Available online at www.sciencedirect.com
ScienceDirect
Atmospheric Environment 41 (2007) 7837–7850
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

Atmospheric concentrations and dry deposition fluxes of particulate trace metals in Salvador, Bahia, Brazil

Pedro A. de P. Pereira[a,b], Wilson A. Lopes[a], Luiz S. Carvalho[a], Gisele O. da Rocha[b,1], Nei de Carvalho Bahia[a], Josiane Loyola[c], Simone L. Quiterio[c], Viviane Escaleira[d], Graciela Arbilla[c], Jailson B. de Andrade[a,b,*]

[a]*Instituto de Química, Universidade Federal da Bahia, Campus de Ondina, 40170-115 Salvador, BA, Brazil*
[b]*Centro Interdisciplinar de Energia e Ambiente—CIEnAm, Campus do Canela, UFBA, 40110-040 Salvador, BA, Brazil*
[c]*Departamento de Físico-Química, Universidade Federal do Rio de Janeiro, CT, Prédio A, Sala 408, 21949-900 Cidade Universitária, Rio de Janeiro, RJ, Brazil*
[d]*Centro Nacional da Pesquisa do Solo, EMBRAPA, Rua Jardim Botânico 1024, 22460-000 Rio de Janeiro, RJ, Brazil*

Received 13 October 2006; received in revised form 8 June 2007; accepted 8 June 2007

Abstract

Respiratory system is the major route of entry for airborne particulates, being the effect on the human organism dependent on chemical composition of the particles, exposure time and individual susceptibility. Airborne particulate trace metals are considered to represent a health hazard since they may be absorbed into human lung tissues during breathing. Fossil fuel and wood combustion, as well as waste incineration and industrial processes, are the main anthropic sources of metals to the atmosphere. In urban areas, vehicular emissions—and dust resuspension associated to road traffic—become the most important manmade source.

This work investigated the atmospheric concentrations of TSP, PM_{10} and elements such as iron, manganese, copper and zinc, from three different sites around Salvador Region (Bahia, Brazil), namely: (i) *Lapa Bus Station*, strongly impacted by heavy-duty diesel vehicles; (ii) *Aratu harbor*, impacted by an intense movement of goods, including metal ores and concentrates and near industrial centers and; (iii) *Bananeira Village* located on Maré Island, a non-vehicle-influenced site, with activities such as handcraft work and fishery, although placed near the port. Results have pointed out that TSP concentrations ranged between 16.9 (Bananeira) and 354.0 $\mu g\,m^{-3}$ (Aratu#1), while for PM_{10} they ranged between 30.9 and 393.0 $\mu g\,m^{-3}$, both in the Lapa Bus Station. Iron was the major element in both Lapa Station and Aratu (#1 and #2), with average concentrations in the PM_{10} samples of 148.9, 79.6 and 205.0 $ng\,m^{-3}$, respectively. Zinc, on the other hand, was predominant in samples from Bananeira, with an average concentration of 145.0 $ng\,m^{-3}$ in TSP samples, since no PM_{10} sample was taken from this site. The main sources of iron in the Lapa Station and Aratu harbor were, respectively, soil resuspension by buses and discharge of solid granaries, as fertilizers and metal ores. On the other hand, zinc and copper in the bus station were mainly from anthropic contributions, probably heavy-duty vehicle ageing and wearing actions releasing off Zn from tires and Cu from brake linings. In the Aratu harbor, the high copper concentrations found were probably due to the port's activities, as discharges of copper concentrate on its terminal, although other sources could

*Corresponding author. Instituto de Química, Universidade Federal da Bahia, Campus de Ondina, 40170-115 Salvador, BA, Brazil. Tel./fax: +55 71 32375524.
E-mail address: jailsong@ufba.br (J.B. de Andrade).
[1]Current address: Instituto Multidisciplinar em Saúde, Universidade Federal da Bahia, 45055-090 Vitória da Conquista, BA, Brazil.

doi:10.1016/j.atmosenv.2007.06.013

be possible, as burning of diesel fuel on ships and heavy oil in heaters. Finally, the Bananeira site has been presented as a different profile, since this remote site has shown zinc as the most abundant element, demonstrating to have an unexpected anthropic contribution. On a mass-to-mass basis, both zinc and manganese were in high levels in the Bananeira site and their presence strongly suggest the impact of other sources, such as the Industrial Center of Aratu and/or a siderurgy plant, not far away from that location.

Keywords: Trace metals; ICP OES; PM_{10}; TSP; Bus station; Harbor and island; Brazil; Salvador

1. Introduction

Respiratory system is the major route of entry for airborne particulates, being the effect on the human organism dependent on chemical composition of the particles, exposure time and individual susceptibility. Airborne particulate trace metals are considered to represent a health hazard since they can be absorbed into human lung tissues during breathing (Finlayson-Pitts and Pitts, 2000; Quiterio et al., 2004a, b). A particular fraction of the particulate matter (PM) which is known to exert toxic effects is metals, such as Fe, Zn, and Cu, which may release free radicals in lung fluid via the Fenton reaction, and are hypothesized to cause cellular inflammation (Birmili et al., 2006). Heavy metals are present in the atmosphere in ever increasing levels as a result of anthropic and natural emissions (Suzuki, 2006). Frequently, anthropic emissions cause the levels of metal in suspended particles to be well above natural background levels (Finlayson-Pitts and Pitts, 2000; Quiterio et al., 2004a, b).

Fossil fuel and wood combustion as well as waste incineration and industrial processes are the main anthropic sources of metals to the atmosphere. In urban areas, vehicular emissions—and dust resuspension associated to road traffic—become the most important manmade source (Birmili et al., 2006; Preciado and Li, 2006; Sternbeck et al., 2002; Lin et al., 2005; Harrison et al., 2003). It is believed that burning of fossil fuels is responsible for Be, Co, Hg, Mo, Ni, Sb, Se, Sn, V, Cr, Cu, Mn and Zn contents, of PM associated with atmospheric particles (Allen et al., 2001; Swaine, 2000), while vehicle ageing and wearing actions release off some heavy metals such as Zn from tires, Cu from brake linings, Mn from moving metal parts and gasoline additives (Preciado and Li, 2006; Swaine, 2000) and Pt, Pd and Rh from catalytic converters of automobiles (Lesniewska et al., 2006). Moreover, there are also indications that heavy-duty vehicles are strong emitters of Ba and Sb, but not of Cu, than light-duty vehicles (Sternbeck et al., 2002). On the other hand, metallurgical processes produce the largest emissions of As, Cd, Cu, Mn and Zn (Allen et al., 2001; Swaine, 2000).

Natural emissions result from a variety of processes acting on crustal minerals, including volcanism, erosion and surface winds, as well as from forest fires and the oceans (Allen et al., 2001; Desboeufs et al., 2005). Even though estimations for natural sources are difficult to be made, on a global scale, resuspended surface dusts make a large contribution to the total natural emission of trace metals to the atmosphere, accounting for $>50\%$ of Cr, Mn and V and $>20\%$ of Cu, Mo, Ni, Pb, Sb and Zn while volcanic activity probably generates up to 20% of atmospheric Cd, Hg, Cr, As, Cu, Ni, Pb and Sb. Sea salt aerosols generated by spray and wave action may contribute with around 10% of total trace metal emissions, while elements contained in biological aerosols are important in forested regions. Cu, Pb and Zn are contained in emissions from biomass combustion (Allen et al., 2001 and references therein; Desboeufs et al., 2005; Swaine, 2000).

