Coarse and fine aerosol source apportionment in Rio de Janeiro, Brazil

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ARTICLE INFO

ABSTRACT

The metropolitan area of Rio de Janeiro is one of the twenty biggest urban agglomerations in the world, with 11 million inhabitants in the metropolitan area, and has a high population density, with 1700 hab. km^{-2}. For this aerosol source apportionment study, the atmospheric aerosol sampling was performed at ten sites distributed in different locations of the metropolitan area from September/2003 to December/2005, with sampling during 24 h on a weekly basis. Stacked filter units (SFU) were used to collect fine and coarse aerosol particles with a flow rate of 17 L min^{-1}. In both size fractions trace elements were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) as well as water-soluble species by Ion-Chromatography (IC). Also gravimetric analysis and reflectance measurements provided aerosol mass and black carbon concentrations. Very good detection limits for up to 42 species were obtained. Mean annual PM_{10} mass concentration ranged from 20 to 37 $\mu g\,m^{-3}$, values that are within the Brazilian air quality standards. Receptor models such as principal factor analysis, cluster analysis and absolute principal factor analysis were applied in order to identify and quantify the aerosol sources. For fine and coarse modes, circa of 100% of the measured mass was quantitatively apportioned to relatively few identified aerosol sources. A very similar and consistent source apportionment was obtained for both fine and coarse modes for all 10 sampling sites. Soil dust is an important component, accounting for 22–72% and for 25–48% of the coarse and fine mass respectively. On the other hand, anthropogenic sources as vehicle traffic and oil combustion represent a relatively high contribution (52–75%) of the fine aerosol mass. The joint use of ICP-MS and IC analysis of species in aerosols has proven to be reliable and feasible for the analysis of large amount of samples, and the coupling with receptor models provided an excellent method for quantitative aerosol source apportionment in large urban areas.

1. Introduction

The metropolitan area of Rio de Janeiro is one of the twenty biggest urban agglomerations in the world, with 11 million inhabitants, and the first, among the Brazilian cities, in respect to the population density, with 1700 hab. km^{-2} (FEEMA, 2003; Fernandes et al., 2002). Among the metropolitan regions in Brazil, Rio de Janeiro has the highest degree of urbanization, 96.8%, and responds for 80% of the internal income of the State and 13% of the country (FEEMA, 2003; Azevedo et al., 1999).

Factors such as local topography, inadequate urban space occupation with sky creepers at the shoreline, close presence of open sea and part of the city surrounding the Guanabara Bay influence the urban atmosphere of the city of Rio de Janeiro. These factors result in an efficient, however complex, regime of atmospheric circulation, combining winds with the canalizations originated from its topography, and, consequently, contributing to an uneven distribution and dispersion of pollutants. The climatological evaluation of the atmospheric circulation in Rio de Janeiro shows that the highest wind direction frequency is from South–Southeast to Northeast sectors, along the year, with average wind velocity of 8 km h^{-1}. The relative humidity is high with small variation along the year, 80–82%. Cloud cover is relatively high and persistent due to the proximity of humidity sources, as the ocean and the Guanabara Bay (FEEMA, 2006).

The region is characteristic of sub-tropical climate, with intense solar radiation and elevated temperatures, favoring enhanced

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photochemical processes as well as the production of secondary aerosols. The regions close to the sea have a natural ventilation that tends to carry pollutants to its inside regions, where physical barriers, as Tijuca and Pedra Branca ridges, parallel to the shoreline, hinder the air circulation (FEEMA, 2003, 2006).

As a result of air pollution control strategies, a decrease in total particle concentration since 1997 has been observed. Despite the observed reduction on air pollution levels, during the year 2003, the mean annual PM_{10} aerosol concentrations was higher than the air quality standards in 3 (Jacarepaguá, Bonsucesso and São Cristovão) from the 8 city sectors monitored, showing the need of the implementation of additional abatement programs (FEEMA, 2003). In order to achieve further reductions on the air pollution level, it is necessary to perform detailed studies of aerosol source apportionment in the metropolitan area (FEEMA, 2003, 2006).

Notwithstanding the fact that Rio de Janeiro is the second largest city in Brazil, very few have been done related to air pollution studies. In particular, the existing information regarding aerosol particulate, and its chemical composition, is even poorer. Besides the Rio de Janeiro state environmental authority (FEEMA) reports, some works have appeared during the last years dealing with some metals and total suspended matter (TSM) (Quitero et al., 2004a,b), or PM_{10} (da Silva et al., 2008; Toledo et al., 2008). However, there is only one publication related to $PM_{2.5}$ and $PM_{2.5-10}$ aerosol particles (Soluri et al., 2007), which represents, in fact, some aspects of the work done during the first year sampling of the present work.

The objective of this work was to contribute to fill the existing gap related to the aerosol source apportionment in the city of Rio de Janeiro. Coarse ($PM_{10-2.5}$) and fine ($PM_{2.5}$) aerosol particles were collected in ten different sites at the metropolitan area during 24 h on a weekly basis during two years. It is important to have such long sampling periods in order to capture the seasonal variability. The aerosol samples were analyzed for trace elements as well as water-soluble ionic species. Also the aerosol mass and black carbon concentrations were determined. Receptor models such as principal factor analysis, cluster analysis and absolute principal factor analysis were applied in order to identify and quantify the aerosol particle sources in each of the aerosol fractions and for all the ten sampling sites.

