

## Concentration of Airborne Trace Metals in a Bus Station with a High Heavy-Duty Diesel Fraction

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Amostras de material particulado total (MPT) e  $MP_{10}$  foram coletadas numa estação de ônibus, no período de agosto de 2006 a fevereiro de 2007. Na área, as únicas fontes importantes de emissão de poluentes são os ônibus, já que os veículos leves representam apenas 1-2% do fluxo total e não são desenvolvidas outras atividades no local. As concentrações de metais foram determinadas por espectroscopia de emissão por plasma indutivamente acoplado (ICP-OES). Os metais mais abundantes foram Ca, Mg, Fe e Al, que correspondem a 50,1%; 24,2%; 6,5% e 18,7%, respectivamente, do conteúdo metálico. O Co, Ni, Cd, Cr e Pb foram encontrados em níveis inferiores ao seu limite de detecção, exceto para algumas poucas amostras. Os fatores de enriquecimento calculados, mostram que o Zn e o Cu são devidos provavelmente à composição do combustível e do óleo lubrificante. O Ca, Mg e Al podem ser atribuídos à resuspensão de poeira, enquanto que o Fe pode ser devido tanto à resuspensão de poeira como as emissões dos veículos.

Total particulate matter (TSP) and  $PM_{10}$  samples were collected in a bus station, in the period of August 2006 to February 2007. Buses are the only significant emission sources in this area once light duty vehicles represent about 1-2% of total flux and no other activities are developed in the location. Concentrations of metals in the samples were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). Ca, Mg, Fe and Al were the most abundant elements and accounted for about 50.1%, 24.2%, 6.5% and 18.7% of the total metal content. Co, Ni, Cd, Cr and Pb were under detection limits except for a few samples. Calculated enrichment factors show that Zn and Cu are probably due to fuel and oil composition. Ca, Mg and Al may be attributed to dust resuspension while Fe may be due to both dust resuspension and contribution of vehicles.

**Keywords:** airborne particulate matter,  $PM_{10}$ , trace metal, diesel emissions

### Introduction

Heavy-duty diesel vehicles contribute significantly to air pollution in urban areas. Previous studies conducted by the California Resources Board estimated that, for instance, heavy-duty vehicles account for nearly 80% of particulate matter (PM) in California.<sup>1</sup>

In Brazil, the government regulatory agencies have estimated mobile source emissions for several urban areas. The Metropolitan Area of São Paulo has the largest running fleet in Brazil: roughly 7.3 million passenger cars and commercial vehicles being composed of approximately 6% of diesel vehicles.<sup>2</sup> In this region, mobile sources are responsible for about 40% of inhalable particulate matter emissions (14,000 t year<sup>-1</sup> due to diesel engines, 4,900 t year<sup>-1</sup> due to light-duty vehicles and 9,100 t year<sup>-1</sup> due to tires of wheels).<sup>2</sup> Other major sources are secondary

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reactions, *i.e.*, gas-to-particle conversion, condensation and coagulation, which contribute with 25% of local  $PM_{10}$  emissions. Resuspension of soil and dust generates 25% of these particles while 10% is attributable to industrial sources.<sup>3</sup> The Metropolitan Area of Rio de Janeiro has the second largest running fleet, with nearly 1.5 million vehicles and about 12% heavy-duty vehicles (mainly buses and trucks) running on diesel.<sup>4</sup> According to the most recent available official emission inventory,<sup>5</sup> approximately 76% of the total air pollution load of  $CO$ ,  $SO_2$ ,  $NO_x$  and  $PM_{10}$  are direct contributions of mobile sources.

Diesel particulate matter consists of an elemental carbon core with a large number of adsorbed substances, such as several organic compounds, sulfates, nitrogen derivatives and metals. The particle size distribution and chemical composition is highly dependable on composition of fuel and lubricating oil, emission control technology, engine type, operating conditions and traffic jams. The properties of Brazilian diesel are presented in Table 1.<sup>6</sup> No analysis of metal content is required and, to our knowledge, there is no information available in the literature.