In a previous work (de Andrade et al., 1996), we studied the metal concentrations in Salvador, Bahia, Brazil in two sites: a residential area and a residential–commercial–industrial neighborhood. The determined metals associated to total suspended particles include Al, Ca, Cr, Cd, Fe, Mg, Mn, V, Zn and Na. The result of factor analysis suggested that the major primary sources in Salvador are: resuspended soil, marine aerosol, vehicular emission, metallurgy and building construction. It was noted that the contribution of natural sources (soil and marine aerosol) accounted for about 50% of the total deposition.

The aim of this work was to determine the atmospheric concentrations and profiles of elements such as iron, manganese, copper, and zinc, present in each site, namely: (i) a bus station, strongly impacted by heavy-duty diesel vehicles, and which

has been already characterized for high molecular weight *n*-alkanes and polycyclic aromatic hydrocarbons (de P. Pereira et al., 2002, 2003); (ii) a harbor, impacted by an intense movement of goods, including metal ores and concentrates and near industrial centers and; (iii) an island, a non vehicle-influenced site, with activities such as handcraft work and fishery, although placed near the port.

2. Experimental

2.1. Collecting sites

The Lapa Bus Station is placed in downtown Salvador City (8°30′00″S and 37°30′00″W), in a region featured by heavy commerce and service activities, with several stores, small office buildings and a large mall at its neighborhood. The station is composed of three floors: the first one being located at underground level, and the second at the ground level, with total areas of about 13,920 m^2, each one has five platforms for arrivals and departures of urban heavy-duty diesel buses. Besides the movements of arrival and departure, the vehicles that are waiting for departure remain with their motors on. Finally, the third floor is occupied by small stores, cafeterias and the administration services. The station makes the confluence for several bus lines coming from all other districts. Samples ($n = 35$) of PM_{10} particles ($d_p \leqslant 10\,\mu m$) were collected between 16 and 28 July 2005 on quartz filters (22.8 × 17.7 cm, Energética, RJ, Brazil), by placing a PM_{10} HI-VOL sampler (Energética, RJ, Brazil and Thermo Andersen, USA) on the ground level at the underground floor of the bus station, at an average flow rate of 1.14 $m^3\,min^{-1}$. Sampling periods along weekdays were 4–6 h during the morning/afternoon and 8–10 h during the night, while on weekends they were 24 h in order to cover—and to be able to compare—rush-to-non-rush and weekday-to-weekend periods.

The Port of Aratu is placed on the Caboto harbor (12°47′00″S and 13°30′00″W), inside the Todos os Santos Bay, Candeias county, 50 km from Salvador (Fig. 1). Its average temperature is 26 °C and the predominant winds are NE (3–37%), E (3–52%) and SE (3–50%). Nowadays, the Port of Aratu is responsible for up to 60% of the total operations in ports of the Salvador basin, giving support to the industrial center of Aratu (CIA) and also to the petrochemical complex of Camaçari. It has four terminals: one for gas, one for liquid and two for solid granaries. The solid granaries received by the Port of Aratu include fertilizers, copper concentrates, manganese ores, mineral coke and phosphate rocks. It is characterized by a very low traffic of light- and heavy-duty vehicles, but an intense movement of charge and discharge of solids, to and from ships (http://www.codeba.com.br/porto_aratu). In this site, particles were sampled for both TSP ($d_p \geqslant 100\,\mu m$) and PM_{10} fractions, by placing the HI-VOL samplers together on the ground level and operating them simultaneously, at average flow rates of 1.16 and 1.14 $m^3\,min^{-1}$, respectively, in two different points: firstly the Aratu#1 (7 samples), near an office building and secondly the Aratu#2 (8 samples), in an open place. The samples were collected from October/2004 to November/2004, in sampling periods of 24 h each one.

Bananeira, Maré Island, is located on the Todos os Santos Bay, about 300 m away from the Port of Aratu, in a north–northwest direction (Fig. 1). It is a "*boat-only access*" place and non vehicle-influenced village composed by ~1000 inhabitants whose activities are essentially based on handcraft work and fishery. In this place, depending on the wind direction, emissions may be coming from the port or from industrial sites, as CIA and Petrochemical Complex of Camaçari. In this site, only samples of TSP particles were collected, by placing the TSP HI-VOL sampler on the roof of the local radio station and operating it at an average flow rate of 1.16 $m^3\,min^{-1}$. Fourteen samples were collected between September and October 2005, in 24 h periods due to the low particle concentrations.

After each sampling, the filters were folded and wrapped in aluminum foils and put inside sealed plastic bags afterwards until weighing. Sample masses were determined by weighing the filters before and after sampling, using an analytical balance (Sartorius Analytic, Goettingen, Germany). According to the standard procedure, before weighing, the blank and sampled filters should be equilibrated for 24 h at a constant relative humidity lower than 50 ± 5% and at a constant temperature between 15 and 30 °C (within ± 3 °C), by placing them inside a desiccator (Method IO-3.1, 1999). After weighing, the filters were folded and wrapped in aluminum foils again, put inside sealed plastic bags and stored in the lab in a refrigerator (4 °C) until analysis.

Summing up, while in the Port of Aratu both TSP and PM_{10} samples were collected, in the Lapa Station only PM_{10} and in the Bananeira only TSP particles were sampled, in different sampling times