2. Material and methods

Aerosol sampling was performed, simultaneously, at ten sites distributed in different location of the Rio de Janeiro metropolitan area (Fig. 1), on a weekly basis with 24 h sampling time, from September 2003 to December 2005, with two interruptions of three months, from December 2003 to February 2004 and from January 2004 to March 2005, providing a total of 80 sampling weeks.

Stacked filter units (SFU) were used to collect fine and coarse aerosol particles with a flow rate of 17 L min^{-1} (Artaxo et al., 1999; Hopke et al., 1997; Maenhaut et al., 1993). The sample volume was obtained with gas volume meters, individually calibrated with a primary standard airflow calibrator, "Gilibrator" (Gilian Instruments Corporation).

The aerosol mass concentrations were obtained through gravimetric analysis using an electronic microbalance with 1 μg sensitivity (Mettler MT5). Samples were kept under controlled temperature $(24 \pm 2)°C$, and relative humidity $(55 \pm 3)\%$, 24 h prior weighting. The detection limit for aerosol mass concentration is about 0.6 μg m^{-3}, while precision is estimated to be lower than 5%. Equivalent black carbon (BC) concentrations in the aerosol fine mode was measured using a reflectance technique (Smoke Stain Reflectometer, Diffusion System, model M43D), calibrated using BC

gravimetric standards (Castanho et al., 2005). In order to determine the water-soluble fraction and the elemental concentrations on the aerosol filters, the samples were divided into two pieces, with a stainless steel blade, one containing one-quarter and the other the remaining three-quarters.

Ten milliliters of ultra-pure water was added to the one-quarter filter fraction, ultra-sonically extracted for 30 min and centrifuged. The obtained extract was kept frozen until its analysis. Ionic concentrations for NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, NO_3^-, SO_4^{2-} and Cl^- were determined in the water-soluble fraction by ion-chromatography with the operational conditions shown in Table 1 of Supplementary material.

On the three-quarter filter fraction, elemental concentrations were determined using the ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) technique, after total chemical dissolution applying high-purity HNO_3 and HF. Filter dissolution was performed by microwave heating in closed Teflon® vessels (CEM MARS 5). After boric acid addition to eliminate HF excess, the solution was evaporated to the dryness under vacuum also by microwave heating and the residue was dissolved with 10 mL 2% HNO_3 (Godoy et al., 2005).

Mass spectrometric analysis was performed in a Perkin–Elmer ELAN 6000 ICP-MS instrument applying an ultra-sonic nebulizer with membrane desolvator (CETAC U-6000AT$^+$) (Table 2 of Supplementary material). Comparing with the previous results, the use of an ultra-sonic nebulizer instead a cross-flow nebulizer, increasing the sensibility by a factor of ten and reducing the achieved detection limit by a factor of five (Godoy et al., 2005). The achieved detection limits are shown in Table 3 of Supplementary material for all species analyzed.

The concentrations of up to 48 elements (Li, Be, Na, Mg, Al, K, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Nb, Mo, Ag, Cd, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, W, Pb, Bi, Th and U) were determined using In and Tl as internal standards. NIST standard reference materials 2783 and 3087a were used to check the analytical procedure applied, including the sample dissolution and the ICP-MS analysis.

Data quality was assessed using a variety of techniques. Histograms, normal and lognormal distributions were generated for each variable to validate the data and to remove outliers. For each variable, a stepwise linear regression was performed on the validated data set to analyze outliers that were above 3 standard deviations. Those variables that could not be significantly predicted by the other variables were not used in the data analysis. Some samples or cases were also excluded from the data set due to equipment failure or unusual activities, such as vegetation burning close to the sampling site. After the data validation, 78–80 cases and 39–49 variables were included in each data set (fine and coarse mode aerosol for each sampling site).

In order to identify and evaluate the contribution of the pollutant sources in the fine and coarse particle fractions in the metropolitan area of Rio de Janeiro, receptor models were used (Hopke, 1999). A multivariate statistical approach was applied including Principal Factor Analysis (PFA), Absolute Principal Factor Analysis (APFA) and Hierarchical Cluster Analysis (Artaxo et al., 1999; Johnson and Wichern, 1998; Legendre and Legendre, 1998). As a general rule (Hair et al., 2005), it is desirable to have at least five times more cases than variables, in order to obtain reliable results of a multivariate model in environmental applications. As a consequence of these criteria, for the multivariate statistical approach we decided to apply a maximum of 17 variables for 80 cases. To reduce the number of variables included in the analysis, additional criteria were used to exclude variables with high similarity as variables included in the analysis, variables that had a significant number of missing values, and variables that could not be associated with any known air pollution sources.
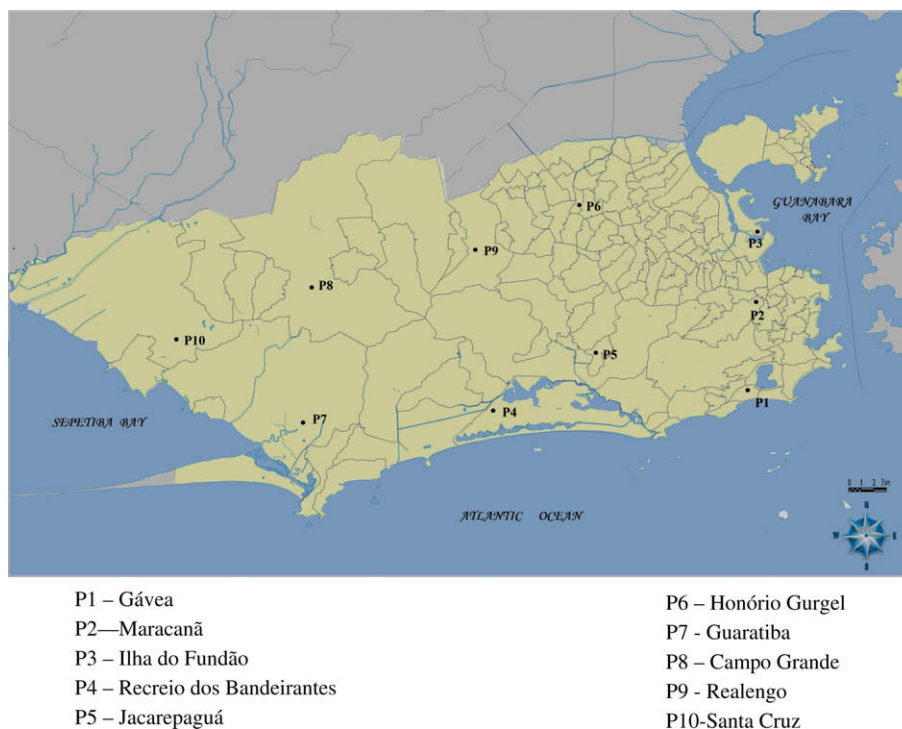
P1 – Gávea
P2—Maracanã
P3 – Ilha do Fundão
P4 – Recreio dos Bandeirantes
P5 – Jacarepaguá

