-duty vehicles (buses and trucks). Light vehicles are mostly run on gasohol (57%) or are flex-fueled (37%). Motorcycles are generally fueled with gasohol (98%), and commercial light vehicles use gasohol (42%) or diesel (28%) or are flex-fueled (26%). Gasohol is a blend of gasoline and ethanol (24%) containing a complex mixture of hydrocarbons, such as paraffin, naphthene, olefin and aromatic hydrocarbon, which are composed between 4 and 12 carbons and are derived from crude petroleum with a small amount of additives.

The Rio de Janeiro Metropolitan Area has the second-largest running fleet with *ca.* 3.3 million vehicles.[2] According to the most recent available official emission inventory,[3] *ca.* 76% of the total air pollution caused by CO, SO_2, NO_X and PM_{10} (particulate matter) are direct contributions from mobile sources. According to the national emission inventory, 96% of emitted particulate matter from vehicles results from diesel exhaust.[1]

National standards of air quality only determine limits for total particulate matter (240 $\mu g\ m^{-3}$ for 24 h and 80 $\mu g\ m^{-3}$ for the annual geometric mean) and PM_{10} (150 $\mu g\ m^{-3}$ for 24 h and 50 $\mu g\ m^{-3}$ for the annual arithmetic mean).[4] However, there is no legislation regarding fine particles ($\leq PM_{2.5}$), and the monitoring was only recently initiated in some locations that have been characterized for exhibiting critical air quality conditions.

In a recent review, Korn *et al.*[5] discussed an analytical method developed for metal and metalloid quantification in automotive fuels. As described in that review, certain metals, such as nickel and vanadium, are natural constituents of petroleum and are found in small concentrations in petroleum-derived products.[5] Other metals, such as iron and zinc, are used in the manufacturing of fuel tanks and may be transferred to fuels during transport and storage. In addition, other metals are introduced in the refinement process or are introduced as additives to promote the desired characteristics. These deliberately introduced metals include Al, Ca, Ce, Cr, Co, Cu, La, Pb, Li, Mg, Mn, Mo, Ni, Si, Ag, Na, Tl, Sn, W, V , Zn and Zr.[6-8]

In previous studies, emissions of coarse particles were found to be dominated by the resuspension of dust and brake wear, while fine particles were mainly due to combustion processes.[9] The various trace metal sources in fine particulate matter emitted from road traffic were characterized in a road tunnel in Nice, France.[10] Using a multivariate analysis (positive matrix factorization), the contribution of the sub-sources were determined as follows: resuspension (43%), vehicular abrasion (36%) and fuel combustion (21%). Resuspended dust may be of anthropogenic or natural origin and is not generally considered in emission inventories.

Metal content in airborne particulate matter collected in the Rio de Janeiro Metropolitan Area was primarily determined in TSP (total suspended particles) and PM_{10}.[11-13] Over the last few years, several studies describing the $PM_{2.5}$ particulate matter were obtained in Rio de Janeiro City.[14,15] In 2009, Godoy *et al.*[15] published results describing aerosol samples that were collected in ten locations in the Rio de Janeiro Metropolitan Area, and the trace elements were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). After applying multivariate analysis, Godoy *et al.*[15] concluded that soil dust is the main source of coarse aerosol particles, with sea-spray and vehicular traffic being the next most common sources. However, for the $PM_{2.5}$ fraction, the anthropogenic sources, such as vehicular traffic and oil combustion, accounted for *ca.* 65%. Similar studies were also performed for Campinas[16] and São Paulo Cities.[17,18]

In a recent study,[13] TSP and PM_{10} samples were collected at the Major José Carlos Lacerda Bus Station in Duque de Caxias City (Rio de Janeiro Metropolitan Area) where buses were the only significant emission sources, representing *ca.* 98% of the total flux. Ca, Mg, Fe and Al were the most abundant elements, accounting for *ca.* 50.1, 24.2, 6.5 and 18.7% of the total metal content, respectively. With the exception of a few samples, Co, Ni, Cd, Cr and Pb levels were below limits of detection. Calculated enrichment factors showed that Zn and Cu likely originated from fuel and oil compositions. Ca, Mg and Al may be attributed to dust resuspension, while Fe may originate from both dust resuspension and vehicular contributions.

The goal of this work was to characterize the metal content of particulate matter at an urban location that is strongly influenced by vehicular traffic and to suggest the metal sources. However, it should be noted that these results are limited, as they are strongly affected by the vehicle operating conditions, quality of fuels, meteorological parameters and air transport. The sampling and analyses were performed using the same conditions as those used in the previous study of diesel emissions,[13] thereby enabling a comparison of the results.

