Wintertime and summertime São Paulo aerosol source apportionment study

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Abstract

A detailed aerosol source apportionment study was performed with two sampling campaigns, during wintertime and summertime in the heavily polluted metropolitan area of São Paulo, Brazil. In addition to 12 h fine and coarse mode filter sampling, several real time aerosol and trace gas monitors were used. PM_{10} was sampled using stacked filter units that collects fine ($d < 2.5\,\mu m$) and coarse ($2.5 < d < 10\,\mu m$) particulate matter, providing mass, black carbon (BC) and elemental concentration for each aerosol mode. The concentration of about 20 elements was determined using the particle induce X-ray emission technique. Real time aerosol monitors provided PM_{10} aerosol mass (TEOM), organic and elemental carbon (Carbon Monitor 5400, R&P) and BC concentration (Aethalometer). A complex system of sources and meteorological conditions modulates the heavy air pollution of the urban area of São Paulo. The boundary layer height and the primary emissions by motor vehicles controls the strong pattern of diurnal cycles obtained for PM_{10}, BC, CO, NO_x, and SO_2. Absolute principal factor analysis results showed a very similar source pattern between winter and summer field campaigns, despite the different locations of the sampling sites of both campaigns, pointing that there are no significant change in the main air pollution sources. The source identified as motor vehicle represented 28% and 24% of the $PM_{2.5}$ for winter and summer, respectively. Resuspended soil dust accounted for 25% and 30%. The oil combustion source represented 18% and 21%. Sulfates accounts for 23% and 17% and finally industrial emissions contributed with 5% and 6% of $PM_{2.5}$, for winter and summer, respectively. The resuspended soil dust accounted for a large fraction (75–78%) of the coarse mode aerosol mass. Certainly automobile traffic and soil dust are the main air pollution sources in São Paulo. The sampling and analytical procedures applied in this study showed that it is possible to perform a quantitative aerosol source apportionment in a complex urban area such as São Paulo. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The urban air pollution issue is a concern in many mega cities, because of its hazardous effect to human health (Macchione et al., 1999; Saldiva et al., 1995; Schwartz, 1994; Spektor et al., 1991). The metropolitan area of São Paulo is possibly the third largest metropolitan conglomerate of the world, with about 17 million inhabitants. It is the most industrialized and developed region of South America, representing 18.5% of the Brazilian GNP. São Paulo city is home of one of the largest urban motor vehicles fleet (5.5 millions automobiles) of the world. It is located in a plateau at about 860 m above sea level (a.s.l.) and it is surrounded by hills of about 1200 m in height. Frequent subsidence and thermal inversion layers provides unfavorable conditions for the dispersion of pollutants during most of the winter season. The strong emissions of trace gases and aerosol particles by vehicles, industry and resuspended soil dust, together with secondary aerosol,

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coupled with the unfavorable natural conditions of dispersion, are responsible for the high concentrations of pollutants observed in the São Paulo metropolitan area (Artaxo and Castanho, 1998).

In São Paulo, PM_{10} concentrations consistently exceed the annual national air quality PM_{10} standard of $50 \mu g m^{-3}$ during the last 20 years for several monitoring stations around the urban area. Concentrations of CO and NO_2 are also high due to high motor vehicle emissions, but the SO_2 concentrations are low because of the consumption of low sulfur fuels in São Paulo, and also probably because of the somewhat fast conversion rate of SO_2 to sulfate in the atmosphere. Concentrations of ozone frequently exceed the air quality standard of $160 \mu g m^{-3}$, 1-h limits, during the spring and summer, when the photochemical processes are efficient. The high level of pollutants occurs in several air pollution monitoring stations distributed over the Metropolitan region of São Paulo (RMSP) (CE-TESB, 1998), indicating that the air pollution issue is actually a regional issue, not limited anymore to the city borders. Several previous works have been done studying air pollution in São Paulo, where the particulate matter has been characterized and sources of pollutants have been identified by receptor models (Andrade et al., 1994; Artaxo et al., 1995; Artaxo and Castanho, 1998; Orsini et al., 1984, 1986). However, this is the first study to use real time aerosol and trace gas monitors that allows the study of the diurnal pattern of pollutants over the metropolitan area during winter and summertime.