National legislation determines the maximum tolerable emissions of diesel vehicles. For new motors, emissions of particulate matter in a current dynamometer test should be less than  $0.10 \text{ g kW h}^{-1}$ .<sup>7</sup> National standards of air quality only determine limits for total particulate matter ( $240 \text{ ng m}^{-3}$  for 24 h and  $80 \text{ ng m}^{-3}$  for the annual geometrical mean) and  $PM_{10}$  ( $150 \text{ ng m}^{-3}$  for 24 h and  $50 \text{ ng m}^{-3}$  for the annual mathematical mean). However, no legislation and no control are done regarding fine particles ( $PM_{2.5}$ ). Literature data obtained for Brazilian cities mainly deals with total suspended particles (TSP)

and  $PM_{10}$ . Recently, Miranda and Andrade<sup>3</sup> determined the main characteristics of particles released into the atmosphere of the city of São Paulo, using a micro-orifice uniform deposit impactor (MOUDI). According to this study, soil-derived elements appeared in the coarse fractions obtained with the impactor, whereas sulfur and black carbon, the latter derived from diesel emissions, were predominant in the fine fraction. Certainly, more studies to assess particulate matter distribution and composition, focused on the fine mode, are necessary.

Several studies have discussed the toxicological effects associated with particle-bound trace metals.<sup>8,9</sup> The size distribution of atmospheric particle-bound trace metals is crucial in determining their health effects by inhalation. Recent literature data show increased toxicity of particles with decreasing size.<sup>10,11</sup>

As discussed by Valavanidis *et al.*,<sup>12</sup> the  $PM_{2.5}$  and  $PM_{10}$  levels in urban atmospheres are mainly related to traffic-pollutants (both diesel and gasoline vehicles) while coarse particles contain crustal material, and resuspended road dust.<sup>13,14</sup> The authors reported that 90% of metals in TSP,  $PM_{10}$  and  $PM_{2.5}$  fractions, collected in the centre of Athens (Greece), were Fe, Zn, Pb and Cu attributed to traffic, static combustion and crustal matter. These results are in general agreement with the majority of previously reported data.

Recently, trace elements and metals in the ultrafine and accumulation particulate matter modes were measured near a Southern California freeway with approximately 20% of diesel traffic. Their results confirmed previous studies which showed that the presence of metals in the 18-32 nm is significantly higher when compared to any other sizes range.<sup>15</sup>

**Table 1.** Diesel fuel properties for diesel formulations A, B and C which are currently used in Brazil<sup>6</sup>

Property	Units	Values following ASTM E 29 specifications <sup>6</sup>		
		A	B	C
Type of Diesel				
Sulfur maximum	% m/m	1.00	0.50	0.30
Volatility				
Distillation				
50%	°C	245-310	245-310	245-310
80%	°C	370	370	360
Density at 20-24°C	$\text{g cm}^{-3}$	0.82-0.88	0.82-0.88	0.82-0.88
Viscosity 40°C	$\text{mm}^4 \text{ s}^{-1}$	1.6-6.0	1.6-6.0	1.6-6.0
Cetane number		40	40	42
Contaminants:				
Water and Sediments	% (v/v)	0.05	0.05	0.05

A – used in all regions of Brazil, including Rio de Janeiro; B – used in the cities of Porto Alegre, Curitiba, Belo Horizonte, Recife and Fortaleza; C – used in the cities of Salvador, São Paulo, Santos and Curitiba.

Direct diesel engine exhaust particles have also received great attention. Using a diesel engine under various driving condition and diesel from Taiwan, it was determined<sup>16</sup> that the emitted concentrations of crustal elements (such as Al, Ca, Fe, Mg and Si) are much higher than those of anthropogenic elements. Nevertheless, the authors concluded that the contribution of these elements to the ambient environment could be quite significant and different results may be expected for diesel fuel used in other countries.

The goal of this paper is to determine diesel buses emissions of metals in particulate matter, under typical conditions of operation in a bus station, which is poorly ventilated and where the buses move at low speed and park for passenger access. Results are limited since they are strongly affected by vehicle's operating conditions and the quality of diesel fuel. Due to instrumental limitations, only TSP and the  $PM_{10}$  fraction were studied.

## Experimental Method

### Sampling site

Samples were collected in Mayor José Carlos Lacerda bus station, placed in Centenário Quarter, in the city of Duque de Caxias (Figure 1). The city occupies an area of 468.3 km<sup>2</sup> and has a population of about 842,890 inhabitants distributed in forty Quarters and four Districts.<sup>17</sup> The total

number of vehicles in the city is about 160,000. Presently, 64.7% of vehicles use gasohol (gasoline with 24% of ethanol), 11.7% use neat ethanol, 12.3% use compressed natural gas (CNG), 2.5% are flex-fueled cars (gasohol and ethanol) and 8.8% use diesel.<sup>4</sup> The city has about 3,000 buses and 690 micro-buses.