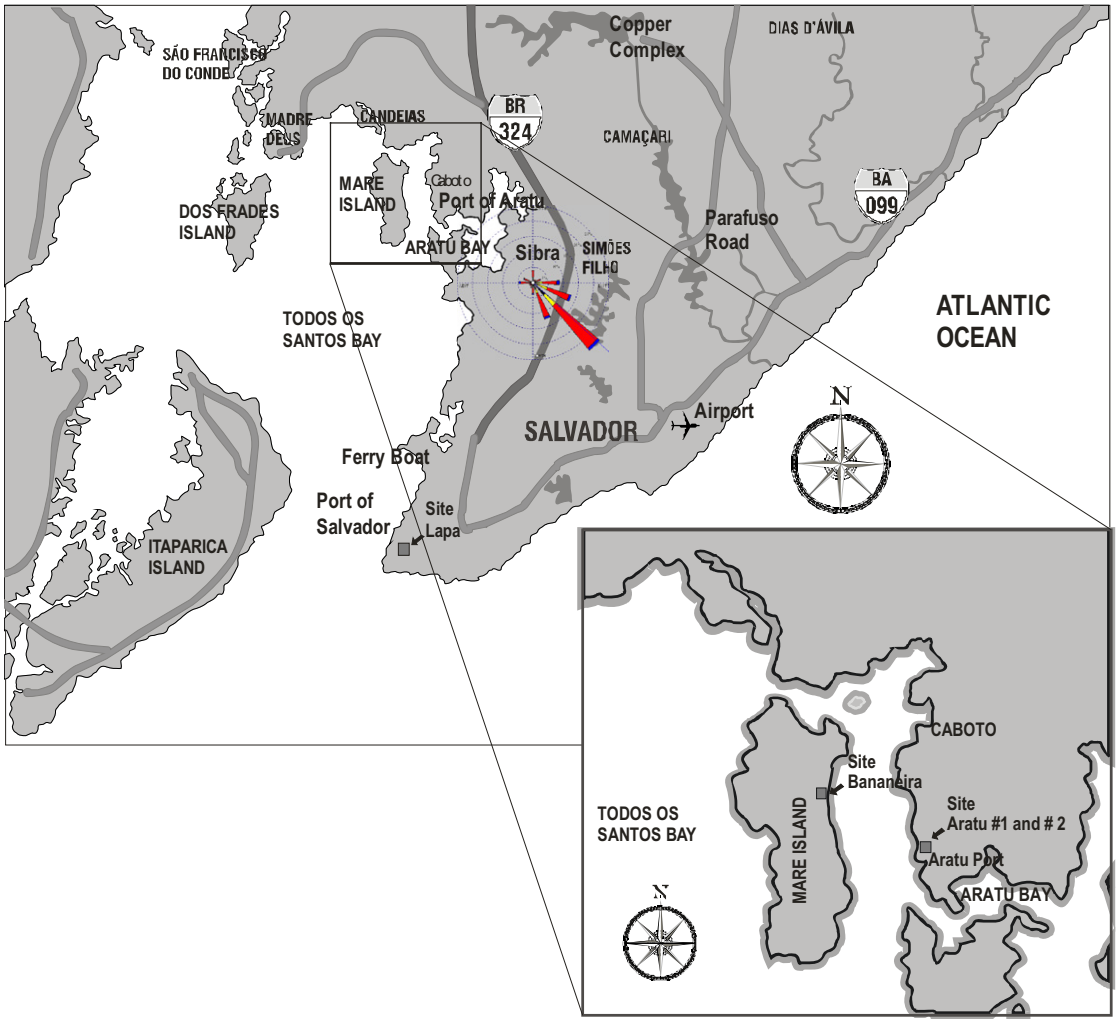

Fig. 1. Map localizing the three sites used in this study for collecting particulate samples.

for each place. The decision to collect samples of different particle sizes was based on two factors: (i) if a site *was* or *was not* supposed to be heavily impacted by important sources of particulate heavy metals, what should reflect on *high* or *low* levels of metal contents on samples and (ii) the adjusted availability of samplers to be used during sampling, always keeping the first aspect as target due to its importance to build a reliable sampling strategy in order to collect representative samples of each local.

2.2. Sample preparation and analysis

A 47 mm diameter section of each filter (17.34 cm^2) was cut and used for the metal analysis, according to the procedure described below.

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 in a pyrex glass tube and let still for 2 h at 95 °C in a heating plate (Fernández et al., 2000). The extracted solution was filtered, using a Whatman#41 (WH1441-110) filter, completed to 50 mL with ultrapure water and kept in pre-cleaned polyethylene bottles in the refrigerator until analysis (Serrano et al., 1996; Beceiro-González et al., 1997). A similar methodology was previously used for TSP (Quiterio et al., 2004a, b).

Filter and reagent blanks were processed with the same treatment. Metals were determined by ICP OES (Perkin-Elmer, Optima 3000), according to the Method IO-3.4 (1999). An external standard

calibration curve was done for the following elements: Mn, Fe, Zn, Cu, Co, Ni, Cd, Cr and Pb. The content of the blanks for these nine elements was <8% of the average content for samples.

Both limit of detection (LOD) and accuracy for the method were determined following Method IO-3.4 (1999). LOD were computed as three times the standard deviation of the distribution of outputs for 10 repeated measurements of the standard, which contained no metals (Boss and Fredeen, 1999). These LOD were calculated as 1.5 ng m^{-3} for Mn; 0.4 ng m^{-3} for Cr, Cd, Ni; 0.5 ng m^{-3} for Cu, Co, 5 ng m^{-3} for Fe, 1 ng m^{-3} for Zn and Pb. The accuracy of the method was evaluated using a standard reference material (111355 ICP multi-element Standard Solution IV from Merck) (Merck, 2006). The obtained results were in the acceptable range of 3–8%. All samples and SRM were determined in triplicate and a difference lower than 1% was considered acceptable.

2.3. Statistical tests

Experimental data were analyzed by calculating the Spearman's correlation coefficients using STATISTICA 6.0 (Stat soft) program. Also Principal Component Analysis (PCA) and Cluster Analysis (CA), using Ward's Method and Euclidian distances, were performed. The calculations were performed using the individual experimental values for each sample.

3. Results and discussion

3.1. TSP and PM_{10} particles in air and statistics

Table 1 shows a statistical summary of metal (ng m^{-3}), TSP and PM_{10} (μg m^{-3}) concentrations for *Port of Aratu*, *Bananeira* and *Lapa Bus Station*. In spite the fact that nine different elements were investigated (Cu, Fe, Mn, Zn, Cr, Co, Ni, Cd and Pb), only Cu, Fe, Mn and Zn were found to be

Table 1
Statistical summary of elements, TSP and PM_{10} concentrations in Aratu, Bananeira and Lapa Bus Station

Site		Element[a] (ng m^{-3})				Particulate matter (μg m^{-3})		
		Cu	Fe	Mn	Zn	TSP	PM_{10}	*n*
Aratu#1 TSP	Mean	21.0	226	19.2	4.53	182		7
	SD	14.3	211	11.3	2.82	87.7		
	Min	7.16	48.6	5.92	1.41	106		
	Max	47.6	596	39.2	9.40	354		
Aratu#2 TSP	Mean	121	328	13.5	3.95	169		8
	SD	91.9	199	4.70	1.26	46.4		
	Min	42.1	93.3	5.14	2.23	95.9		
	Max	293	650	20.0	6.35	222.6		
Aratu#1 PM_{10}	Mean	8.79	79.6	8.32	1.83		64.6	7
	SD	3.30	60.1	5.81	0.33		30.1	
	Min	5.19	18.5	2.47	1.43		44.2	
	Max	13.2	165	16.8	2.20		123	
Aratu#2 PM_{10}	Mean	79.2	205	9.52	2.80		71.7	8
	SD	82.8	119	6.36	0.72		13.9	
	Min	17.8	75.0	2.61	1.96		49.2	
	Max	257	470	21.2	3.69		88.2	
Bananeira TSP	Mean	3.37	26.8	19.5	145	36.1		15
	SD	2.54	17.6	22.3	56.9	10.1		
	Min	0.49	7.03	1.60	68.0	16.9		
	Max	8.57	75.0	81.8	243	54.5		
Lapa Bus Station PM_{10}	Mean	1.87	149	9.68	5.78		112	35
	SD	1.04	72.9	9.22	7.31		68.9	
	Min	0.59	52.0	1.81	1.49		30.9	
	Max	5.88	343	44.9	40.8		393	

[a]Elements with mean concentration below their LOD were not included (Cr, Co, Ni, Cd and Pb).

above their limits of detection, evidencing that those studied sites have no important sources of Cr, Co, Ni, Cd and Pb until the present. These five elements were disconsidered in all samples collected in the four locations (Aratu#1 $n = 7$ for TSP and PM_{10}; Aratu#2 $n = 8$ for TSP and PM_{10}; Bananeira $n = 15$ and Lapa Station $n = 35$) because individual determinations and the arithmetic mean concentrations were below the LOD. Even though keeping in mind that particulate matter of different size fractions were collected on each site and by considering only arithmetic means from Table 1, it was found that Fe was the element in the highest concentrations in all sites, except for Bananeira, where Zn presented the highest concentration.

Because Port of Aratu was the unique site where both TSP and PM_{10} samples were simultaneously collected in two different places, the *F*-test was performed in order to find whether these factors could be affecting the determined concentrations of the samples. It was found (Table 2) that neither the two chosen places for collection nor TSP and PM_{10} fractions should be considered as "similar" for following comparisons. Although they were not so far from each other, Aratu#1 was near a building, while Aratu#2 was in an open place. This geographical peculiarity could contribute, for example, to differences in the wind's predominant direction and velocity that each one would receive. Also, and maybe more important, the samples in the two places were collected in different periods. By consequence throughout this paper, samples from Aratu#1 and Aratu#2 were computed separately, not trying to compare them in any way. On the other hand, since TSP and PM_{10} samples were collected simultaneously in each of these two sites, they could be compared when it would be necessary.