This paper reports quantitative source apportionment calculations for winter and summertime aerosols collected in the São Paulo metropolitan area. Fine and coarse mode aerosol particles were collected and analyzed for mass, black carbon (BC) and up to 20 trace elements using particle induced X-ray emission analysis. The carbonaceous component was measured using several techniques, including an aerosol carbon monitor, to measure organic and total carbon with a time resolution of 60 min. The aerosol optical absorption component was determined using one Aethalometer from Magee Scientific. The measurement of gaseous component, mostly SO_2, CO and NO_2 has helped to apportion aerosol sources. Meteorological influence in the PM_{10} concentrations was studied using real time aerosol mass monitors such as the TEOM sampler. This study includes measurements during summertime in addition to wintertime, to allow comparison of source strengths in different seasons.

2. Experimental and analytical methodologies

Two sampling campaigns were carried out continuously during the wintertime of 1997 (10 June until 10 September) and summertime of 1998 (16 January until 6 March). The wintertime study was carried out in a site located about 6 km from São Paulo downtown at the Medical School building at the University of São Paulo, indicated in Fig. 1. The sampling sites and meteorological station locations in the city are indicated in this figure. The region is characterized by heavy traffic and the local activity is mainly commercial. The summertime campaign was carried out in the University of São Paulo campus located about 10 km from downtown. The site is also characterized by a heavy traffic and the local activity is mainly residential and commercial. The comparison of atmospheric characteristics between two different sampling sites for winter and summer has its limitations, because you aren't under identical sampling condition for both studies. However, São Paulo is a very large urban area and the small distance between the two sampling site and the well mixed characteristics of the urban area makes the comparison valid. The comparison between the two sites for different seasons was valid, and the results confirm that. In both campaigns the equipment inlets were located 3 m above the ground on the flat roof of the 3-floor buildings to minimize direct influence of emissions from local vehicles and nearby resuspended soil dust by the local traffic. Both sites were at about 760 m a.s.l.

During the wintertime campaign the SFU operated with an integration time of 12 h from 10 AM to 10 PM from 10 June until 10 September. The Aethalometer also operated during all the campaign period with a time resolution of 10 min. The carbon monitor operated with a time resolution of 1 h in the last month, from 10 August until 10 September, at the same period the TEOM operated with a time resolution of 10 min. Trace gas data were available from July until September with a time resolution of 1 h. During the summer campaign of 1998, the SFU operated for 24 h integration time, from
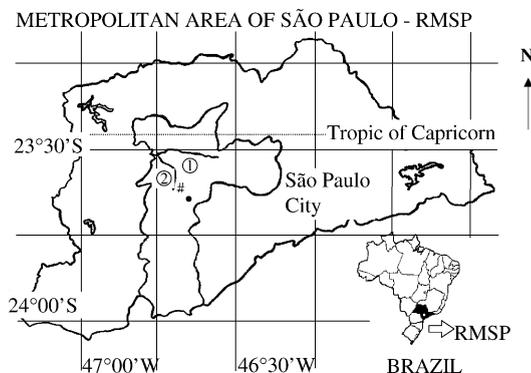
Fig. 1. São Paulo metropolitan region map with the sampling locations indicated: (1) Medical School—USP, site of the winter campaign; (2) São Paulo University Campus—USP, site of the summer campaign; #, Congonhas Airport; ●, Meteorological Station.

10 AM until 10 AM during all period from 16 January until 6 March. The real time monitors in the summer campaign operated during most of the period, with the same time resolution as they operated during wintertime.

The inhalable particulate matter was sampled using stacked filter units (SFU) (Hopke et al., 1997) on 47 mm diameter nuclepore polycarbonate filters, in two separated size fractions (John et al., 1983). The inlet have an impactor stage designed to have a 50% collection efficiency at 10 μm equivalent aerodynamic diameter. The coarse particles ($2.5 < d_p < 10$ μm) were collected in an 8.0 μm pore size filter while fine particles ($d_p < 2.5$ μm) were collected on 0.4 μm pore size filters. At a flow rate of 16 lpm, the SFU was fully characterized in Hopke et al. (1997).

Mass concentrations of the fine and coarse modes were obtained gravimetrically in a 1 μg sensitivity electronic microbalance, in a controlled atmosphere room (20°C, 50% relative humidity, with fluctuations less than 10% of these set points). The filters were equilibrated in this room for 24 h before weighing. Electrostatic charges were controlled using radioactive sources. The concentration of BC on the fine fraction of the SFU was determined using a reflectance technique (Reid et al., 1998) that was calibrated using Monarch soot carbon standard. Elemental composition was determined by particle induce X-ray emission (PIXE) (Campbell, 1995) at the 1.7 MV tandem Pelletron accelerator at the Laboratory of Analysis of Materials by Ionic Beam (LAMFI) in the São Paulo University (Artaxo and Orsini, 1987; Tabacniks et al., 1987). It was possible to measure the elemental concentration of up to 20 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sn, Zr and Pb). The typical precision of the elemental concentration is 4–8%.