Experimental

Sampling site

The city occupies an area of 1,200.3 km^2 and has a population of 6,320,446 inhabitants[19] and approximately 2,416,823 vehicles.[20] Gasohol is used by 50.85% of the vehicles (gasoline with 24.00% ethanol), neat ethanol 8.95%, compressed natural gas 16.03% (CNG), flex-fueled (gasohol and ethanol) cars are 19.50% of the vehicles (gasohol and ethanol) and diesel 3.97%.[20]

Sampling was conducted in an urban area that was strongly affected by vehicle emissions at Jardim Botanico Street, which is a busy roadway that provides access to the André Rebouças Tunnel and links the Jardim Botanico and Rodrigo de Freitas Lagoon neighborhoods, from Southern district of the city to the Northern areas. Samplers were placed *ca.* 145 m from the entrance of the tunnel and *ca.* 5 m from the street in an open area of the tunnel administrative building. The administrative building is constructed of concrete, and the samplers were placed more than 50 m from the walls. The tunnel is two-bored and has two galleries, one of which is 2040 m long and connects Jardim Botanico and Cosme Velho, while the other gallery is 800 m long and connects Cosme Velho and Rio Comprido.[21] The flux of vehicles is almost constant during the daylight hours and is approximately eight times greater than the flux observed at night. In the South entrance, where the samples were collected, the mean traffic from 7 a.m. to 7 p.m. on Mondays through Fridays was *ca.* 5,500 vehicles *per* h. Light-duty vehicles represent *ca.* 97% of the total flux, and the distribution by fuel type is similar to the mean distribution for Rio de Janeiro. A map of the area (Figure S1) is available in the Supplementary Information section.

The sampling area is mainly affected by vehicular emissions, though the resuspension of dust and marine aerosol should also be considered. Data collected by the INEA (Rio de Janeiro State Environmental Institute, Brazil) show that industrial facilities are mainly located in the Western and Northern districts of the metropolitan area.[3] Climatological evaluation of the wind patterns for Rio de Janeiro City shows a larger frequency of the South-Southeast to North-Northwest winds in virtually every month of the year, with an average wind speed of 8 km h^{-1}. Data collected in downtown neighborhoods during the year of 2009 showed a predominance of weak winds in the Southeast and Northwest directions.[3] The frequencies of winds over the sampling period were plotted by wind directions to show the direction with the greatest frequency. The data were collected in the Santos Dumont Airport and showed a predominance of winds from the Southeast (135^o) to Northwest (180^o) and wind speeds ranging up to 30 km h^{-1}. The Santos Dumont Airport is located adjacent to the Guanabara Bay, being approximately 1 km from downtown and 9 km from the sampling area. The wind rose (Figure S2) is shown in the Supplementary Information section.

The air circulation in the Rio de Janeiro Metropolitan Area is largely affected by topographical conditions. The Tijuca Forest (a mountainous rainforest area) forms a natural barrier to air circulation and divides the city into Northern and Southern sections. Using topographical and meteorological criteria, the Rio de Janeiro Metropolitan Area was divided into four air basins.[3] The sampling area was located in Air Basin II, while the main industrial facilities were located in Basins I (West) and III (North). Considering the geographical position of the sampling site and the physical barrier of Pedra Branca and Tijuca Mountains, the sampling site mainly receives marine and urban air from the South and only a small contribution from the industrial areas.

Sampling

The selection of the points and the sampling procedures took into account the minimum sampler siting criteria, calibration and filter handling procedures recommended by the U. S. Environmental Protection Agency (U.S. EPA).[22] Briefly, following EPA recommendations, the height above ground should be 2 to 7 m, the distance from samples to obstacles should be at least twice the height of the obstacle and the air flow around the sampler inlet should be unrestricted.

TSP and PM$_{10}$ were collected using high-volume samplers (Sibata, model HVC500) and borosilicate glass microfiber filters (Sibata, diameter of 110 mm, thickness of 0.40 mm and porosity of 0.6 μm). The flow rate was 0.5 m^3 min^{-1}. A total of 62 samples (31 TSP and 31 PM$_{10}$ samples) was collected on weekdays without rainfall in the period of January to April 2009.

PM$_{2.5}$ was collected using a high volume sampler (Hi-vol, Energetica) that was equipped with an impactor design size-select inlet (Andersen, model G1200-2.5) and quartz fiber filters (Millipore filters with an area of 20 × 25 cm and a thickness of 0.5 mm). The flow rate was 1.05 to 1.21 m^3 min^{-1}. A total of 50 samples was collected during weekdays and Saturdays during the period of January to April 2009.

Samplings of TSP and PM$_{10}$ were performed at a height of 4 m using 6 h sampling periods (from 8 a.m. to 2 p.m.). PM$_{2.5}$ samples were collected at a height of 2 m over 24 h. It was not the objective of this study to assess such comparisons as rush and non-rush hours, weekdays to Saturdays and Sundays or daytime to nighttime periods. Although these comparisons would be useful in clearly linking the metal content to gasohol, experiments at night and during the weekends were not possible due to security reasons and restricted access to equipment.