The bus station region is a residential area with reduced commercial activity and no industries. The station has one floor (10,621 m<sup>2</sup>) with 8 platforms for arrivals and departures of urban heavy-duty diesel buses. Each platform has capacity for four buses. Besides movements of arrivals and departures, many vehicles that are waiting for departure keep their motors on. The station makes the confluence for 181 buses from 14 bus lines coming from all other districts of Duque de Caxias (6) and other cities of the Metropolitan Region of Rio de Janeiro (8). The samplers were installed beside one of the platforms at a height of 2 m. The flux of buses is higher during the morning and in the evening. In those periods, the departure interval between buses is nearly five minutes and the frequency of leaving buses in the bus station is less than one minute. Since light duty cars represent about 1-2% of the total flux, buses are the only significant emission sources. Moreover, no other activities are developed in the location and its surroundings, and no other possible significative sources may be considered. In particular, there are no fast-food restaurants in the area near the platforms.

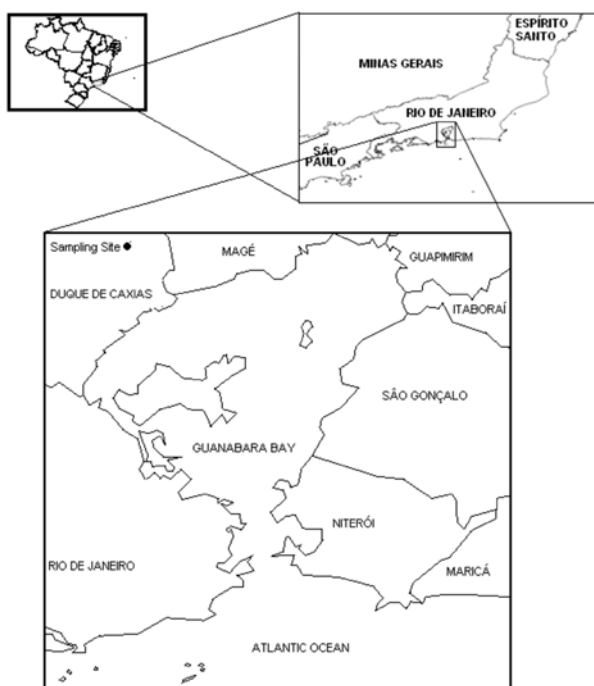
The bus station has a paved platform and is covered by a roof. Since the sides are opened and the roof is about 10 m high, it is a well ventilated area.

### Sampling

The selection of the points and the sampling procedure took into account the U.S. Environmental Protection Agency<sup>18</sup> (EPA) recommendations.

Samplings were performed, in Mayor José Carlos Lacerda bus station on week days using 6 h sampling periods of time (from 6:00 am to midday). No samplings were performed in the afternoon and at night because the main goal of this work was to identify typical emissions of diesel-powered vehicles. It was not the objective of this study to assess comparisons such as rush-to-non-rush hours or daytime-to-nighttime periods. Furthermore, these comparisons should have been useful to qualify clearly diesel burning but experiments at night were not possible to be performed because of security reasons and availability of the equipment.

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 0.22  $\mu$ m). The flow rate was aspiration of 500 L min<sup>-1</sup>.



**Figure 1.** Location of the sampling site, Major José Carlos Lacerda, in the city of Duque de Caxias (Rio de Janeiro Metropolitan Area).

A total of 66 samples (33 TSP and 33 PM<sub>10</sub> respectively) were collected, on week days, from August 2006 to February 2007.

#### Extraction procedure and analysis

Levels of TSP and PM<sub>10</sub> were determined by gravimetry.<sup>19-21</sup> For analysis of trace metals, the same procedure of our previous studies was followed.<sup>19-21</sup> 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<sup>-1</sup> of specific resistivity) in a Pyrex™ tube and let still for 2 h at 95 °C in a heating plate.<sup>22,23</sup> The extracted solution was filtered by using a Whatman n° 41 (WH1441-110) filter, completed to 50 mL with ultrapure water and kept in pre-cleaned polyethylene bottles in the refrigerator until analyses.<sup>24,25</sup>

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

Metals were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) following Method IO-3.4.<sup>23</sup>

Both, detection limits and accuracy for the method were determined following Method IO-3.4.<sup>23</sup> Detection limits were computed as three times the standard deviation of the distribution of outputs for ten repeated measurements of the standard, which contained no metals.<sup>26</sup> These limits were calculated as 80 ng m<sup>-3</sup> for Al and Cr, 10 ng m<sup>-3</sup> for Zn, 8 ng m<sup>-3</sup> for Fe, Co and Cu, 4 ng m<sup>-3</sup> for Mn, 2 ng m<sup>-3</sup> for Ni, 0.2 ng m<sup>-3</sup> for Cd and 0.1 ng m<sup>-3</sup> for Pb.