A real time aerosol mass monitor, the tapered element oscillating microbalance (TEOM) series 1400a from Rupprecht & Patashnick Inc., with a PM$_{10}$ inlet was operated, with a time resolution of 10 min. The TEOM was operated with a collection stage heated to 50°C. A detailed comparison between the PM$_{10}$ measured by the SFU and by the TEOM monitor was done to assure the quality of the data for both sampling campaigns. The TEOM high time resolution measurements were integrated to 12 h to be compared to the respective interval of time used by the SFU. As the TEOM had operated for only one month in winter, the samples to be compared resulted in a total of 55 data points. The regression results for concentrations measured in μg m^{-3} were

$$PM_{10}(TEOM) = 0.90(\pm 0.03) \times PM_{10}(SFU)$$
$$- 8(\pm 3) \quad \text{with } R^2 = 0.95.$$

The regression equation shows a difference of 10% between the SFU gravimetric mass concentrations and the TEOM PM$_{10}$ measurements, and that the TEOM is systematically lower than the SFU mass concentration. It is well known and reported in the literature that the TEOM aerosol monitor always measures smaller mass concentrations than gravimetric methods. This effect is due to the heating (50°C) that the instrument must apply to the aerosol flow, causing some loss of semi-volatile organic compounds (Ayers et al., 1999; Meyer et al., 1992). The study of Meyer et al. (1992) carried out in a California mountain site during wintertime where wood smoke dominate the PM$_{10}$ obtained a loss of 45% of aerosol mass. Ayers et al. (1999) experiment carried out in Australian cities in the winter revealed differences from PM$_{2.5}$ of more than 30%, whereas Soutar et al. (1999) experiment carried out in UK cities obtained loss of 35% for PM$_{10}$. The reason for the smaller volatile component in São Paulo is the higher impact of resuspended soil dust in São Paulo, compared to the other studies, with relatively smaller impact of ammonium nitrate and sulfate.

The organic and total carbon concentration were measured with 1 h time resolution, in the PM$_{2.5}$ fraction by a direct automatic thermal-CO_2 technique, performed by the Ambient Carbon Particulate Monitor, series 5400 from Rupprecht & Patashnick, Inc. During the analysis the collected sample is heated first to 340°C and then to 750°C determining the concentrations of organic and total carbon, respectively. The elemental carbon is derived as the difference between the total and the organic carbon (OC). A high time resolution BC monitor, the Aethalometer, manufactured by Magee Scientific Co., measured the BC concentration in the fine fraction (Hansen et al., 1984). The Aethalometer was operated with 5 min time resolution, and an absorption cross section of 10 m^2 g^{-1} was used to convert optical absorption to BC equivalent (Reid et al., 1998).

The BC measured from the aethalometer was compared to the elemental carbon acquired by the carbon analyzer. Despite of being two very different measurements the comparison between EC and BC shows a good agreement. The regression result was

$$BC(Aethalometer) = 1.00(\pm 0.02) \times EC(Carbon Analyzer)$$
$$+ 2.3(\pm 0.1) \text{ with } R^2 = 0.88.$$

The measurement of CO, NO$_2$, and SO$_2$ concentrations were performed by the State of São Paulo Environmental Protection Agency (CETESB, 1998), with an automatic air pollution monitoring station located near the sampling site building during wintertime and at the same site during the summer. The time resolution of these aerosol and trace gas instruments enabled the measurement of diurnal cycles and allowed the identification of the factors that influence on it, complementary to the traditional 12 or 24 h aerosol analyses (Artaxo, 1999a).

Meteorological variables were monitored at the University of São Paulo automatic weather station, located in the southeast part of the city. Despite of being in a different site, the data was only used to classify weather patterns. The products of the analysis of these meteorological data helped to classify the general meteorological conditions in the region of São Paulo, basically if the weather was favorable or not to the dispersion of the pollutants. It was analyzed atmospheric pressure at surface level, temperature, relative humidity, precipitation, and cloudiness observations. Radiosondes were done at Congonhas Airport, twice a day and also analyzed (9 AM and 9 PM local time).