The PM_{10} concentrations, as function of the sampling period in the Lapa station, are shown in Fig. 2. The highest concentrations were generally found in the afternoon, since the rush hours—when there were an increase in the frequency of arrivals and departures of buses—were covered during this sampling period. Since an increase in commuting could promote high concentrations of particulate matter, coming from diesel burning in heavy-duty vehicles and particles resuspension associated to the local traffic, it seems reasonable that afternoon period has shown higher levels of the determined elements and PM_{10}. The lowest levels, on the contrary, were found at night due to a reduction in the number of vehicles circulating in the station *and/or* in particles resuspension. This trend has been already observed with polycyclic aromatic hydrocarbons (PAH) concentrations, in samples collected in 1991 at the same place. (de P. Pereira et al., 2002). It should be highlighted that almost all samples (91%) presented concentrations higher than the $50\,\mu g\,m^{-3}$ Brazilian primary standard for PM_{10}, while six (17%) were higher than the secondary standard of $150\,\mu g\,m^{-3}$ for 24 h exposure.

Table 2
F test for analyzing PM_{10} and TSP fractions from Port of Aratu (95% of confidence limit)

Analyzes	F_{calc}	F_{crit}	Conclusion
Aratu#1 (TSP) vs. Aratu#2 (TSP)	3.57	3.87	Similar
Aratu#1 (PM_{10}) vs. Aratu#2 (PM_{10})	4.69	3.97	Non-similar
Aratu#1 (TSP) vs. Aratu#1 (PM_{10})	8.49	4.95	Non-similar
Aratu#2 (TSP) vs. Aratu#2 (PM_{10})	11.1	3.79	Non-similar

A *F*-test was performed in order to find the statistical significance of differences in concentrations reported in Fig. 2. Data were compared in pairs: morning vs. afternoon ($F_{calc} = 0.37$), morning vs. night ($F_{calc} = 0.37$) and afternoon vs. night ($F_{calc} = 0.99$). In the three situations, the critic *F*-value was 0.26, indicating that data are non-similar.

Pearson's correlation (Table 3) shows low-to-moderate correlations among studied metals for Lapa Station, while the PCA analysis (which explains only 59% of results) shows that Fe, Cu, Mn and Zn form only one component (Table 4). In the Cluster Analysis (Fig. 3), a sub-group is formed between Zn and Cu and a second, with a more strong linkage, between Fe and Mn, and both associating with each other. Also, the stronger correlation among metal concentrations was found for Mn and Fe ($r = 0.78$). This could be indicative of soil resuspension associated to buses traffic as the main sources responsible for those metal concentrations.

TSP and PM_{10} average concentrations in Aratu were higher than the maximum allowable by the Brazilian standards for annual values. For TSP, they were in Aratu#1 and Aratu#2, respectively, 182 and $169\,\mu g\,m^{-3}$, while for PM_{10} they were 64.6 and $71.7\,\mu g\,m^{-3}$ in the same sites. Both Lapa Station and Port of Aratu show a not so much different profile for the metals determined, with iron being the most abundant one (Table 1, Figs. 2 and 4). Average concentrations for iron in PM_{10} filters were, respectively, 149, 79.6 and $205\,ng\,m^{-3}$ for Lapa, Aratu#1 and Aratu#2. Despite these high

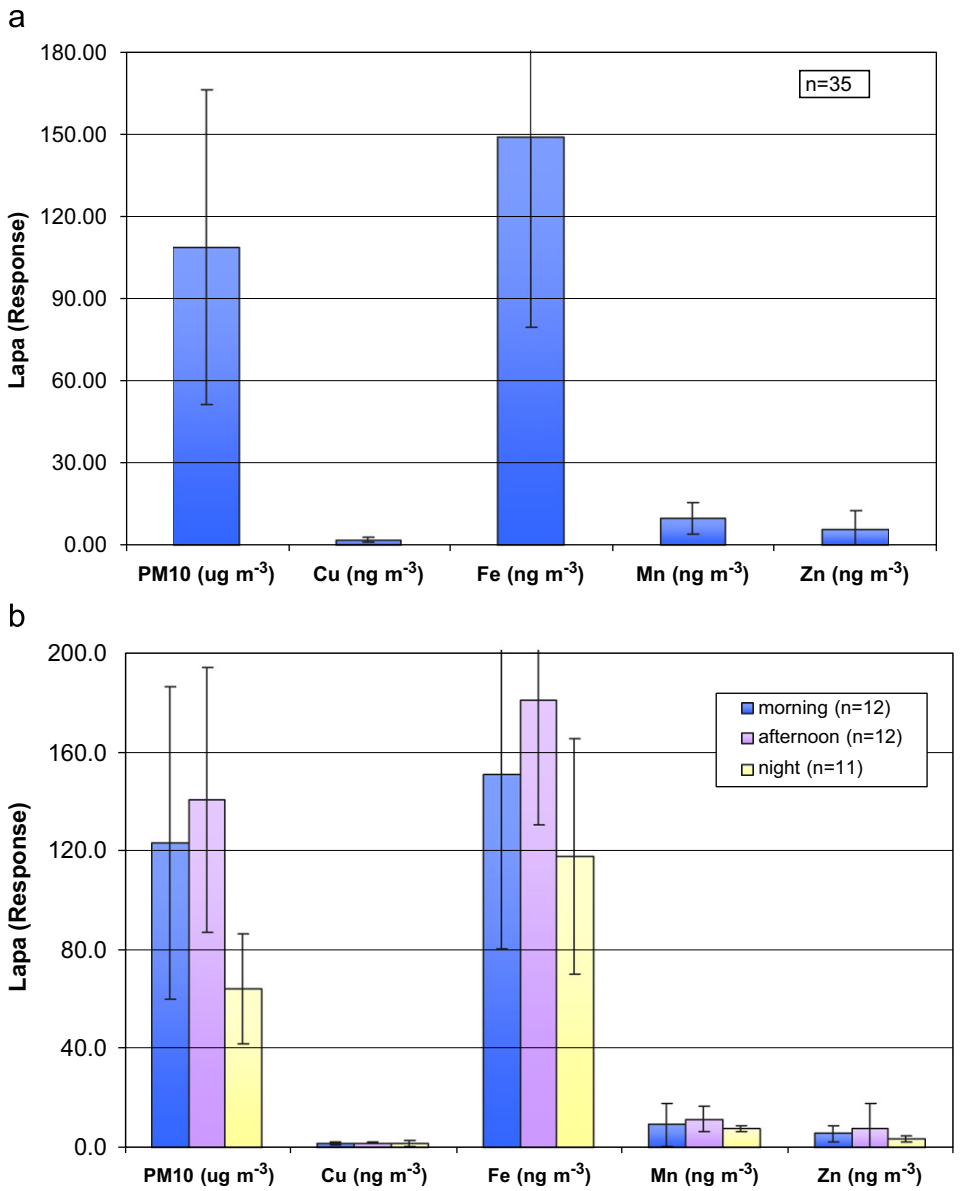

Fig. 2. (a) Arithmetic mean values for PM_{10} and metal concentration for Lapa Bus Station and (b) morning-to-afternoon-to-night comparisons for PM_{10} and metal concentrations based on arithmetic means for Lapa Bus Station. In both cases, bars indicate ± standard errors.

values, they were usually lower than those found, for example, in seven districts of the Baixada Fluminense, in Rio de Janeiro, where pollution sources are mainly local industries and vehicular emissions (Quiterio et al., 2005).