Extraction procedure and analysis

The levels of TSP, PM_{10} and $PM_{2.5}$ were determined by gravimetry using an electronic microbalance with a 1 μg sensitivity. For the analysis of trace metals, the same procedures were followed as in our previous studies.[12,13,23] The 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 and subsequently heating for 2 h at 95 °C on a heating plate. The extracted solution was filtered with a Whatman No. 41 (WH1441-110) filter, diluted to a volume of 20 mL with ultrapure water and stored in pre-cleaned polyethylene bottles in the refrigerator for further analyses.

The metals were determined by ICP-OES (inductively coupled plasma-optical emission spectroscopy) following Method IO-3.4. Limits of detection and accuracy were determined using the same method.[24] Data quality, accuracy and reproducibility, and limits of detection and quantification were determined using the same procedures as the used in our previous study at the bus station.[13]

Limits of detection and quantification computed as three and ten times, respectively, the standard deviation of the distribution of outputs for ten repeated measurements of the standard, which contained no metals.[25] These limits of detection were calculated as 30 ng m^{-3} for Ca, 20 ng m^{-3} for Mg and Ni, 35 ng m^{-3} for Al, 3 ng m^{-3} for Cu, 40 ng m^{-3} for Fe and Pb, 1 ng m^{-3} for Mn, Zn and V, 7 ng m^{-3} for Cr and Co, 2 ng m^{-3} for Cd and 9 ng m^{-3} for Mo.

The accuracy of the method was evaluated using a standard reference material (SRM, 2783 Air Particulate on Filter Media, National Institute of Standards and Technology (NIST), Maryland, U. S. A.). Three samples of the reference material were analyzed in triplicate, and the results were compared with the concentrations reported in the certificate of analysis. The obtained concentrations differed by less than 8%. All samples and SRM were determined in triplicate, and a difference of less than 1% was considered acceptable.

Filter and reagent blanks were processed following the same procedure. The metal content of the blanks for Ca, Mg, Mn, Fe, Zn, Cu, Cr, Co, Ni, Al, Cd, Pb, Mo and V was less than 5% of the sample average contents. For Cr, the metal content represented less than 8%.

Statistical analysis

Experimental data were analyzed using Statistica 7.0 (StatSoft). The data were previously analyzed using descriptive statistics. After removing outliers, a multivariate statistical analysis was performed that included the evaluation of Spearman's correlation coefficients, cluster analysis (CA) using Euclidian distances and Ward's method and principal component analysis (PCA).

Results and Discussion

PM_{10} and total particulate matter

TSP levels were in the range of 35.04 to 95.6 μg m^{-3}. The mean concentration for all samples (n = 31) was 53.7 μg m^{-3}. Similarly, values for PM_{10} (n = 31) ranged from 13.1 to 47.0 μg m^{-3} with a mean value of 22.9 μg m^{-3}.

Because TSP and PM_{10} samples were simultaneously collected using Sibata portable samplers, their levels may be directly compared. The PM_{10}/TSP ratios calculated for the same sampling date were in the range of 0.30 to 0.75 with an average value of 0.42. In a previous study,[13] the PM_{10}/TSP ratios for a location with 95% diesel vehicles were calculated to be in the range of 0.11 to 0.65 with an average value of 0.24. The coarse mode is mainly related to primary particles that are usually mechanically-generated. So, the main contribution to particulate matter in the TSP and PM_{10} range is from the resuspension of dust and particles from natural sources (plants, microorganisms and ocean spray).[26] This is due to the proximity of the Jardim Botanico Park, Tijuca Forest, Rodrigo de Freitas Lagoon and the Atlantic Ocean.

Fine particulate matter

$PM_{2.5}$ levels were also determined by gravimetry. The values for $PM_{2.5}$ (n = 50) ranged from 7.6 to 117.2 μg m^{-3} with a mean value of 29.2 μg m^{-3}. Fine particles may be secondary in origin, being generated by chemical reactions between gases and particles, or primary in origin, being generated by combustion processes.[26] Marine aerosols may also contain fine particles (5-10%) that result from the evaporation of sea-spray produced by bursting bubbles or wind-induced wave breaking. Other probable sources of particles smaller than 2.5 μm in diameter include tire wear and brake linings.

Levels of trace metals

Fourteen metals were analyzed in the samples: Ca, Mg, Mn, Fe, Zn, Cu, Co, Ni, Al, Cd, Cr, Pb, Mo and V. Mean concentrations, standard derivations, minima and maxima are shown in Table 1.

Ca, Mg, Fe and Al were the most abundant metals in TSP and PM$_{10}$ with mean concentrations higher than 427 ng m^{-3}. In PM$_{2.5}$, the most abundant metals were Fe and Ca (307 and 60 ng m^{-3}, respectively), while Mg, Zn and Cu were detected at similar levels (*ca.* 20-35 ng m^{-3}). All concentrations were under the limits of detection. These results agree with those seen by Lough *et al.*,[27] who reported that the most abundant elements found in PM$_{10}$ in two tunnels in Milwaukee (U. S. A.) were Fe, Ca, Si, Na, Mg, Al, S and K. These accounted for an average of 94% of the total PM$_{10}$ content for the 42 measured elements. These metals were also present in PM$_{2.5}$ in much lower amounts and were significantly different from the limits of detection in few samples.[27]

For PM$_{10}$, the average metal contents were 55.7,14.9, 8.0 and 18.5% for Ca, Mg, Al and Fe, respectively. The values determined for the diesel emissions were 50.2, 24.1, 18.7 and 6.5%, respectively for the same metals.[13] The differences are probably due to the composition of soils, aerosol particles, mechanical parts and , also, to the composition of fuels.