P6 – Honório Gurgel
P7 - Guaratiba
P8 – Campo Grande
P9 - Realengo
P10-Santa Cruz

Fig. 1. Localization of the 10 sampling sites used in this aerosol source apportionment study at the metropolitan area of Rio de Janeiro, Brazil.

3. Results and discussion

The obtained results using the NIST SRM to check the analytical procedure applied, including the sample dissolution and the ICP-MS analysis are given in Table 4 of Supplementary material. The precision of the elemental concentration measurements were better than 10 % and the accuracy better than 15% for the majority of the analyzed elements.

Table 1 presents the mass concentration results of $PM_{2.5}$, $PM_{2.5–10}$, PM_{10} and BC, for each of the ten sampling sites. No violation to the PM_{10} Brazilian air quality standards (50 µg m^{-3} annual mean and 150 µg m^{-3} daily values) was observed. One of the possible reasons for this is the fact that the chosen sampling sites were located not directly over heavy traffic avenues. The air pollution regulatory agency in the Rio de Janeiro metropolitan area (FEEMA) has two automatic air monitoring stations installed in the area, one Downtown and the other in Jacapepaguá, the same neighborhood of sampling site number 5. The PM_{10} mean

annual values reported by the official monitoring station for the year 2006 were 30 µg m^{-3}, for both sampling sites (FEEMA, 2006). These findings are quite in agreement with the observed in the present work, with averages ranging from 20 µg m^{-3} for sampling site 7–37 µg m^{-3} for sampling site 6. On the other hand, during the same year, 2 from 7 sites of FEEMA's manual PM_{10} sampling network have shown mean annual value higher than 50 µg m^{-3} (Bonsucesso and São Cristovão). Mariani (2001) has reported a PM_{10} mean annual value of 62 µg m^{-3} during the year 1999 at sampling site 2 (Maracanã), where lower values were observed, both, by FEEMA, for the year 2006, and in the present work. Sampling site 6 (Honório Gurgel) showed the highest mean black carbon, coarse mode ($PM_{2.5–10}$) and inhalable (PM_{10}) particle mass concentrations, while sampling site 5 (Jacarepaguá) has shown the highest fine ($PM_{2.5}$) particle mean mass concentration. Sampling site 6 is located near regions with the influence of industries and one of the main Rio de Janeiro avenue (Av. Brasil), with a very heavy traffic of buses and autos. However, for all sampling sites it was observed that the coarse particle fraction shows very similar values and represents a high 62–72% of the PM_{10} mass concentration (Table 5 of Supplementary material). Black carbon contribution is more variable but also accounts for a high 18–31% of the fine particle fraction. This large BC fraction indicates that traffic emissions are responsible for a significant fraction of the aerosol mass in the fine mode aerosol fraction, since buses and truck emissions are the largest contributors to black carbon in the urban area (Artaxo et al., 1999). The same fraction for São Paulo is 26%, showing the same impact of diesel emissions in $PM_{2.5}$ in both cities. The lowest values were observed on sampling sites 4 (Recreio dos Bandeirantes), 7 (Guaratiba) and 10 (Santa Cruz). Sampling sites 4, 7 and 10 are located at the Western area of the city, a region of the city in which the city is expanding rapidly and the present values could be used in the future to evaluate the influence of the present growing urbanization on the local air quality.

Table 1
Descriptive statistics of the aerosol mass concentration, as well as black carbon concentration, according to the different sampling sites.

Sampling site	$PM_{2.5}$ (µg m^{-3})		$PM_{2.5–10}$ (µg m^{-3})		PM_{10} (µg m^{-3})		BC (µg m^{-3})	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	7.3	4	12.7	5.9	21	11	2.2	1.3
2	9.8	4.9	18.1	9.0	28	13	3.1	1.6
3	11.1	6.0	18.3	8.1	29	13	2.6	1.5
4	7.7	4.9	14.1	5.6	21.9	9.5	1.6	1.0
5	11.4	4.6	23.1	9.4	34	13	3.1	1.4
6	10.5	4.6	27	14	37	17	3.3	1.7
7	7.9	5.0	12.6	5.1	20.4	8.1	1.43	0.98
8	10.5	4.7	19.4	8.4	30	12	2.4	1.2
9	11	5.5	21	10	32	14	2.5	1.3
10	10.3	4.9	20	10	30	14	1.9	1.0

Mean = arithmetic mean; SD = distribution standard deviation.