The Pearson's statistics for Aratu#1 TSP and Aratu#2 TSP shows that correlations are slightly better only for Aratu#1, while in Aratu#2 metals were not correlated, except for Cu and Mn (Table 3). By Cluster Analysis it is shown a more clear correlation between Cu and Mn, while Fe is located in another group, giving support to the hypothesis of Fe is coming mainly from soil resuspension, for both sites (Fig. 3). These results are consistent with low correlations between Fe and Cu (0.05 and −0.48, respectively) and Fe and Mn (−0.04 and −0.54, respectively). Aratu#1 and Aratu#2 PM_{10} presented higher scores for Pearson's correlations when compared to TSP samples. This fact may be explained by the different contributions

to fine and coarse particulate matter composition. The Cluster analysis shows Zn, Mn and Cu together in one group and Fe in the other one. Discharge of solid granaries, as fertilizers and metal ores, in the port's terminal may be the main sources for Cu, Mn and Zn while, as previously stated, Fe may be due to soil resuspension.

The receptor site of Bananeira, on the other hand, has presented a different profile when compared to the other sites. Primarily, the mean TSP concentration (36.1 $\mu g\,m^{-3}$) was, as expected due to characteristics of the site, not only much lower than the other two places studied, but also lower than values reported for two urban districts in Salvador and localities in Rio de Janeiro and other cities (de Andrade et al., 1996). The stronger correlation among metals was found for Mn and Fe ($r = 0.75$) indicating that soil resuspension may be the main source of these metals.

In terms of the elements determined (Fig. 5), zinc was the most abundant, presenting average concentration of 145 $ng\,m^{-3}$ and ranging from 68 to 243 $ng\,m^{-3}$, measured in TSP samples. Iron, instead, was comparatively low (26.8 $ng\,m^{-3}$ average), while copper was lower than in Aratu but higher than in the Lapa Station.

Zinc, to our present knowledge, has no significant source contributions coming from the Port of Aratu. Thus, its high concentrations strongly suggest the hypothesis that there are other probable sources impacting the Bananeira site, besides Aratu, and these could be the Industrial Center of Aratu and/or the siderurgy plant, not too distant from the location.

Table 3
Pearson's correlations of metals from all sites (significant values at 95% of confidence limit are in bold)

	Cu	Fe	Mn	Zn
Lapa Station				
Cu	1.0			
Fe	**0.35**	1.0		
Mn	**0.45**	**0.78**	1.0	
Zn	0.18	**0.52**	**0.37**	1.0
Aratu#1 TSP				
Cu	1.0			
Fe	0.05	1.0		
Mn	**0.19**	−0.04	1.0	
Zn	**0.57**	**0.57**	**0.32**	1.0
Aratu#1 PM_{10}				
Cu	1.0			
Fe	0.15	1.0		
Mn	**0.48**	**0.41**	1.0	
Zn	**0.98**	−0.19	**0.57**	1.0
Bananeira				
Cu	1.0			
Fe	**0.33**	1.0		
Mn	0.07	**0.75**	1.0	
Zn	−0.33	**0.30**	**0.46**	1.0
Aratu#2 TSP				
Cu	1.0			
Fe	−0.48	1.0		
Mn	**0.52**	−0.54	1.0	
Zn	−0.71	−0.07	−0.05	1.0
Aratu#2 PM_{10}				
Cu	1.0			
Fe	-0.25	1.0		
Mn	**0.82**	0.16	1.0	
Zn	**0.21**	**0.51**	**0.41**	1.0

3.2. Enrichment factors

Trace metals in aerosols are derived from a variety of sources which include the Earth's crust, the oceans, volcanic activity, the biosphere, and a number of anthropogenic processes (e.g., fossil fuel burning, waste incineration, the processing of ores, etc.). The degree to which a trace metal in an aerosol is enriched, or depleted, relative to a specific source can be assessed to a first approximation using an enrichment factor (EF). It has been the practice to

Table 4
Principal Component Analysis (at 95% of confidence limit)

	Lapa	Bananeira		Aratu#1 TSP		Aratu#2 TSP		Aratu#1 PM_{10}		Aratu#2 PM_{10}	
	PC1	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2
Cu	−0.57	−0.01	**−0.92**	0.67	−0.12	**−0.93**	−0.28	**0.93**	0.06	**0.92**	−0.32
Fe	**−0.89**	**0.85**	−0.37	0.63	0.59	0.68	−0.57	−0.20	**−0.93**	−0.10	**0.93**
Mn	**−0.87**	**0.92**	−0.06	0.34	**−0.82**	**−0.74**	0.44	0.68	−0.41	**0.96**	−0.001
Zn	−0.69	0.67	0.55	**0.96**	−0.01	0.55	**0.82**	**0.99**	0.03	0.52	**0.75**