To compare the results of the atmospheric particulate matter with motor emissions, the exhaust of a 1.8 gasohol engine was analyzed using the ABNT NBR 6601:2005 Protocol. The engine was operated with the gasohol that is currently used in Brazil. Two samples (one of TSP and the other of PM$_{10}$) were collected. In the TSP sample, the following metals were detected: Ca (52.0%), Mg (26.7%), Fe (1.5%), Zn (0.1%), Cu (1.6%) and Al (18.1%). In the PM$_{10}$ sample, the following metals were detected: Ca (51.6%), Mg (26.9%), Fe (0.8%), Zn (0.1%), Cu (1.9%) and Al (18.7%). Because of operational restrictions, it was not possible to collect more samples for the purpose of studying the PM$_{2.5}$ emissions.

The results obtained for the engine exhaust were notably different from those obtained for the atmospheric particulate matter, and this conclusion should be confirmed with further experiments. For TSP, the concentration ratios of metal/Ca were 0.51, 0.03, 0.35 and 0.002 for Mg, Fe, Al and Zn, respectively, in the motor exhaust, and 0.26, 0.81, 0.22 and 0.02 for the same metals in the ambient aerosol. Clearly, the Zn and Fe contents were higher for the airborne particulate samples, indicating that there are other sources of these metals. As reported by Thorpe and Harrinson,[28] Fe is present in high concentrations in car brake linings and car brake dust, and Zn is usually associated with tire wear.[29] Mg and Al are present in relatively high concentrations in motor exhaust. For PM$_{10}$ samples, a similar conclusion may be obtained.

The results for the TSP and PM$_{10}$ samples were significantly different from those obtained for fine particles in which Ca, Mg, Al and Fe represent 14.2, 4.5, 3.9 and 61.9% of the total metal content, respectively. This finding may be due to the different sources of these metals. Ca, Mg and Al are mainly related to soil dust and marine aerosols, while Fe may also be related to combustion

Table 1. Statistical summary of metal concentrations determined in TSP, PM$_{10}$ and PM$_{2.5}$. Samples were collected in the André Rebouças Tunnel in the period of January-April 2009. Standard deviations (SD), minimum (Min.) and maximum (Max.) values are also shown

		Concentration / (ng m^{-3})								
		Ca	Mg	Mn	Fe	Zn	Cu	Cr	Al	V
TSP	Mean	5038	1320	54	4101	128	179	13	1095	7
(n = 33)	SD	1285	297	14	1068	29	29	3	309	3
	Min.	2878	744	30	2479	73	130	8	527	4
	Max.	7800	1933	90	6490	182	253	19	1804	16
PM$_{10}$	Mean	2997	803	14	994	39	87	< LOD[a]	427	5
(n = 33)	SD	981	252	5	314	18	25	< LOD[a]	133	3
	Min.	811	244	5	418	17	58	< LOD[a]	124	1
	Max.	4867	1256	24	1779	94	167	< LOD[a]	660	10
PM$_{2.5}$	Mean	60	21	5	307	20	35	< LOD[a]	< LOD[a]	2
(n = 50)	SD	25	9	2	94	10	29	< LOD[a]	< LOD[a]	1
	Min.	28	9	< LOD[a]	183	6	16	< LOD[a]	< LOD[a]	< LOD[a]
	Max.	143	51	11	570	42	135	< LOD[a]	< LOD[a]	4

[a] LOD: limit of detection

sources. High concentrations of Fe were observed by Silva[29] in the exhaust of diesel and gasoline engines and were attributed to the corrosion of internal components and exhaust pipes.

For the TSP and PM$_{10}$ samples, Co, Ni, Cd, Pb and Mo were always observed in concentrations lower than their limits of detection. Cr was only observed in TSP samples. In our previous study[13] in which TSP and PM$_{10}$ samples were collected at the bus station, Mn, Co, Ni, Cd, Cr and Pb levels were under the limits of detection in all, but a few samples. It should be noted that in our previous work,[13] final sample volumes of 50 mL were used. In the present work, smaller final sample volumes were adopted (20 mL), but the trace metal concentrations were still too low to be determined. A more sensitive method of detection was not available.

The pattern observed in the atmospheric particulate matter may be attributed to the influence of several sources, such as tail pipe emissions, brake wear, tire wear, resuspended dust and marine aerosols.