Tables 6 and 7 of Supplementary material show the number of samples, the mean concentration and the standard deviation of the variables observed in the fine and in the coarse particles fractions for each sampling site. It can be observed that elements associated with sea-spray, as Na and Mg, and with soil dust, like Al and Fe, are mainly present in the coarse mode aerosol fraction. On the other hand, volatile elements such as As, Cd, Sb and Pb, are predominantly in the fine mode. Sampling site 6 (Honório Gurgel), with the highest observed coarse particle mass concentration, represents also the region with the highest elemental concentration in this mode. Similarly, sampling sites 1 (Gávea), 4 (Recreio dos Bandeirantes) and 7 (Guaratiba) shows the lowest coarse particle concentration and presented the lowest elemental concentration in this mode. However, relative to sampling sites 1 and 7, sampling point 4 show high Cd, Sb and Pb concentration in the fine mode indicating a consequence of the building construction activities at this city area and the related increasing in the circulation of vehicles. The highest concentration of soil related elements in the fine mode were observed in sampling site 10 (Santa Cruz), while sampling site 3 (Ilha do Fundão), close to an express road and industrial zone, represents the site with highest concentration of elements related to oil combustion, as Ni and V, in this mode. Sampling point 6, with the highest concentration for several elements in the coarse mode, represents also the local with the highest As, Cd, Cu, Pb, Se and Zn concentration in the fine mode.

As observed for the aerosol mass concentration, in general, sampling sites 4 and 7 are those with the lowest nitrate and sulfate concentrations and sampling site 6 presented the highest concentration of the same substances. Water-soluble sodium and chloride are mainly present in the $PM_{2.5-10}$ fraction reflecting the sea-spray contribution. Due to the secondary aerosol formation, sulfate was predominately found in the fine aerosol fraction.

Tables 8 and 9 of Supplementary material show a comparison of the present values with some studies published in the literature involving similar sampling methodology. $PM_{2.5}$ and $PM_{2.5-10}$ mass concentrations are in a similar range of reported values for Auckland (Wang and Shooter, 2005), Brisbane (Chan et al., 1999) Edinburgh (Heal et al., 2005) and Zurich (Hueglin et al., 2005), but lower than Bern (Hueglin et al., 2005), Ho Chi Minh (Hien et al., 2001) and Santiago de Chile (Artaxo et al., 1999). Proximity to the seacoast and different precipitation patterns that could change airborne soil dust particles could be the reason for the difference. Comparing the measurements in this study with measurements in Brazilian cities, Porto Alegre, Niteroi and São Paulo, the results obtained in the present work are quite compatible with the values observed in Porto Alegre (Braga et al., 2005) and those found during the summer season in São Paulo (Castanho and Artaxo, 2001), but lower than the winter season results in this city, when thermal inversion layers provide unfavorable conditions for the dispersion of pollutants and concentrations are enhanced (Castanho and Artaxo, 2001). Our results are also lower than Niteroi, a 500,000-inhabitant city close to Rio de Janeiro, and also lower than the results published by the same author for Rio de Janeiro city at sampling site 3 (Mariani, 2001). However, more recent publication of the same author (Mariani and de Mello, 2007) shows lower mean annual values for $PM_{2.5}$ and $PM_{2.5-10}$ mass concentrations in Niteroi at the same sampling site, 17.1 and 25.7 $\mu g\,m^{-3}$, respectively.

As Rio de Janeiro presented significant lower aerosol mass concentration than São Paulo (Castanho and Artaxo, 2001), lower elemental concentrations are also observed in both fine and coarse aerosol modes. Since the aerosol mass concentrations are similar to those found in Porto Alegre (Braga et al., 2005) similar elemental concentration of elements related to the soil dust as Fe and Al were observed. But, the elemental concentration of elements related to the diesel fuel and oil combustion as Ni and V (Ho et al., 2006;

Table 2
Initial eigenvalues obtained for each retained factor and the total variance explained for each sampling site, in the fine mode.

Sampling site	Initial eigenvalues				Variance explained (%)
	Factor 1	Factor 2	Factor 3	Factor 4	
1	8.7	2.4	1.6	1.2	87.2
2	8.4	1.9	1.7	1.4	83.7
3	7.3	2.3	1.9	1.4	80.7
4	7.8	2.4	1.5	1.4	82.2
5	6.3	2.9	2.2	1.7	82.1
6	6.2	2.5	2.1	1.7	78.3
7	8.6	2.5	1.5	1.0	85.7
8	7.4	2.9	1.6	1.3	83.1
9	7.2	2.3	2.0	1.4	80.3
10	6.2	2.8	2.4	1.2	79.2

Valavanidis et al., 2006; Vasconcellos et al., 2007) are lower in Rio de Janeiro when compared to Porto Alegre (Table 9, Supplementary material). When comparing concentrations with values measured in cities abroad, for elements more related to anthropogenic sources, such as Cd, Ni and V, the results found in Rio de Janeiro are of the same order of magnitude of those observed in Edinburgh (Heal et al., 2005), Zurich and Bern (Hueglin et al., 2005), but lower than the results reported by Hien et al. (2001) for Ho Chi Minh city. As lead is not added anymore to the gasoline in Brazil, the Pb elemental concentration, in particular, in the fine mode is lower than those observed in other countries as Vietnam (Hien et al., 2001). On the other hand, the concentrations of crustal elements as Al, Fe, Mn and Ti are higher than in cities as Auckland (Wang and Shooter, 2005), Brisbane (Chan et al., 1999), Edinburgh (Heal et al., 2005) and Zurich and Bern (Hueglin et al., 2005). Probably the effect of road cleaning plays a role in the ressuspended road dust.