Receptor model methodologies are based on statistical multivariate analysis to infer source contributions at the receptor sites (Henry, 1991; Puri et al., 1996). Absolute principal factor analysis (APFA) was applied to identify the absolute source profiles and quantify the source apportionment (Thurston and Spengler, 1985). The APFA model is based on the eigenvalue and eigenvector analysis of the correlation matrix of the normalized elemental concentration. The aim is to obtain a reduced number of factors that are independent and uncorrelated that could explain most of the original data variability. The factor-loading matrix represents the association between the trace elements and each factor obtained. The factor-scores are an indication of the strength of each sample to each retained factor. The percentage of variance explained for each variable can be used to test the effectiveness of the factor model to that particular variable. Also the total variance explained by the model can be used as a check if the number of factors and their composition is adequate to the original database (Hopke, 1991).

3. Results and discussion

In this experiment, a careful quality assurance and data validation procedure was implemented. Several key related aerosol properties were measured by different samplers and techniques, allowing a detailed analysis of the data quality. To facilitate discussion of the results, the time series of the SFU, TEOM and related bulk aerosol properties will be first presented and discussed, followed by a presentation of the aerosol source apportionment with the measured aerosol elemental composition. Summer and wintertime and fine and coarse aerosol fraction will be discussed separately.

The time series of PM_{10} concentrations measured by the SFU separated in the fine and coarse fractions are shown in Fig. 2. Fig. 2 presents the temporal series of PM_{10} in 24 h average in order to compare the variability of winter and summer concentrations, and also to compare the PM_{10} measurements to the Brazilian air pollution standard limit for PM_{10} that is $150\,\mu g\,m^{-3}$

averaged over 24 h. During the winter period PM_{10} concentrations from 20 up to $160\,\mu g\,m^{-3}$ were measured. The meteorological analysis identified that the period with low concentrations in wintertime are coincident with days with synoptic systems of low pressure associated with high wind speed and occasional rain. This condition is favorable to dispersion and deposition of the pollutants. However, periods were also observed where the meteorological conditions are characterized by synoptic systems of high pressure that brought mostly sunny weather, low wind speed and a low height thermal inversion layer, a meteorological condition unfavorable to the dispersion of the pollutants. If this meteorological condition persists for more than 3 days, the resulting accumulation of pollutants in the atmosphere brings high PM_{10} concentrations. During the summertime campaign, a very different pattern was observed, as can be seen in the right pane in Fig. 2. The PM_{10} concentrations are relatively low, with an average of $32\,\mu g\,m^{-3}$ in the summer, compared to $77\,\mu g\,m^{-3}$ during wintertime. This pattern can be explained by the favorable conditions to the dispersion of pollutants during the summer, with frequent rains in the metropolitan region of São Paulo. Comparing winter and summertime periods, the fine fraction had a reduction of about 50% while the coarse fraction had a greater reduction of 60%. This is probably due to the difference of deposition efficiency between the coarse and fine modes in the summer when there are more frequently rainy periods. Artaxo et al. (1999b) in a similar study in Santiago de Chile, obtained average concentrations of PM_{10} of $148\,\mu g\,m^{-3}$ downtown. Similar fractions of PM_{10} for the fine (40% $PM_{2.5}/PM_{10}$) and coarse mode (60% of CPM/PM_{10}) were obtained for Santiago and São Paulo.