Ca, Mg, Fe and Al are major components of crustal materials and soil and, are predominantly attributed to the resuspension of dust.[30] Road dust and roadside soils are often enriched with many elements emitted from anthropogenic sources, including Pb, Cu, Cd and Zn.[28] For PM$_{10}$ and total particulate matter, Zn and Cu are present in all of the samples in much higher ratios than the ratios found in crustal materials, indicating that these two elements (which are anthropogenic in origin) are enriched in the soil (Table 2).

Additionally, Ca and Mg (PM$_{10}$) and Fe (TSP) are present in higher ratios in the samples than in typical crustal material, which may indicate that vehicles also contribute to the emissions of these elements. It was reported that brake wear emissions contain significant amounts of metals, mainly Fe, Cu, Zn, Ca and Mn,[28] and Zn is usually considered a fingerprint of tire wear.[30]

Additionally, metal-based oil additives containing Zn and Mg, Zn-based anti-wear agents and Ca- and Mg-based detergents are added to fuels and lubricating oils, influencing the sizes of emitted particles and their composition.[31]

Our previous results from studies[13] at the bus station (TSP and PM$_{10}$) showed that for diesel emissions, Fe and Al were not enriched in the soil and were probably not due to vehicle emissions.

For fine particles, Mn, Fe, Zn and Cu were presentin higher ratios than in crustal material. Because these particles mainly originate from combustion processes, being present in gasoline, oil and lubricants. Al, Cr, Co, Ni, Cd, Pb and Mo were always observed in lower concentrations than their limits of detection. As previously observed,[29] Cu, Cr, Fe, Mn, Pb and Zn were present in the exhaust of gasoline-fueled vehicles, while Cd, Cu, Pb and Zn were found in alcohol engine emissions and Cr, Cu and Zn were also found in additives. Cu, Fe, Pb and Ni were determined by electrothermal atomic absorption spectrometry in Brazilian gasoline.[32] The presence of metals in automotive fuels is associated with the corrosion of engine parts, deposition and oxidative decomposition reactions of the fuel compounds.[33-35] Zn may also originate from the production process of ethanol and the transportation and storage of the fuel.[29]

Enrichment factors

For TSP and PM$_{10}$ samples, enrichment factors (EF) relative to the earth crust were calculated using Al as a

Table 2. Typical crust concentration (second column) and relative concentration of each metal in the earth crust (third column). Relative concentration of each crust metal in TSP, PM$_{10}$ and PM$_{2.5}$ samples (fourth, fifth and sixth columns). Enrichment factors (EF) for each metal in TSP, PM$_{10}$ and PM$_{2.5}$ samples (three last columns) were calculated using Al and Mg as references for TSP/PM$_{10}$ and PM$_{2.5}$ samples, respectively

Metals	Crust concentration / ppb by weight	% of metal crust	% of metal in TSP	% of metal in PM$_{10}$	% of metal in PM$_{2.5}$	EF[b] in TSP	EF[b] in PM$_{10}$	EF[c] in PM$_{2.5}$
Ca	5.0 x 10^7	22.1	42.2	55.7	14.2	7.8	11.8	1.8
Mg	2.9 x 10^7	12.8	10.8	14.9	4.5	3.1	4.9	1.0
Mn	1.1 x 10^6	0.5	0.5	0.3	0.9	1.9	2.8	7.1
Fe	6.3 x 10^7	27.9	34.3	18.5	62.0	5.4	3.3	8.4
Zn	7.9 x 10^4	[a]	1.1	0.8	4.6	259.6	192.1	835.2
Cu	6.8 x 10^4	[a]	1.5	1.7	8.8	191.2	238.4	1001.5
Cr	1.4 x 10^5	[a]	0.1	–	–	4.1	–	–
Al	8.2 x 10^7	36.3	9.2	8.0	3.9	1.0	1.0	–
V	1.9 x 10^5	[a]	0.1	0.1	0.3	0.1	[a]	[a]

[a] < 0.01; [b] Al was used as the reference metal; [c] Mg was used as the reference metal.

reference. Al is traditionally considered to be a relatively stable soil tracer that is not affected by contamination.[36] The selection of a metal as the normalization element is rather arbitrary and would lead to misleading conclusions if the metal were significantly enriched in the samples. For TSP and PM_{10}, Al is the only a crustal-origin metal that is not enriched in the samples (Table 2). For $PM_{2.5}$, it was not possible to use Al as the reference element because Al concentrations were under the limits of detection in all samples. Mg was considered a suitable reference element, as it was present in lower ratios in $PM_{2.5}$ than in crustal material. The following expression was used for the calculations:

$$EF_X = \frac{\left(X/_{Ref}\right)_{air}}{\left(X/_{Ref}\right)_{crust}} \quad (1)$$

where EF_X is the enrichment factor of species X, $(X/Ref)_{air}$ is the ratio of species X to the reference metal in the aerosol sample and $(X/Ref)_{crust}$ is the ratio of species X to the reference metal in the earth crust. The values for the composition of the earth crust were the same as those used in our previous work[13] and related papers.[37]

The interpretation of EF is based on the fact that metals originating from well-defined sources, such as the earth crust, can be distinguished from other metals derived from anthropogenic processes.[36,38,39] Because crustal metals are also present in direct exhaust emissions from vehicles, the choice of a reference material is rather difficult. However, the dependence of calculated values on this choice does not (in general) affect the conclusions that may be obtained from EF factors.