The accuracy of the method was evaluated using a standard reference material (SRM, 2783 Air particulate on Filter Media-NIST). Three samples of the reference material were determined in triplicate and the results were compared with the concentration reported in the certificate of analysis. The obtained concentrations differed less than 8%. All samples, as well as SRM, were in the range of the reference material (3-8%). All samples and SRM were determined in triplicate and a difference lower than 1% was considered acceptable.

#### Statistical analysis

Experimental data were analysed by calculating the Spearman's correlation coefficients using STATISTICA 6.0 (Stat soft) programme. Also principal component analysis (PCA) and cluster analysis (CA), using Euclidian distances

and Ward's Method, were performed, as a classification and ordination method.

## Results and Discussion

#### Particulate matter

TSP levels, determined by gravimetry, were in the range of 177.6 to 524.2 µg m<sup>-3</sup>. The mean concentration for all samples (n=33) was 335.9 µg m<sup>-3</sup>. Similarly, values for PM<sub>10</sub> (n=33) ranged from 38.6 to 120.6 µg m<sup>-3</sup>, with a mean value of 74.6 µg m<sup>-3</sup>.

The ratios PM<sub>10</sub>/TSP were in the range 0.11 to 0.65 with an average value of 0.24. Literature data<sup>27,28</sup> show that most diesel exhaust particle mass is associated with accumulation mode particles, ranging from 0.05 to 0.7 µm and centered at about 0.02 µm. The coarse mode (1-10 µm) accounts for 5-20% of diesel exhaust particle mass, containing accumulation mode particles that have been deposited on cylinder and exhaust system surfaces and are later reentrained. Since in this work only the TSP and PM<sub>10</sub> fractions were studied and clearly the fraction of diameter > 10 µm is the most abundant, the main contribution to the studied particulate matter in the bus station is the resuspension of dust.

#### Levels of trace metals

Twelve metals were studied in TSP and PM<sub>10</sub> samples: Ca, Mg, Mn, Fe, Zn, Cu, Co, Ni, Al, Cd, Cr and Pb.

Table 2 shows the mean concentrations as well as standard derivation, minimum and maximum for Ca, Mg, Fe, Zn, Cu and Al which were determined in all samples. Ca, Mg and Fe were the most abundant elements and accounted for about 50.1%, 24.2%, 6.5% and 18.7% of the total metal content.

This result agrees with Wang *et al.*<sup>16</sup> who reported that Al, Ca, Fe, Mg and Si (not determined in the present study) accounted for about 80% of the total metal content in diesel fuel and in the exhaust of a diesel engine. Aerosol samples from the exhaust of a diesel motor car, in the size range 0.1-2.5 µm, determined by total reflection X-ray fluorescence presented considerable amounts of Si, Ca, Al, Fe, Zn and Mg.<sup>29</sup>

Also, Lough *et al.*<sup>30</sup> reported that the most abundant elements determined in PM<sub>10</sub> in two tunnels in Milwaukee, USA, were Fe, Ca, Si, Na, Mg, Al, S and K, which accounted for an average of 94% of the total PM<sub>10</sub> content of 42 measured elements. They were also present in PM<sub>2.5</sub> in much lower amounts and were significantly different from zero in PM<sub>2.5</sub> in only a few tests.