There are two clear meteorological conditions that influence the pattern of pollutants in São Paulo. They can be classified by clear and sunny days, versus cloudy days. In the first condition, the so-called '*sunny days*' represent 12 days of the total data set of 29 days. During these days the region was under a high-pressure synoptic system and the boundary layer has a very well defined cycle during the day. They are characterized by absence of clouds, high thermal amplitude (13°C nighttime to 27°C daytime) and by low daytime relative humidity (from 20% to 36%). The nighttime stable layer could reach heights very low as 20–60 m. In the second weather classification, '*cloudy days*' represent 7 days of 29 days of the data set. During these days the region was mainly under low-pressure synoptic system, characterizing the arrival of cold fronts. Cloudy skies with or without rain, low thermal amplitude (15°C nighttime to 22°C daytime) and high humidity (60% daytime and 90% nighttime) characterized these days. The other 10 days represent a mix of the two situations listed above, they were transitions from one extreme of high stable
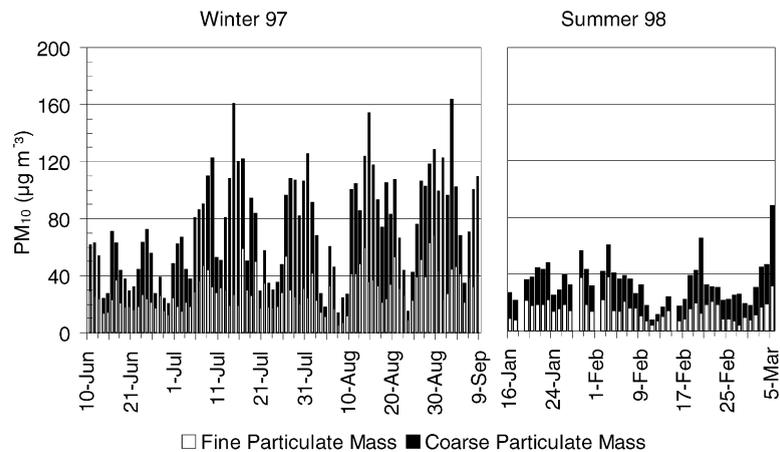
Fig. 2. Fine and coarse mode aerosol mass concentration (24 h average, from 10 AM to 10 AM) for the wintertime and summertime SFU measurements. The sum of the two aerosol fractions provides the PM_{10} concentrations. Measurements in wintertime are from 10 June to 10 September 1997 and measurements in summertime are from 16 January to 6 March in 1998 in São Paulo. The average PM_{10} was 77 $\mu g\,m^{-3}$ in wintertime and 32 $\mu g\,m^{-3}$ in summertime. The average $PM_{2.5}$ during wintertime was 30 $\mu g\,m^{-3}$ and 15 $\mu g\,m^{-3}$ during summertime.
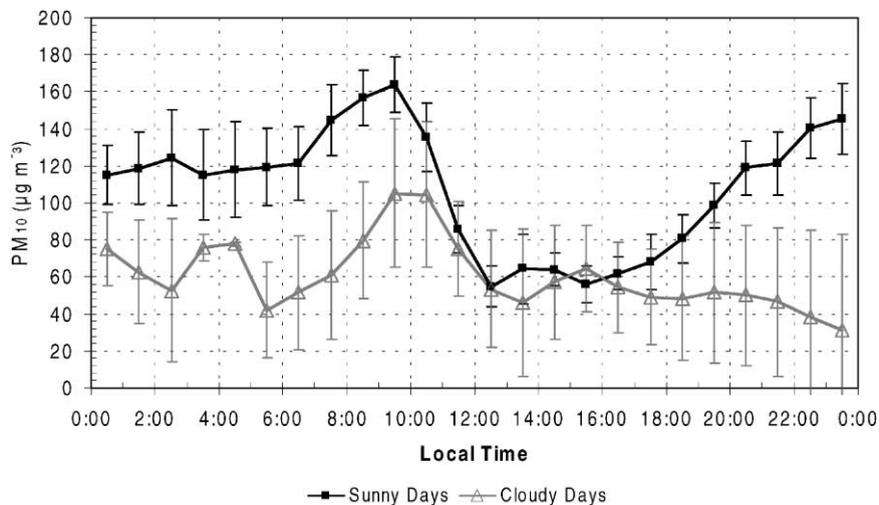
Fig. 3. Average diurnal cycle of PM_{10} concentrations during weekdays. The plot presents 1-h average of sunny (8 days) and cloudy (3 days) weekdays measured in wintertime from 10 July to 10 September in 1997 in São Paulo by the TEOM PM_{10} monitor.

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Fig. 3 shows the average PM_{10} diurnal variability obtained by the TEOM monitor in the winter season. Analyzing the pattern for the days classified as 'sunny days' during the week (8 days), it is possible to observe the influence of the traffic, with a peak in concentrations at 8–10 o'clock in the morning and an increase in concentrations after the 18:00–20:00 rush hours peak. The variation of the planetary boundary layer (PBL) height during the day is clearly modulating the atmo-

spheric particulate concentrations in the 'sunny days'. In the early morning a turbulent layer starts to form, called mixing boundary layer (MBL), due to the solar heating. This MBL reaches its maximum depth in the afternoon when the temperature reaches its maximum. This atmosphere layer is characterized by an intense mixing and instability (Stull, 1991). This condition results in low concentrations values during the afternoon as can be seen in Fig. 3 with a minimum at 13:00–15:00 o'clock. During the night a low and stable boundary layer (SBL) is formed due to the thermal inversion and the intense

subsidence in the region. This added to the early evening vehicle emissions results in an increase of the concentrations during all the night. The concentration of particulate matter in the early morning can reach very high values (250 $\mu g\,m^{-3}$ for PM_{10}). A different pattern is observed in the 'cloudy days' during the week (average of 3 days during the campaign) when a low concentration pattern during the night due to atmospheric instability and therefore efficient dispersion of the pollutants are noticed.