Nitrate and sulfate mean annual concentrations in the fine mode are lower than the values reported by Mariani (2001) for sampling site 2 (Maracanã) and Niteroi, and than those reported by Hueglin et al. (2005) for Bern and Zurich (Switzerland). But, higher than the mean annual values reported by Chan et al. (1999) for Brisbane (Australia) and Wang and Shooter (2005) for Auckland (New Zealand), two large sub-tropical coastal cities, indicating a larger secondary aerosol production. One possible reason for this higher sulfate concentration is related to the sulfur content in the Brazilian diesel fuel, 0.5%. Similar values for water-soluble species as chloride, sodium and magnesium ionic concentrations in the coarse mode are observed for coastal cities like Auckland (Wang and Shooter, 2005), Brisbane (Chan et al., 1999), Niteroi (Mariani, 2001; Mariani and de Mello, 2007) and Rio de Janeiro.

The climate seasonality in Rio de Janeiro is characterized by two seasons with different characteristics. The rainy season (October–March) corresponds also to the summer with higher temperatures

Table 3
Initial eigenvalues obtained for each retained factor and the total variance explained for each sampling site, in the coarse mode.

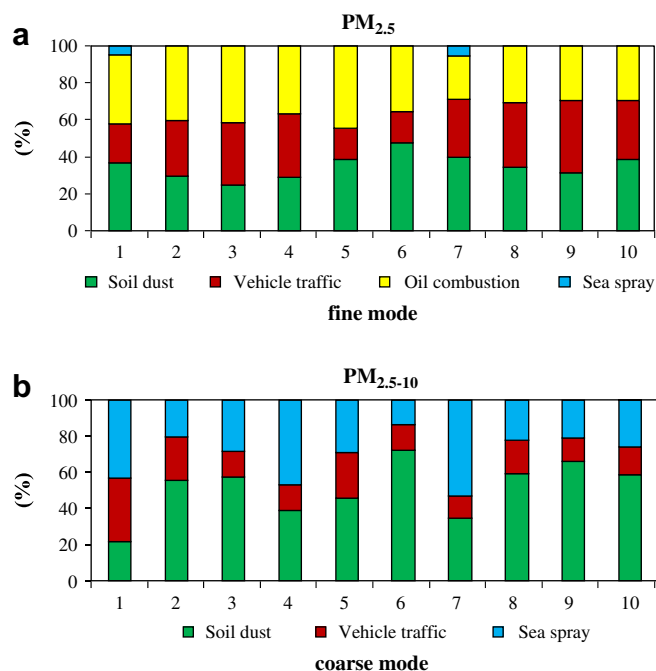| Sampling site	Initial eigenvalues			Variance explained (%)
	Factor 1	Factor 2	Factor 3	
1	9.7	4.1	1.1	87.5
2	10.4	3.7	1.0	89,2
3	9.4	3.7	1.5	85.9
4	9.4	3.9	1.2	85.1
5	9.2	3.7	1.4	84.3
6	10.2	3.0	1.4	85.9
7	9.6	3.8	1.0	85.1
8	10.5	3.3	1.0	87.6
9	10.0	3.1	1.3	84.7
10	9.9	3.2	1.2	84.1

a

fine mode

b

coarse mode

Fig. 2. Distribution according to the largest factor loading of each variable by principal factor analysis and by each sampling site: (a) fine mode and (b) coarse mode.

and insulation, what led from one side to a more intense atmospheric washing-out process and from the other to more favorable conditions for secondary aerosol formation. The winter season corresponds to a dryer period (April–September) with more soil dust and there are frequent vegetation fires. The winter is also characterized by the occurrence of frequent thermal inversions. Figs. 1 and 2 in Supplementary material show the seasonality of some studied parameters for the fine and coarse mode aerosol. For both modes, the observed mass concentration in winter is about 40% higher than in the summer. However, some parameters show higher seasonality than others. Black carbon follows the same

proportionality as observed for the aerosol mass concentration, indicating a similar mass fraction ratio in the emissions that should actually be the case if diesel emissions from buses are the main source of BC. Aluminum and potassium concentration in both aerosol fractions have shown a strong seasonality, with twice concentrations at wintertime. Two factors combined leads to this profile: a more intensive washing-out and larger soil coverage by vegetation during the summer. Sea-spray is constant over the seasons, therefore, water-soluble sodium in the coarse mode shows almost no seasonal effect. The more intense secondary aerosol formation in summer than in winter seems to be compensated by

Fig. 3. Mass concentration distribution according to the absolute principal factor analysis results for each sampling site: (a) fine mode and (b) coarse mode.

the scavenging removal process by rain and, therefore, sulfate in the fine mode shows a low seasonal effect, as observed by Mariani and de Mello (2007). Vanadium has shown a different seasonal behavior for fine and coarse modes, where in the coarse mode,

vanadium is probably associated with the soil dust and, therefore, shows the same strong seasonal behavior as aluminum. On the other hand, in the fine mode, vanadium seems to be more related to residual oil combustion and its seasonal effect, as observed for sulfate, is not very significant.