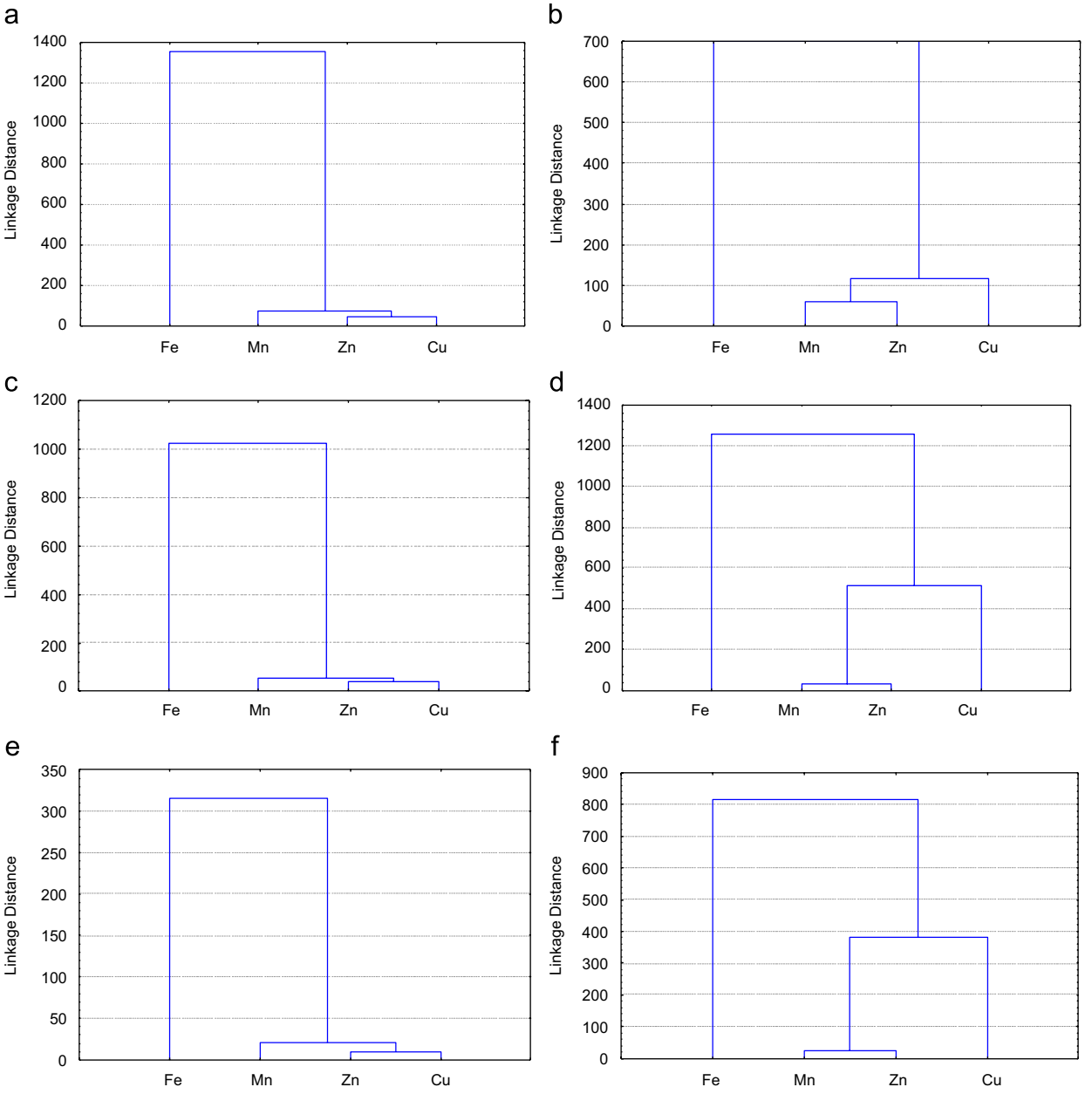

Fig. 3. Cluster analyses at 95% of confidence limit: (a) Lapa's Station; (b) Bananeira; (c) Aratu#1 TSP; (d) Aratu#2 TSP; (e) Aratu#1 PM_{10}; (f) Aratu#2 PM_{10}.

categorise trace metals in the aerosol on the basis of their crustal EFs, calculated according to Al or Fe contents as follows:

$$EF_{crust} = (C_{xp}/C_{Fep})/(C_{xc}/C_{Fec}), \quad (1)$$

where (C_{xp}) and (C_{Fep}) are the concentrations of a trace metal X and Fe (or Al) (which are used as crustal reference element), respectively, in the aerosol, and (C_{xc}) and (C_{Fec}) are their concentrations in average crustal material. By convention, an arbitrary average EF value of <10 is taken as an indication that a crust trace metal in an aerosol has a significant crustal source, and these are termed the non-enriched elements (NEEs). In contrast, an EF value of >10 crust is considered to indicate that a significant proportion of an element has a non-crustal source, and these are referred to the anomalously enriched elements (AEEs); however,

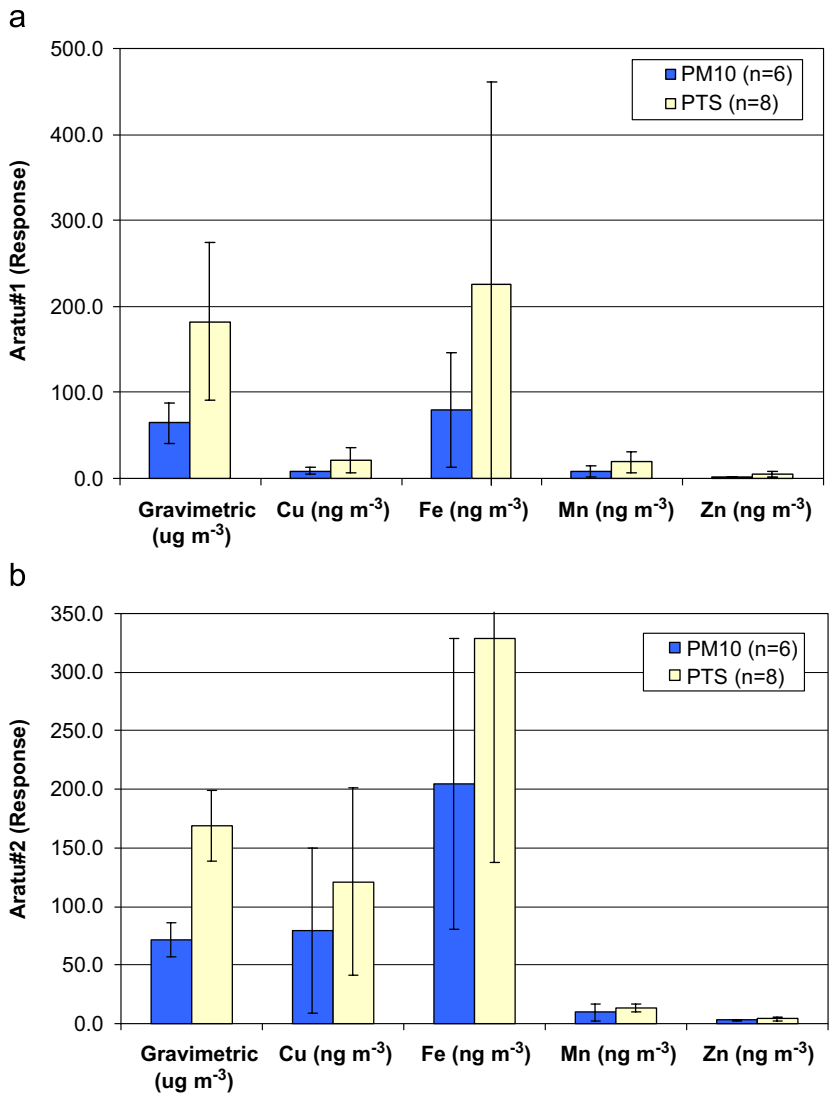

Fig. 4. Arithmetic mean values for TPS, PM_{10} and metal concentrations for (a) Aratu#1 and (b) Aratu#2 sites. Bars indicate ± standard errors.

when sufficient crustal material is present in the air the AEEs can switch character and behave as NEEs. This is an essentially crude classification, but is useful in interpreting aerosol chemistry (Caroli et al., 1996; Ure and Davidson, 1995; Wedepohl, 1995; Chester et al., 1999; Odabasi et al., 2002; Herut et al., 2001; Sardans and Peñuelas, 2006).

EFs in this study (Table 5) were calculated based on Fe natural content, since due to previously assumed storage protocols for determination of the organic species, in the same filters, aluminum foils were used to wrap the filters before and after sampling and thus that element could not be analyzed.

When EFs based in the iron concentration were calculated for the Lapa samples, high values were found for zinc and copper, 28 and 19, respectively, and low for manganese (4). This low EF for manganese, together with its high Pearson's correlation with iron (0.78) suggests that soil resuspension is the unique or the main source of that element. The high EF values for zinc and copper, on the other hand, could denote them as AEEs although Pearson's correlation between Zn and Fe (0.52) and Cu and Fe (0.35) support the hypothesis that soil resuspension by buses circulation is also an important source for both elements in the Lapa site. In spite of this fact, previous works (Pacyna 1986;

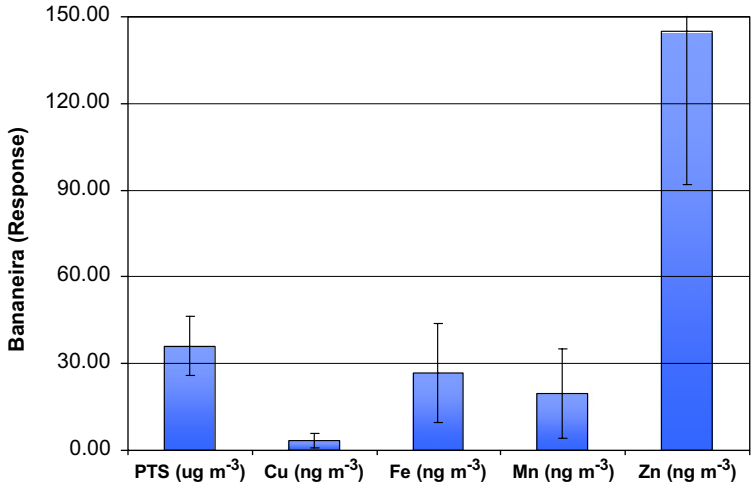

Fig. 5. Arithmetic mean values for TPS and metal concentrations for Bananeira's site. Bars indicate ± standard errors.