Fig. 4 presents the diurnal cycle of weekend averages of the PM_{10} (4 sunny days and 4 cloudy days), which shows a slight different pattern. It presents a decrease in the peak concentrations of PM_{10} in rush hours compared to weekdays, when the traffic of vehicles is much higher, reinforcing the evidence of the importance of vehicles emissions in the urban area of São Paulo. A similar analysis was done for the BC concentration and trace gases such as CO and NO_2 and the diurnal cycle obtained had a similar pattern as the observed for the PM_{10}. Diesel and vehicle emissions are the main sources of BC, CO and NO_2 in São Paulo. These analyses showed the critical role of the effect of the vehicle emissions in addition to the PBL diurnal cycle in the modulation of diurnal pattern of the pollutants concentration.

The OC aerosol is originated from direct emissions of particles, such as automobile exhaust, and also from atmospheric secondary formation from gaseous precursors. The diurnal cycle of OC measured by the 5400 Ambient Carbon Particulate Monitor presents a similar pattern as the BC concentration. However, the ratio of BC/OC varies significantly along the day, as can be observed in Fig. 5. The maximum value of the ratio BC/OC occurs in the early morning, at about 70%,

coincident with the time of traffic peak. This is an evidence of the higher influence of direct vehicle emissions of BC relatively to OC. During the day it is possible to observe a sharp decrease in the ratio (BC/OC < 40%), indicating two processes: a reduction in the direct emission of BC by the motor vehicles, and the secondary production of OC particulate in the atmosphere mostly from the motor vehicle emissions of volatile organic compounds (VOC). Chow et al. (1996) has pointed out that the limit of 50% of (BC/OC) indicates the presence of secondary organic aerosols in the urban atmosphere. The cloudy days do not show a strong gradient in the ratio, presenting a BC/OC ratio in the afternoon around 10% higher than in sunny days. This fact points to the possibility of changes in the production of OC related to atmospheric radiation.

Fig. 6 shows a comparison of the diurnal cycle of BC concentration observed in wintertime and summertime measurements. It is possible to observe that the maximum concentration in the rush hours is similar in the two periods, besides the most unfavorable dispersion conditions during wintertime. At nighttime the pattern is very different. During wintertime, a large accumulation of BC during nighttime occurs, showing average concentrations of 8–$10\,\mu g\,m^{-3}$. A similar mechanism during summertime measurements was not observed. This effect could be caused by more favorable conditions of dispersion of the pollutant during the night in summertime. From the absolute magnitude of the BC concentrations during the rush hours, it is possible to observe similar amounts of BC emissions in the two seasons, again showing the effect of direct vehicle emission on BC concentrations.