The EF values calculated in this work are shown in Table 2. Zn and Cu have EF values higher than 10 and may be considered to be of anthropogenic origin in all samples of particulate matter. As previously noted, Cu is typically linked to the abrasion of brakes, and Zn is generally linked to tire wear. These values are *ca.* 10 times higher than those obtained from our previous studies at the bus station.[13] The EF results are in close agreement with the calculated relative concentrations. Other metals, such as Ni, Cd and Pb, which are frequently identified as being of anthropogenic origin, were under their limits of detection and thus were not included in these calculations.

Trace metal dry deposition fluxes

Dry deposition can be an important mechanism for removing pollutants in the absence of precipitation and is characterized by the deposition velocity. The net flux of a species to the surface is proportional to the concentration of the species.[40] The deposition processes include gravitational settling, impaction and diffusion,[41] and these processes are dependent upon wind speed, humidity, viscosity and surface roughness. Dry deposition velocities are higher for coarse particles than for fine particles, and a range of settling velocities has been reported in the literature.[23,40,42,43]

In this work, dry deposition fluxes were calculated using an approximate model:[38,40]

$$F_d = V_d\, C_i \quad (2)$$

where F_d is the dry deposition flux, C_i is the trace metal geometric mean concentration and V_d is the elemental deposition velocity. The settling velocities reported by Yi *et al.*[43] were adopted. They determined their velocities by dividing measured fluxes by measured airborne concentrations. Flux measurements were performed with a smooth surrogate surface on an automated dry deposition sampler, and ambient particle concentrations were collected using a dichotomous sampler and analyzed by X-ray fluorescence spectrometry.[43] It should be emphasized, however, that the flux calculations might vary by more than one order of magnitude due to differences in the methods used and the uncertainties in V_d. Approximated values were estimated in order to compare our current data with data obtained in the bus station study[13] and in several locations in Salvador City (Bahia State, Brazil).[23] Calculated values are presented in Table 3.

When considering the calculated flux of TSP as the overall dry deposition, the main contribution is due to the crustal elements Ca, Mg and Fe. These fluxes are at least one order of magnitude greater than those ones of the metals of anthropogenic origin (Mn, Zn and Cu). For TSP and PM_{10}, Ca shows a higher flux due to the higher concentration. Considering the uncertainties and the wide range of dry settling velocities used in the literature, these results are in a range that is equivalent to the previously reported values taken at the bus station[13] and at other locations in Brazil and worldwide.[23,40,43] This was an expected result since dry deposition fluxes depend on element concentrations, which do not drastically differ for the studied areas.

In the fine particle fraction, the dry deposition flux for Ca was considerably lower than in the previously described fractions (*ca.* 10 times lower than in the TSP fraction). For primarily anthropogenic elements that are associated with smaller particle sizes, the dry deposition fluxes are mainly lower in the TSP and PM_{10} fractions due to the smaller concentrations of these elements compared to the crustal elements. When comparing the deposition flux of the elements in the different fractions, rates of flux for

Table 3. Estimated trace element dry deposition fluxes in the André Rebouças Tunnel (F_d). Dry settling velocities (V_d) are from reported literature data[40,43]

TSP (6 h)	Ca[a]	Mg	Fe[a]	Mn	Zn	Cu	Al
Mean concentration / (ng m^{-3})	5037.6	1319.3	4101.1	53.8	178.6	182.1	1095.5
Dry settling velocity (Vd) / (cm s^{-1})	1.839[b]	4.6[a]	1.405[b]	1.1[a]	3[a]	3[a]	1.1[a]
Dry deposition flux (Fd) / (mg m^{-2} yr^{-1})	17529.2	11482.7.1	10902.7	11.9	727.4	1013.8	2280.1
PM$_{10}$ (6 h)							
Mean concentration / (ng m^{-3})	2996.8	803.2	994.4	13.8	39.1	87.4	429.7
Dry settling velocity (Vd) / (cm s^{-1})	1.839[b]	4.6[a]	1.405[b]	1.1[a]	3[a]	3[a]	1.1[a]
Dry deposition flux (Fd) / (mg m^{-2} yr^{-1})	10427.9	6991.0	2643.6	28.6	238.4	495.9	894.4
PM$_{2.5}$ (24 h)							
Mean concentration / (ng m^{-3})	59.5	21.2	321	4.4	20.8	47.2	–
Dry settling velocity (Vd) / (cm s^{-1})	0.317[b]	23.1[a]	0.385[b]	12.3[a]	2.8[a]	2.8[a]	12.3[a]
Dry deposition flux (Fd) / (mg m^{-2} yr^{-1})	142.9	3704.9.0	935.3	413.7	521.3	999.4	–

[a]Reference 43; [b]Reference 40.

anthropogenic metals (Zn and Cu) are relatively higher in the PM$_{2.5}$ fraction. Again, this finding is a result of the trace metal levels and distribution.