Table 5
Enrichment Factors based on arithmetic means and relative to Fe for all sites (Enrichment Factors based on arithmetic means and relative to Fe for all sites (values in bold indicate anthropogenic contributions as the main source)

	Lapa	Bananeira	Aratu#1 TSP	Aratu#1 PM_{10}	Aratu#2 TSP	Aratu#2 PM_{10}
Cu	**19**	**192**	**142**	**168**	**564**	**589**
Fe	1.0	1.0	1.0	1.0	1.0	1.0
Mn	4.0	45	5.2	6.4	2.5	2.9
Zn	**28**	**3909**	**15**	**17**	**8.7**	**9.9**

López et al., 2005) have reported copper as a component in emissions from both gasoline and diesel fueled vehicles and in wearing of brakes, and zinc as a component of tire rubber debris. Furthermore, the low correlation between these two elements (0.18) suggests yet other sources for them.

Besides the larger amounts of iron than Aratu#1, Aratu#2 had also an increase in the copper concentration and in the EF of this element (Tables 1 and 5 and Fig. 4). Looking to the EFs for copper they were, respectively, 142 and 564 for TSP and 168 and 589 for PM_{10}, showing the relative increase of the copper concentration and EF in Aratu#2 and denoting this element as an AEE. Firstly, these high concentrations and EFs of copper may probably be due to the port's activities, since discharges of copper concentrate are frequent at its terminal. Also, other possible sources would be the burning, in ships, of diesel fuel and heavy oil in heaters. The low correlations shown between this element and iron ($r = 0.05$ and -0.48 for TSP and 0.15 and -0.25 for PM_{10} for Aratu#1 and #2, respectively) reinforces the hypothesis of other sources for it, besides soil resuspension. Thus, soil resuspension does not seem to be the predominant source for these two locations. Actually, copper content in PM mostly reflects *both* port's activities and burning of diesel *and* heavy oil on the terminal as main sources.

The EF for zinc in Bananeira was very high (3909), showing strong anthropic contributions, and this was followed by copper (192) and manganese (45). Because of its unexpected high EF and that there are no significant sources of this element neither on Aratu Harbor nor on Bananeira, other very significant emission sources of zinc seem to be acting on this scenery. They probably would be the Industrial Center of Aratu (CIA) and/or the Sibra/RDM siderurgy plant, not too distant from the island.

It should be highlighted that while copper had also a high EF (192), its correlation with zinc was poor (-0.33), what suggests different sources for both elements. Manganese, despite its moderately high EF (45), had a good correlation with iron (0.75) and its main source could be the soil resuspension.

3.3. Estimate of dry deposition fluxes

The dry atmospheric deposition fluxes (F_d) were calculated by multiplying the geometric mean particulate concentration in air of the element of interest (i) by the elemental dry settling velocity (V_d):

$$F_d = C_i \times V_d. \quad (2)$$

The term V_d varies with particle size and is dependent on climatological and physical conditions in the troposphere, especially in coastal environments (Herut et al., 2001). The values used here follow the mean values used by Duce et al. (1991). For Zn and Cu a mean value of $0.1\,cm\,s^{-1}$ was applied, and for Fe and Mn a mean value of $2\,cm\,s^{-1}$ was adopted. These values fall close to the V_d range given in other studies (Rojas et al., 1993; Migon et al., 1997; Herut et al., 2001 and references therein). It should be emphasized, however, that the flux calculations might vary by approximately an order of magnitude due to the uncertainties in V_d.

Table 6 shows dry deposition fluxes for Cu, Fe, Mn and Zn content of particulate matter from Lapa Bus Station, Port of Aratu and Bananeira. Fe is the element which demonstrated higher dry deposition flux, followed by Mn, Cu and Zn.

Table 6
Estimates of trace element dry deposition fluxes (F_d)

	Cu	Fe	Mn	Zn
Dry settling velocity[a] (V_d) ($cm\,s^{-1}$)	0.1	2.0	2.0	0.1
Lapa				
Geometric Mean ($ng\,m^{-3}$)	1.6	133.5	7.1	4.2
Dry deposition Flux (F_d) ($mg\,m^{-2}\,yr^{-1}$)	*0.4*	*674*	*36*	*1*
Bananeira				
Geometric Mean ($ng\,m^{-3}$)	2.5	22	11	134
Dry deposition Flux (F_d) ($mg\,m^{-2}\,yr^{-1}$)	*2*	*338*	*159*	*101*
Aratu#1 TSP				
Geometric Mean ($ng\,m^{-3}$)	18	160	16	4
Dry deposition Flux (F_d) ($mg\,m^{-2}\,yr^{-1}$)	*13*	*2416*	*243*	*3*
Aratu#1 PM_{10}				
Geometric Mean ($ng\,m^{-3}$)	8	61	7	2
Dry deposition Flux (F_d) ($mg\,m^{-2}\,yr^{-1}$)	*6*	*925*	*102*	*1*
Aratu#2 TSP				
Geometric Mean ($ng\,m^{-3}$)	96	269	13	4
Dry deposition Flux (F_d) ($mg\,m^{-2}\,yr^{-1}$)	*73*	*4072*	*190*	*3*
Aratu#2 PM_{10}				
Geometric Mean ($ng\,m^{-3}$)	52	181	8	3
Dry deposition Flux (F_d) ($mg\,m^{-2}\,yr^{-1}$)	*40*	*2742*	*117*	*2*

[a]According to Herut et al. (2001).

4. Conclusions

In this work, the atmospheric concentrations and profiles for iron, manganese, copper and zinc were determined in three different sites, namely: (i) a bus station, strongly impacted by heavy-duty diesel vehicles, (ii) a harbor, impacted by an intense movement of goods, including metal ores and concentrates and near industrial centers and; (iii) an island, a non-vehicle-influenced site, with activities such as handcraft work and fishery. Metals were determined by ICP OES with external standard calibration curves. The average concentrations for PM_{10} and TSP, in the bus station and in the Aratu harbor, were higher than the values allowable by the Brazilian standards, while for the Bananeira site it was lower, as expected due to the local characteristics.

The main sources for iron in the Lapa Station and Aratu harbor were, respectively, the soil resuspension by buses and discharge of solid granaries, as fertilizers and metal ores.

Zinc and copper in the Lapa station were mainly from anthropic contributions as, for example, components in emissions from both gasoline and diesel fueled vehicles, wearing of brakes and tire rubber debris. Nevertheless, the soil resuspension provoked by buses movement has also contributed.

In the Aratu site, copper predominant sources were either the port's activities such as discharges of copper concentrates on its terminal or burning of diesel fuel and heavy oil in heaters in ships although other minor sources may be acting as well.

The Bananeira site has presented a different profile, with zinc as the most abundant element, with concentrations ranging from 68 to $243\,ng\,m^{-3}$, measured in TSP samples. The EF for zinc was very high (3909), showing strong anthropic contributions, followed by copper (192) and manganese (45). Zinc, to our present knowledge, has no significant source contributions coming from the Port of Aratu, and its high concentrations strongly suggest the hypothesis of other probable sources, as the

Industrial Center of Aratu and/or the siderurgy plant, not too distant from the location.

Copper had also a high EF (192), but its correlation with zinc was poor (−0.33), what suggests different sources for both elements. Manganese, despite its moderately high EF (45), had a good correlation with iron (0.75) and its main source could be the soil resuspension.

Finally, in the Aratu samples, iron, manganese and copper were present predominantly in the PM_{10} fraction of the particulate matter, instead of TSP, what might be contributing to health risks to the local workers.