**Table 2.** Statistical summary of metal concentrations determined in TSP and PM<sub>10</sub>. Samples were collected in Mayor José Carlos Lacerda Bus Station in the period of August 2006 to February 2007. Standard deviations (SD), minimum (Min) and maximum (Max) values are also shown

		Concentration (ng m <sup>-3</sup> )					
		Ca	Mg	Fe	Zn	Cu	Al
TSP (n=33)	Mean	11907	5754	2597	141	66	4811
	SD	3581	1784	1849	110	178	1815
	Min	4270	1902	6	0	6	1423
	Max	19215	8568	5715	509	1049	8273
PM <sub>10</sub> (n=33)	Mean	11145	5361	1446	77	26	4160
	SD	2648	1545	1625	75	13	1189
	Min	4270	1902	218	Udt	Udt	1423
	Max	15548	7902	5299	313	51	7106

Udt = Under detection limit

The pattern observed in the bus station may be attributed to the influence of several sources such as tail pipe emissions from buses, brake wear, tire wear and resuspended dust. Literature results confirm that diesel fuels and lubricating oils contain significant amounts of Ca, Mg, Fe and Zn.<sup>16,31,32</sup> Lubricating oils contain trace amounts of Ti, Mn, Co, Cd and Pb used as additives.<sup>31</sup>

The exhaust of a 4 cylinders diesel engine, with a rotatory fuel pump and a mechanical injection system was analyzed using the US EPA protocol. The engine was operated with diesel A, currently used in Brazil. Two samples, one of TSP and other of PM<sub>10</sub>, were collected. In TSP, the following metals were detected: Ca (47%), Mg (23%), Fe (10%), Zn (0.6%), Cu (0.3%) and Al (19%). In PM<sub>10</sub> the following metals were detected: Ca (50%), Mg (24%), Fe (6.5%), Zn (0.3%), Cu (0.1%) and Al (19%). Mn, Co, Ni, Cd and Pb were under detection limits.

Ca, Mg, Fe and Al are major components of crustal materials and soil and are predominantly attributed to resuspension of dust.<sup>30</sup> It has been previously shown that the dust resuspended from roadways is enriched with many

elements emitted from anthropogenic sources. The fact that Zn and Cu are present in the samples in higher ratios than those found in crustal materials, while Ca, Mg, Fe and Al are present in lower levels, indicates that these two elements may have important combustion sources and are enriched in the soil (Table 3). It may be noted that, as previously stated, metal-based oil additives containing Zn and Mg, anti-wear agents (Zn based) and detergents (Ca and Mg based) are added to fuels and lubricating oils, influencing the sizes of emitted particles and their composition.<sup>31</sup> Also, it was reported that brake wear emissions contain significant amounts of metals, including Zn, Cu, Fe and crustal elements.<sup>30,33</sup>

Mn, Co, Ni, Cd, Cr and Pb levels were under detection limits except for a few samples: PM<sub>10</sub>, one sample presented 129 ng m<sup>-3</sup> of Pb, five samples presented concentrations in the range 1.1-9.7 ng m<sup>-3</sup> and another sample contained 6.9 ng m<sup>-3</sup> of Ni. For TSP, one sample contained 1.7 ng m<sup>-3</sup> of Cd, Ni and Cd is present in batteries. It is worth noting that the extraction procedure, mainly the final sample volume, may have a negative contribution to the detection

**Table 3.** Relative concentration of each metal in TSP and PM<sub>10</sub> samples (first and second columns). Typical crust concentration in units of ng m<sup>-3</sup> (third column) and relative concentration of each metal in the earth's crust (fourth column). Enrichment factors (EF) for each metal in TSP and PM<sub>10</sub> samples (two last columns) calculated using Al as reference

Metals	% of metal in TSP	% of metal in PM <sub>10</sub>	Crust concentration	EF (in TSP)	EF (in PM <sub>10</sub> )	% of metal in crust
Ca	47.0	50.2	4.9x10 <sup>13</sup>	4.2	4.5	22.3
Mg	22.7	24.1	3.2x10 <sup>13</sup>	3.1	3.1	14.5
Fe	10.3	6.5	5.7x10 <sup>13</sup>	0.8	0.5	25.9
Zn	0.6	0.3	7.9x10 <sup>10</sup>	30.6	19.3	0.0
Cu	0.3	0.1	3.7x10 <sup>10</sup>	30.0	13.9	0.0
Al	19.0	18.7	8.2x10 <sup>13</sup>	1.0	1.0	37.3



**Table 4.** Estimated trace element dry deposition fluxes in Mayor José Carlos Lacerda Bus Station ( $F_d$ ). Dry settling velocities ( $V_d$ ) are literature data<sup>34-36</sup>