Statistical analysis

A multivariate statistical approach was applied to determine the relationship between measured trace metals. A combination of Spearman's correlation coefficients, cluster analysis and principal component analysis (PCA) were used. Spearman's correlation coefficients were calculated using the individual metal concentrations and are presented in Table 4.

For PM$_{10}$ and total particulate matter, high correlations were obtained with Ca, Mg and Al (0.89-0.99). The correlation of Ca and Mg with Fe was poor (0.36-0.55),

Table 4. Spearman's correlation factors calculated for metals in TSP, PM$_{10}$ and PM$_{2.5}$ samples collected from the André Rebouças Tunnel

TSP	Ca	Mg	Mn	Fe	Zn	Cu	Cr	Al	V
Ca	1								
Mg	0.89	1							
Mn	0.44	0.31	1						
Fe	0.55	0.37	0.87	1					
Zn	0.61	0.42	0.58	0.73	1				
Cu	0.58	0.45	0.55	0.67	0.35	1			
Cr	0.61	0.40	0.85	0.98	0.74	0.69	1		
Al	0.92	0.76	0.66	0.76	0.70	0.66	0.79	1	
V	0.42	0.21	0.46	0.54	0.41	0.59	0.52	0.5	1
PM$_{10}$	Ca	Mg	Mn	Fe	Zn	Cu	Al	V	
Ca	1								
Mg	0.99	1							
Mn	0.35	0.34	1						
Fe	0.37	0.36	0.93	1					
Zn	0.64	0.60	0.50	0.58	1				
Cu	0.55	0.53	0.30	0.36	0.48	1			
Al	0.95	0.97	0.41	0.45	0.57	0.60	1		
V	0.19	0.15	0.34	0.33	0.28	0.39	0.15	1	
PM$_{2.5}$	Ca	Mg	Mn	Fe	Zn	Cu	V		
Ca	1								
Mg	0.58	1							
Mn	0.44	0.42	1						
Fe	0.32	0.49	0.74	1					
Zn	0.49	0.37	0.63	0.58	1				
Cu	–0.26	–0.13	0.05	0.05	–0.35	1			
V	0.30	–0.09	0.2	0.33	0.40	–0.30	1		

which is an important difference when comparing these results with those obtained at the bus station.[13] These results indicate that Ca, Mg and Al are probably due to the resuspension of dust, while Fe may also have additional source. A similar conclusion is obtained from Figure 1 in which Al, Mg and Ca are grouped in the same sub-group, and Fe is closely related to Cr (in TSP) and Mn (in TSP and PM_{10}) (correlation factors in the range of 0.87-0.98).