Acknowledgments

The authors wish to thank to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo a Pesquisa do Estado da Bahia (FAPESB), Financiadora de Estudos e Projetos (FINEP), Agência Nacional de Energia Elétrica (ANEEL), Nordeste Generation, RECOMBIO/CNPq/CTENERG and to Eng. Oscar A. Reis Martinez, for helpful discussions.

References

Allen, A.G., Nemitz, E., Shi, J.P., Harrison, R.M., Greenwood, J.C., 2001. Size distributions of trace metals in atmospheric aerosols in the United Kingdom. Atmospheric Environment 35, 4581–4591.

de Andrade, J.B., Macedo, M.A., Korn, M., Oliveira, E., Gennari, R.F., 1996. A comparison study of aerosol emissions sources in two receptor sites in Salvador (Brazil) city. Technological and Environmental Chemistry 54, 23–28.

Beceiro-González, E., Andrade-Garda, J.M., Serrano-Velasco, E., Lópes-Mahía, P., 1997. Metals in airborne particulate matter in La Coruña (NW Spain). Science of the Total Environment 196, 131–139.

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

Boss, C.B., Fredeen, K.J., 1999. Concepts, Instrumentation, and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry, second ed. Perkin-Elmer Corp., Norwalk.

Caroli, S., La Torre, F., Petrucci, F., Violante, N., 1996. Element Speciation in Bioinorganic Chemistry. Wiley-Interscience, New York.

Chester, R., Nimmo, M., Preston, M.R., 1999. The trace metal chemistry of atmospheric dry deposion samples collected at Cap Ferrat: a coastal site in the Western Mediterranean. Marine Chemistry 68, 15–30.

Desboeufs, K.V., Sofitikis, A., Losno, R., Colin, J.L., Ausset, P., 2005. Dissolution and solubility of trace metals from natural and anthropogenic aerosol particulate matter. Chemosphere 58, 195–203.

Duce, R.A., Liss, P.S., Merril, J.T., Atlas, E.L., Buat-Menard, P., Hickes, B.B., Miller, J.M., Prospero, J.M., Arimoto, R., Church, T.M., Ellis, W., Galloway, J.N., Hansen, L., Jickells, T.D., Knap, A.H., Reinhardt, K.H., Schneider, B., Soudine, A., Tokos, J.J., Tsunogai, S., Wollast, R., Zhou, M., 1991. The atmospheric input of trace species to the world ocean. Global Biogeochemical Cycles 5, 193–259.

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

Finlayson-Pitts, B.J., Pitts Jr., J.N., 2000. Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications, first ed. Academic Press, San Diego.

Harrison, R.M., Tilling, R., Romero, M.S.C., Harrad, S., Jarvis, K., 2003. A study of trace metals and polycyclic aromatic hydrocarbons in the roadside. Environmental Science and Technology 37, 2391–2402.

Herut, B., Nimmo, M., Medway, A., Chester, R., Krom, M.D., 2001. Dry atmospheric inputs of trace metals at the Mediterranean coast of Israel (SE Mediterranean): sources and fluxes. Atmospheric Environment 35, 803–813.

〈http://www.codeba.com.br/porto_aratu〉; accessed on June, 2006.

Lesniewska, B.A., Godlewska-Zylkiewicz, B., Ruszczynska, A., Bulska, E., Hulanicki, A., 2006. Elimination of interferences in determination of platinum and palladium in environmental samples by inductively coupled plasma mass spectrometry. Analytica Chimica Acta 564, 236–242.

Lin, C.-C., Chen, S.-I., Huang, K.-L., Hwang, W.-I., Chang-Chien, G.-P., Lin, W.-Y., 2005. Characteristics of metals in nano/ultrafine/fine/coarse particles collected beside a heavily trafficked road. Environmental Science and Technology 39, 8113–8122.

López, J.M., Callén, M.S., Murillo, R., García, T., Navarro, M.V., de la Cruz, M.T., Mastral, A.M., 2005. Levels of selected metals in ambient air PM_{10} in an urban site of Zaragoza (Spain). Environmental Research 99, 58–67.

Merck, 2006. Retrieved June 05, 2006, from 〈http://chemdat.merck.de/pls/pi03/web2.zoom_in?text=111355&screen=110&cid=xcsfs&pg=0&s=&lang=15〉.

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

Method IO-3.4, 1999. Determination of metals in ambient particulate matter using inductively coupled plasma (ICP) spectroscopy. US-EPA.

Migon, C., Journel, B., Nicolas, E., 1997. Measurement of trace metal wet, dry and total atmospheric fluxes over the Ligurian Sea. Atmospheric Environment 31, 889–896.

Odabasi, M., Muezzinoglu, A., Bozlaker, A., 2002. Ambient concentrations and dry deposition fluxes of trace elements in Izmir, Turkey. Atmospheric Environment 36, 5841–5851.

Pacyna, J.M., 1986. In: Nriagu, J.O., Davidson, C.I. (Eds.), Toxic Metals in the Atmosphere. Wiley, New York.

de P. Pereira, P.A., de Andrade, J.B., Miguel, A.H., 2002. Measurements of semivolatile polycyclic aromatic hydrocarbons in a bus station and an urban tunnel of Salvador, Brazil. Journal of Environmental Monitoring 4 (4), 558–561.

de P. Pereira, P.A., de Andrade, J.B.; Miguel, A.H., 2003. PAHs and aliphatic hydrocarbons (C19 to C29) in a bus station and

an urban tunnel of Salvador, Bahia, Brazil. In: A & WMA'S 96TH Annual Conference & Exhibition, 2003, San Diego—CA. Energy, Economic and Global Challenges—Environment in the Balance.

Preciado, H.F., Li, L.Y., 2006. Evaluation of metal loadings and bioavailability in air, water and soil along two highways of British Columbia, Canada. Water, Air, and Soil Pollution 172, 81–108.

Quiterio, S.L., Arbilla, G., Silva, C.R.S., Escaleira, V., 2004a. Metals in airborne particulate matter in the Industrial District of Santa Cruz, Rio de Janeiro, in an annual period. Atmospheric Environment 38, 321–331.

Quiterio, S.L., Arbilla, G., Escaleira, V., Silva, C.R.S., Maia, L.F.P.G., 2004b. Metals in airborne particulate matter in downtown Rio de Janeiro (Brazil). Bulletin of Environmental Contamination and Toxicology 72, 916–922.

Quiterio, S.L., Sousa, 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. Atmospheric Environment 39, 3503–3512.

Rojas, C.M., Injuk, J., Van Grieken, R.E., Laane, R.W., 1993. Dry and wet depostion fluyes of Cd, Cu, Pb and Zn into the sourthern Bight of the North Sea. Atmospheric Environment 27A, 251–259.

Sardans, J., Peñuelas, J., 2006. Introduction of the factor of portioning in the lithogenic enrichment of trace element bioaccumulation in plant tissues. Environmental Monitoring and Assessment 115, 473–498.

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

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

Suzuki, K., 2006. Characterization of airborne particulates and associated trace metals deposited on tree bark by ICP-OES, ICP-MS, SEM-EDX and laser ablation ICP-MS. Atmospheric Environment 40, 2626–2634.

Swaine, D.J., 2000. Why trace elements are important. Fuel Processing Technology 65–66, 21–33.

Ure, A.M., Davidson, C.M., 1995. Chemical Speciation in the Environment. Academic & Professional, London, Blackie, p. 408.

Wedepohl, K.H., 1995. The composition of the continental crust. Geochimica et Cosmochimica Acta 59, 1217–1232.