A multivariate statistical approach was applied to study the inter-relationship between the measured compounds and elements. A combination of Principal Factor Analysis (PFA), Absolute Principal Factor Analysis (APFA) and Hierarchical Cluster Analysis was used to investigate the relationship between the elemental concentrations, and its possible sources. Principal factor analysis was applied individually on each sampling site. The factor loading matrix is obtained. Only factors with initial eigenvalues higher than 1 were retained. Tables 2 and 3 show the initial eigenvalues obtained for each retained factor and also the total variance explained for each sampling site, for the fine and coarse modes. The statistically significant factor loadings higher than 0.40 were used in order to interpret the possible aerosol sources associated with each factor retained by the model (Heidam, 1982).

Four factors were identified for the fine particles in all sampling sites, and they explain around 78–87% of the data variability for each site. In general, the communality, that expresses the adequacy of the factor model, was high for most of the elements, indicating that the identified factors explain most of the data variability of these elements. One factor was identified as soil dust based on the presence of elements such as Al, Fe and Ce. High factor loadings for BC (Artaxo et al., 1999; Castanho and Artaxo, 2001; Heal et al., 2005; Ho et al., 2006; Pakkanen et al., 2003), Cu (Castanho and Artaxo, 2001; Heal et al., 2005; Ho et al., 2006; Pakkanen et al., 2003; Swietlicki et al., 1996; Wahlin et al., 2006) and Cd (Ho et al., 2006; Valavanidis et al., 2006; Wang et al., 2006) were used to characterize the vehicle traffic factor. The presence of Ni (Artaxo et al.,
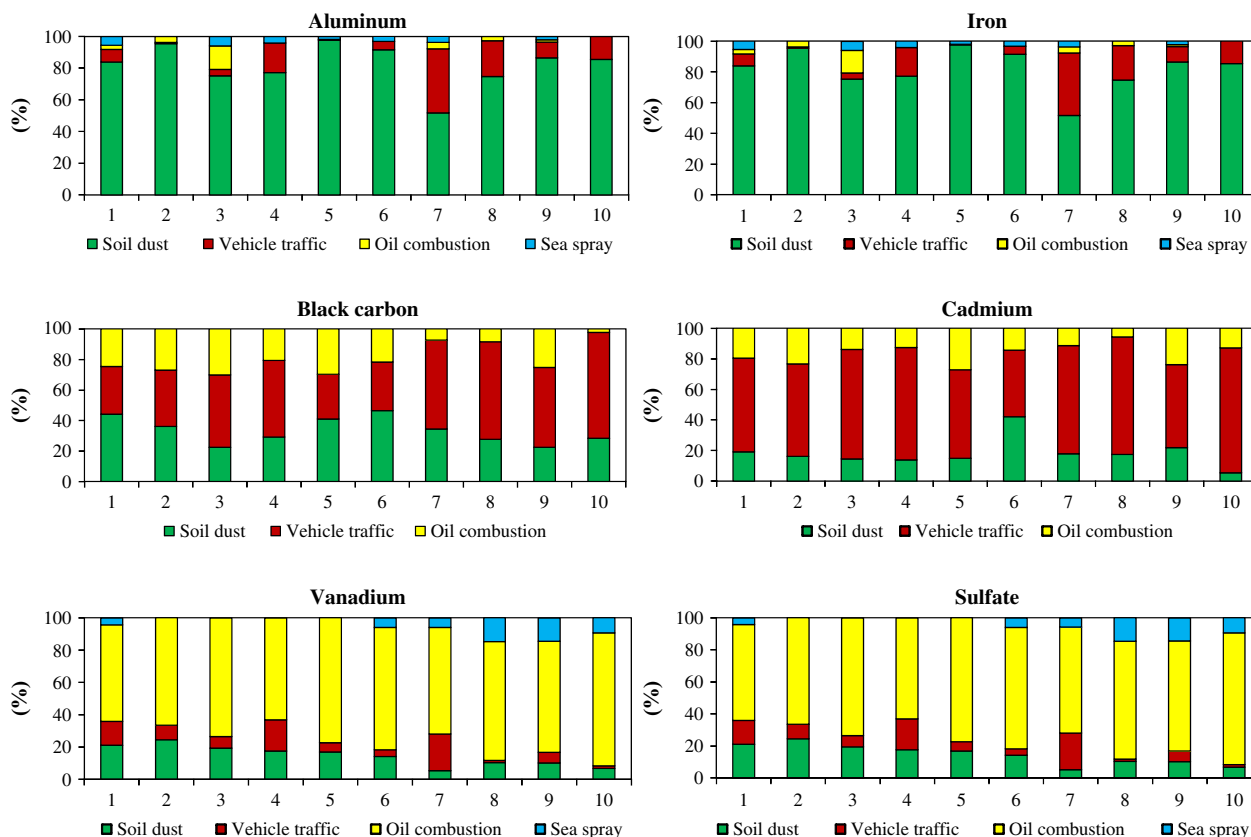

Fig. 4. Aluminum, iron, black carbon, cadmium, vanadium and sulfate distribution in the fine mode according to the absolute principal factor analysis results.