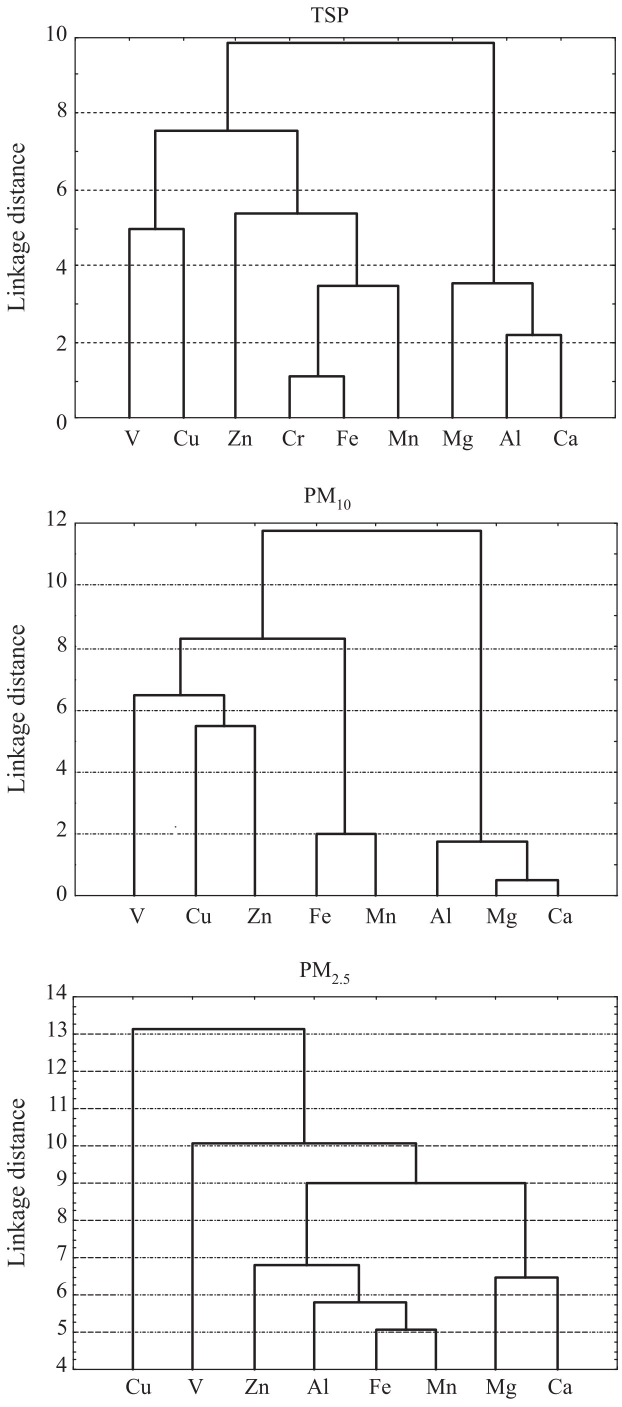

Figure 1. Cluster analysis at 95% confidence level for TSP, PM_{10} and $PM_{2.5}$ samples collected from the André Rebouças Tunnel.

As previously cited, Fe and Mn are important elements of brake wear, and their levels were determined in the exhaust of gasoline-fueled vehicles. Anthropogenic elements (Zn and Cu) have low correlation factors. This suggests that they have different emission sources.

Principal component analysis gave similar results. Two factors showing eigenvalues higher than 1 (accounting for a total of 81% of the data variability) were identified for TSP. One factor was attributed to soil dust based on the presence of crustal elements (Ca, Mg and Al). The other factor concerned the high loadings of Mn, Fe, Zn and Cr, which characterize the vehicular traffic factor. For PM_{10}, three factors with eigenvalues higher than 1 were obtained, thereby explaining 79% of data variance. The first factor was attributed to soil dust (Ca, Mg and Al), the second factor was attributed to high loadings of Fe and Mn and may be associated to vehicular traffic and the third factor (V) may be attributed to diesel fuel and oil combustion.

For fine particles, the correlation factor between Ca and Mg was relatively low (0.58), and Fe was found to be related to Mn (0.74). The weak correlation between metals may be indicative of a variety of sources related to vehicular flux. Principal components analysis showed three factors with eigenvalues higher than 1, which account for 71% of the data variability. These factors are related to natural inputs (Ca and Mg), vehicular emissions (Mn, Fe and Zn) and diesel and oil combustion (V).

Principal component analysis, Figure 2, clearly suggests that natural sources, dust resuspension and vehicular traffic may be related to particulate matter. Nevertheless, the relative contributions of these components are different: for TSP and PM_{10}, the soil dust and , to a lesser extent, the marine aerosols are the main sources of contribution, while for $PM_{2.5}$ fraction, the soil dust and vehicular emissions contribute to a similar extent.

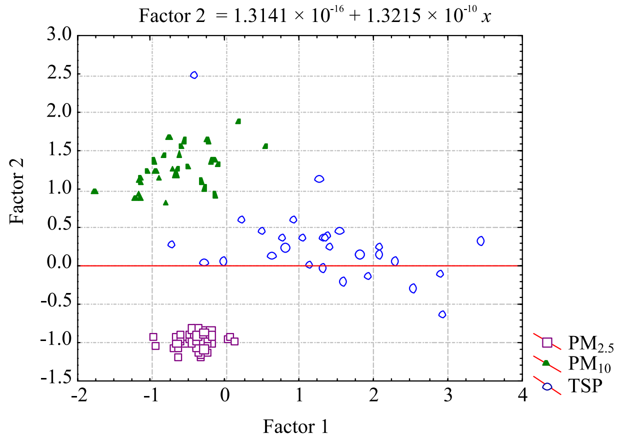

Figure 2. Principal component analysis for TSP, PM_{10} and $PM_{2.5}$ samples.

When the present results are compared with results obtained for TSP and PM_{10} at the bus station in the Rio de Janeiro Metropolitan Area[13] and the PM_{10} at the Lapa Bus Station in Salvador[23] using the same analytical method, several differences are observed. Enrichment factors for Cu and Zn in both bus stations were in the range 20-30, while the values obtained in this work were approximately an order of magnitude higher. Also, in both bus stations, in the high diesel-fueled vehicle fraction, Cu and Zn were highly correlated, while no significant correlation was observed in the present work.

Conclusions

Exhaust emissions of metals were determined in coarse and fine particulate matter collected in a location characterized by light-duty vehicular flux. The results for coarse particles are significantly different from those obtained for fine particles, confirming that they originate from different sources. For coarse particles, Ca, Mg and Al may be attributed to marine aerosols and the resuspension of dust, while Fe and anthropogenic metals (Zn and Cu) may originate from brake and tire wear. In fine particulate matter, the presence of these metals may be attributed to the corrosion of internal vehicular components and exhaust pipes.

Supplementary Information

Supplementary information concerning the experimental procedures is available free of charge at http://jbcs.sbq.org.br as a PDF file.

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