PM <sub>10</sub>	Ca	Mg	Fe	Zn	Cu	Al
Mean concentration (ng m <sup>-3</sup> )	11907	5754	2597	141	66	4811
Dry settling velocity ( $V_d$ ) (cm s <sup>-1</sup> )	2.0	2.0	2.0	0.1	0.1	2.0
Dry deposition Flux ( $F_d$ ) (mg m <sup>-2</sup> yr <sup>-1</sup> )	60078	29035	13103	36	17	24275
TSP	Ca	Mg	Fe	Zn	Cu	Al
Mean concentration (ng m <sup>-3</sup> )	11145	5361	1446	77	26	4160
Dry settling velocity ( $V_d$ ) (cm s <sup>-1</sup> )	2.0	2.0	2.0	0.1	0.1	2.0
Dry deposition Flux ( $F_d$ ) (mg m <sup>-2</sup> yr <sup>-1</sup> )	168703	81149	21893	58	20	62965

of these metals. Eventually, using smaller volumes, they would be determined in concentrations higher than the detection limit.

#### Enrichment factors

Enrichment factors (EF) were also calculated using Fe as reference and the expression:

$$Ef_X = (X/Ref)_{air} / (X/Ref)_{crust}$$

The interpretation of EF is based on the fact that metals originated from well defined sources, such as the earth's crust can be distinguished from other metals derived from anthropogenic processes.<sup>34-36</sup> Since crustal metals are also present in direct exhausts emissions from the diesel motors, the choice of a reference material is rather difficult.

When using Al as reference, which is traditionally considered a soil tracer, enrichment factors for Zn and Cu in the range from 13.8 to 30.6 are obtained, confirming the possibility of anthropogenic sources.

#### Trace metal dry deposition fluxes

Dry deposition fluxes were calculated using the equation:

$$F_d = C_i \times V_d$$

where  $F_d$  is the dry deposition flux,  $C_i$  the trace metal geometric mean concentration taken from a prolonged sampling period and  $V_d$  is the elemental settling velocity.<sup>37</sup> The deposition processes include gravitational settling, impaction and diffusion,<sup>38</sup> which are dependent upon wind speed, humidity, viscosity and surface roughness. A range of settling velocities have been applied to dry deposition flux calculations in the past, these were determined by a number of approaches including mass-size distributions in the aerosol population, usually evaluated from cascade

impactor data.<sup>39-41</sup> For Zn and Cu, a mean value of 0.1 cm s<sup>-1</sup> was applied, and for Ca, Mg, Fe and Al a mean value of 2 cm s<sup>-1</sup> was adopted. These values fall close to the  $V_d$  range given in other studies<sup>42-44</sup> (and references there in). It should be emphasized, however, that the flux calculations might vary by approximately one order of magnitude due to the uncertainties in  $V_d$ .

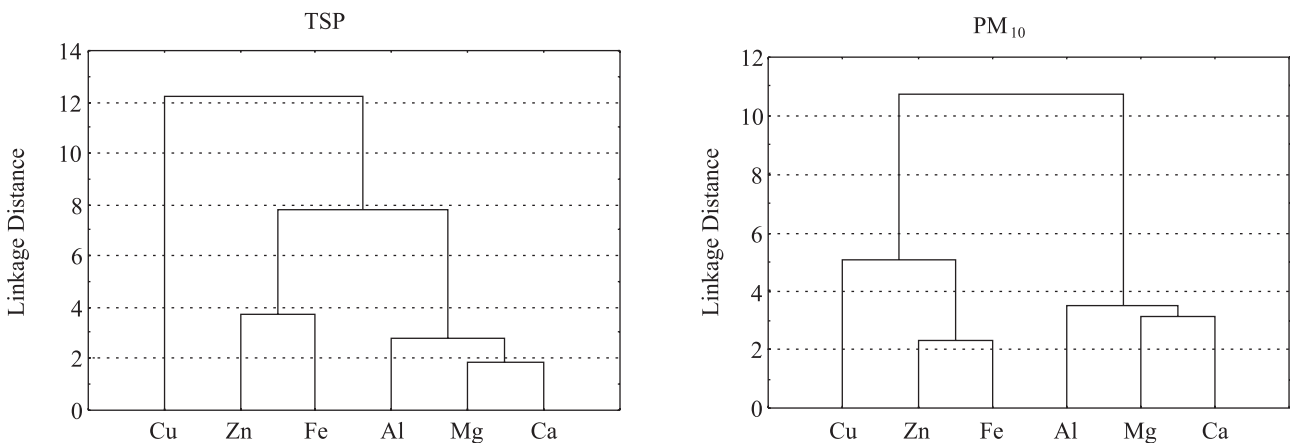
Calculated values are presented in Table 4. Dry deposition fluxes are higher for Ca, Mg, Al and Fe, in decreasing order, due to their high concentration and settling velocities. Fluxes for Zn and Cu are three orders of magnitude lower.