1999; Castanho and Artaxo, 2001; Ho et al., 2006; Johnson et al., 2006; Pakkanen et al., 2003), V (Artaxo et al., 1999; Castanho and Artaxo, 2001; Heal et al., 2005; Ho et al., 2006; Johnson et al., 2006; Pakkanen et al., 2003; Swietlicki et al., 1996) and SO_4^{2-} in another factor is an indication of diesel fuel, residual oil combustion sources plus secondary aerosol. The Na and Mg association in a factor is an indication that it represents the sea-spray influence.

Three factors were identified for the coarse particles samples in all sampling sites, and they explain a high 84–89% of the data variability. Also for the coarse particles, the communality was high for most of the elements. One factor was attributed to soil dust based on the presence of elements such as Al, Fe and Ce. High factor loadings for Cu (Castanho and Artaxo, 2001; Heal et al., 2005; Pakkanen et al., 2003; Swietlicki et al., 1996) and Cd were used to characterize the vehicle traffic. The presence of Na, Mg and SO_4^{2-} in another factor is an indication of the sea-spray influence. The distribution according to the higher factor loading of each variable by Principal Factor and by sampling site is summarized in Fig. 2a (for the fine mode aerosol) and 2b (for the coarse mode aerosol).

In order to verify the orthogonality of the identified factors, the factor scores that represent the individual identification of each sample to each factor, were added as new variables to each database. A hierarchical cluster analysis was then carried out and a dendrogram of the clusters were obtained. Each cluster contains one of the factor scores, and a similar pattern of elements as obtained in the PFA, showing consistency between the independent multivariate procedures as shown in Fig. 3a of Supplementary material (for the fine mode aerosol) and 3b (for the coarse mode aerosol) for sampling site 1, as an example. In order to perform a quantification of the factor structure a source apportionment based on APFA was carried out (Swietlicki et al., 1996). The absolute amounts apportioned to the different sources in the fine and

coarse mode for each sampling site are shown in Fig. 3a and b respectively. The absolute amounts explained 97.4–104.5% of the fine mode mass and 95.3–97.4% of the coarse mode mass, which represent an improvement when compared to the previous results (Soluri et al., 2007). According to the results of this study, only three aerosol sources were responsible for the fine mode mass concentration, soil dust, vehicle traffic and oil combustion, a relatively even and similar partitioning among them was calculated (36, 29 and 35%, respectively), which could indicate a well-mixed atmosphere with a regional transport of the fine particles. For two sampling sites, 1 and 7, a fourth component was identified in the fine mode, sea-spray, but due to its relatively small participation (4 and 6%, respectively) and to the fact that the sea-spray contribution is more relevant to the coarse mode than to the fine mode, this contribution was not considered further. Similarly, three sources were responsible for the coarse mode mass concentration, soil dust, vehicle traffic and sea-spray. However, the distribution among these sources was quite uneven showing a quite local character of the sources contributing for the coarse mode, as expected. Soil dust contribution ranged from 21% in sampling site 1 up to 70% in sampling site 6. Sampling site 1 has the highest vehicle traffic contribution, 35%, due to its proximity to a heavy loaded road nearby. The sampling sites closest to the shoreline (1, 4 and 7) have the highest sea-spray contribution, while sampling site 6 far from the coast has the lowest. Sampling site 3 is located close the shoreline at the Guanabara Bay, but inside the bay a flat surface with small waves is generally observed and, therefore, the sea-spray contribution is smaller if compared with sampling site 1 close to a shoreline with larger waves and visible sea-spray formation. Sampling sites 2 and 5 are located also in a region with known heavy traffic and about 25% of the mass concentration on the coarse mode was attributed to this source, while for the others
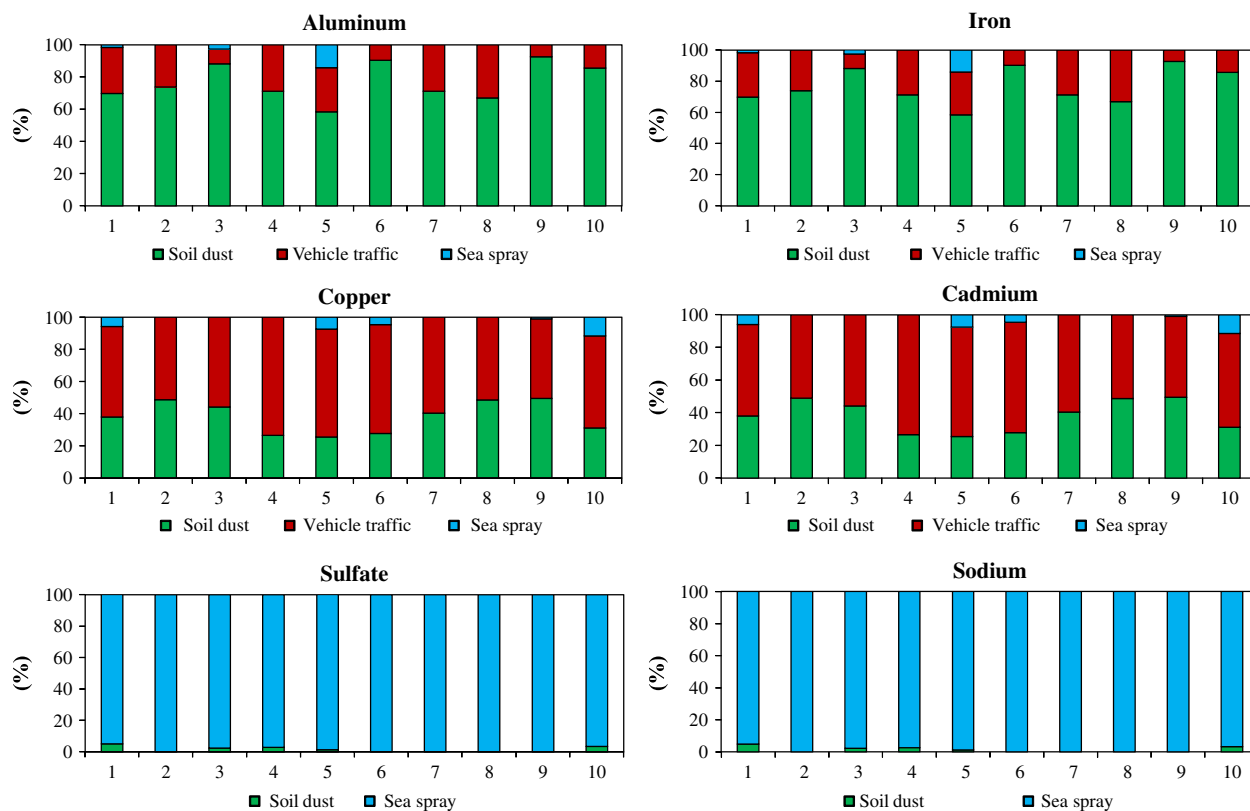