#### Statistical analysis

Spearman correlation coefficients, calculated using the individual concentrations (n=33 for TSP and n=33 for PM<sub>10</sub>), are presented in Table 5.

**Table 5.** Spearman's correlation factors calculated for metals in TSP and PM<sub>10</sub> samples collected of metals in Mayor José Carlos Lacerda Bus Station (significant values at 95% of confidence limit are in bold)

TSP	Ca	Mg	Fe	Zn	Cu	Al
Ca	1.0					
Mg	<b>0.95</b>	1.0				
Fe	<b>0.65</b>	0.58	1.0			
Zn	0.49	0.39	<b>0.79</b>	1.0		
Cu	-0.33	-0.20	-0.18	-0.16	1.0	
Al	<b>0.92</b>	<b>0.88</b>	<b>0.84</b>	<b>0.68</b>	-0.42	1.0
PM <sub>10</sub>	Ca	Mg	Fe	Zn	Cu	Al
Ca	1.0					
Mg	<b>0.84</b>	1.0				
Fe	0.38	0.11	1.0			
Zn	0.40	0.18	<b>0.92</b>	1.0		
Cu	0.50	0.35	<b>0.69</b>	<b>0.71</b>	1.0	
Al	<b>0.84</b>	<b>0.79</b>	<b>0.66</b>	<b>0.65</b>	<b>0.67</b>	1.0



**Figure 2.** Cluster analysis, at 95% confidence limit, for TSP and PM<sub>10</sub> samples collected at Major José Carlos Lacerda Bus Station.

High correlations (0.88-0.92) were obtained for Ca, Mg, Fe and Al in TSP samples. Furthermore, Zn and Fe show a high correlation (0.79) while the value for Zn and Cu is very low. A similar result is shown in Figure 2 in which the cluster analysis is displayed. Al, Mg and Ca are grouped in the same sub-group, as well as Zn and Fe. The five elements are in the same group in the dendrogram of Figure 2.

Besides, the principal component analysis shows three groups. Component 1, which accounts for 66.8% of the total variance, contains Fe and Zn. Ca, Mg, and Al are included in component 3 (96.0% of total variance).

Data for PM<sub>10</sub> also show a high correlation between Ca, Mg and Al with Spearman correlation coefficients in the range of 0.79-0.84 (see Table 5). Fe and Zn also show high correlation (0.92) and Zn-Cu has a coefficient of 0.71. These data are consistent with the dendrogram displayed in Figure 2: two clusters are obtained, one grouping Cu, Zn and Fe and the other containing Al, Mg and Ca.

Principal components analysis leads to two factors: factor 1, (which represents 65.6% of variance) groups Fe, Zn and Cu, and factor 2 contains Ca, Mg and Al accounts for 89.9% of total variance.

When comparing TSP and PM<sub>10</sub> data, it can be seen that Ca, Mg and Al are highly correlated in both particulate matter fractions. As previously stated, they are major components of crustal materials and are indicative of the significant contribution of dust resuspension to particulate matter contribution.

As suggested by the enrichment factors, Zn and Cu, which may have an important anthropogenic contribution, only show a good correlation in PM<sub>10</sub>. Fe also shows a good correlation with Zn, mainly in PM<sub>10</sub>. These results may be explained considering that it was reported that brake emissions contain significant amounts of metals, including Zn, Cu, Fe and crustal elements.<sup>30,33</sup>

## Conclusions

The results of this study showed that diesel vehicles significantly contribute to the emissions of Ca, Mg, Zn and Cu. The pattern observed may be attributed to the contribution of several sources such as tail pipe emissions, brake wear, tire wear and resuspended dust. The analysis of the exhaust of a diesel motor confirmed that these metals are emitted by diesel combustion. Oil additive also contains trace quantities of these metals, while brake wear emissions contain significant amounts of Zn, Cu and crustal elements.

Due to instrumental limitations, only the TSP and PM<sub>10</sub> fractions were determined but, clearly, the characterization of trace metals in the fine and ultrafine ranges is important due to the toxicological impacts of some of the metals studied.

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