Fig. 5. Aluminum, iron, copper, cadmium, sulfate and sodium distribution in the coarse mode according to the absolute principal factor analysis results.

sampling site the traffic contribution is similar and around 14% of the aerosol mass.

The attribution in the fine mode of the presence of Ni and V to oil combustion can be corroborated by the V/Ni ratio observed (mean value = 1.36) which is similar to the V/Ni ratio of 1.25, in the petroleum produced in Brazil (Fonseca, 2000). On the other hand, on the coarse mode these elements appeared in the soil dust factor meaning that the soil is contaminated with the residue of oil combustion deposited over roads.

The quantitative aerosol source apportionment for some variables on the fine and coarse mode fractions is shown in Figs. 4 and 5. Elements such as Al and Fe are present on fine and coarse modes associated to soil dust, with some contribution from the vehicular traffic factor. Curiously, black carbon has relevant contribution of three different sources: oil combustion, vehicle traffic and soil dust. The BC quantitative apportionment changes according to each sampling site-specific characteristics. BC association with combustion processes (oil combustion and vehicular traffic) is expected, but also the high loading of soil dust absorbs light in the visible due to the soil dust itself, as well as deposition of diesel emission on the roads. As could be expected, sulfate in the fine and coarse mode is apportioned to different sources, oil combustion in the fine mode and sea-spray in the coarse mode. Cadmium is an element usually associated to smelters, but it can be also associated to the vehicular traffic (Ho et al., 2006; Valavanidis et al., 2006; Wang et al., 2006) and this association appears in both modes. Similarly, copper is also associated to vehicular traffic due to the presence of Cu in brake wear (Heal et al., 2005; Ho et al., 2006; Pakkanen et al., 2003; Swietlicki et al., 1996; Wahlin et al., 2006), but, in the Brazilian, distilled alcohol is used as fuel in cars able to run with 100% ethanol and also mixed in the gasoline in Brazil with a 22% proportion all over the country (Castanho and Artaxo, 2001) (Fig. 5). Sodium in the coarse mode is supposed to be related to the sea-spray as effectively shown in Fig. 5, where almost 100% of this element was apportioned to sea-spray.

4. Conclusions

Levels of air pollution for particulate matter are not very high for the 10 sampling sites in Rio de Janeiro. A quite similar air pollution source structure for the 10 sampling sites in this study was obtained. Sampling site 6 (site Honório Gurgel) was identified with the highest mean BC, $PM_{2.5-10}$ and PM_{10} particle mass concentration, while sampling site 3 (Ilha do Fundão) has shown the highest $PM_{2.5}$ particle mass concentration. Both are sampling sites located on a region under the influence of industrial emissions as well as a region with heavy vehicular traffic. However, for all sampling sites it was observed that the $PM_{2.5-10}$ fraction represents a high 60–70% of the PM_{10} mass concentration. On the other hand, BC accounts for 17–29% of the fine mode particle fraction. The lowest observed BC concentrations were observed on sampling sites 4 (Recreio dos Bandeirantes) and 7 (Guaratiba) both located at the Western area of the city. The Western area of the city represents a new area that is showing a growing urbanization with important effects on the local air quality.

Applying the APCA almost 100% of the observed mass for fine and coarse modes were identified, which represents an improvement related to previous results obtained applying a simpler methodology. Three sources were apportioned to the coarse aerosol particles, soil dust, sea-spray and vehicle traffic, being the soil dust the more important one followed by the sea-spray and the vehicle traffic. In general, at the $PM_{2.5-10}$ fraction, the soil dust accounts for 50% of the coarse mode mass; consequently, the implementation of actions aiming the reduction of ressuspended dust should improve considerably the air quality of the Rio de Janeiro city. On the other hand sources related to anthropogenic sources as vehicle traffic and oil combustion, represents about 65% of the $PM_{2.5}$ fraction. Taking into account the association between the fine mode aerosol and respiratory diseases (Marmur et al., 2006; Hopke et al., 2006), a reduction of this contribution could have a substantial impact on the population health.

Acknowledgements

Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.atmosenv.2008.12.046.

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