Table 1 shows the mean concentration, standard deviation and number of samples for all the measure-
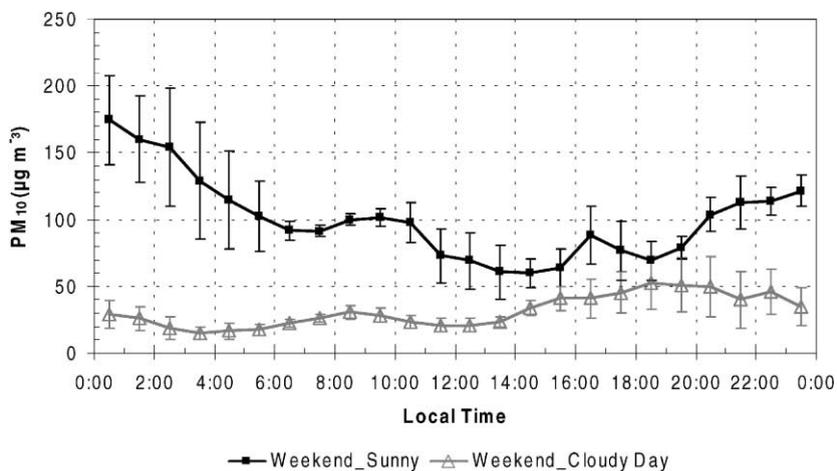
Fig. 4. Diurnal cycle of mass concentration of PM_{10} on weekend's days. The figure shows 1-h average of sunny (4 days) and cloudy (4 days) days data measured in wintertime from 10 July to 10 September in 1997 in São Paulo by the TEOM PM_{10} monitor.
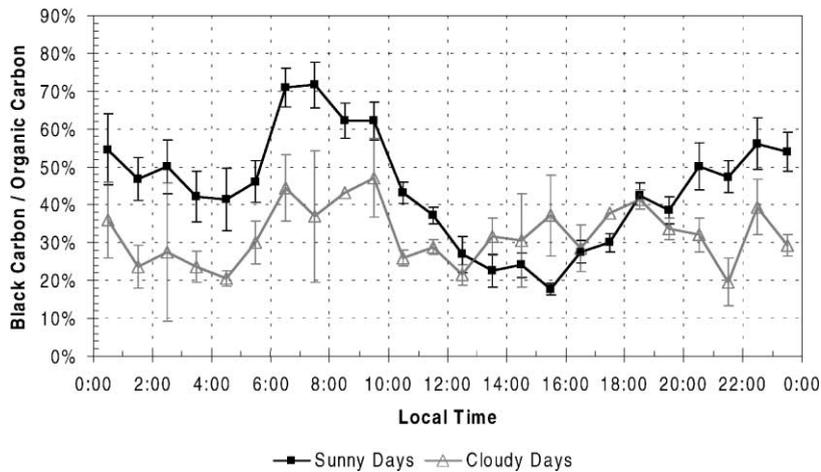
Fig. 5. Diurnal cycle of mass concentration ratio between black carbon (BC) measured by the Aethalometer and the organic carbon (OC) measured by the carbon monitor. The figure presents 1-h average of Sunny (8 days) and Cloudy (3 days) weekday's data in wintertime in São Paulo.
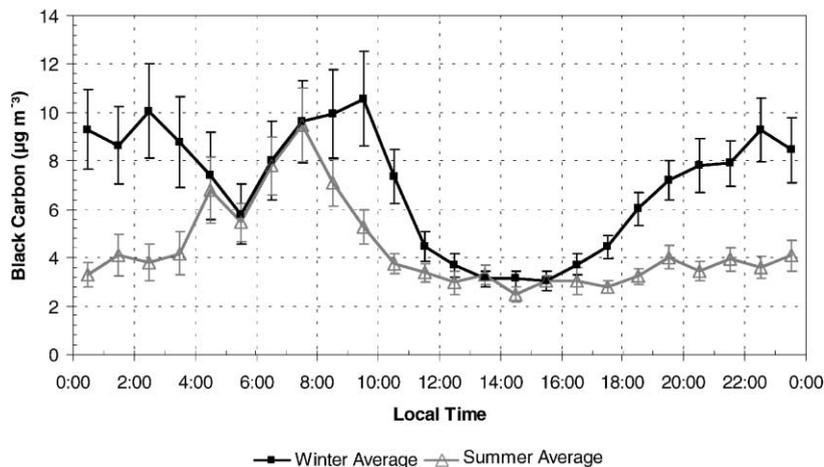
Fig. 6. Diurnal cycle concentrations of black carbon observed in wintertime and summertime. The figure presents 1-h average of data obtained in wintertime (29 days) and summertime (33 days) in São Paulo.

ments in the fine and coarse fractions of the aerosol for the wintertime sampling campaign. Table 2 shows similar data for the summertime campaign. A general reduction in the absolute elemental concentrations between the winter and summer periods, more remarkable for crustal elements (Si, Al, Fe, Ti and others) that is more susceptible to the seasonal variability, due to the emission and deposition processes can be observed. Comparing the fine and coarse fractions it is evident that the sulfur concentration is predominantly in the fine fraction of the particulate matter due to its formation process, the gas-to-particulate conversion of SO_2. The concentrations of soil dust characteristics elements (Si, Al, Ti, Fe) are much higher in the coarse mode of the

aerosol also reflecting the formation process of this kind of aerosol particles. The fine sulfur concentration in Santiago de Chile has a similar absolute magnitude as São Paulo at $1.5 \, \mu g \, m^{-3}$ (Artaxo et al., 1999b; Rojas et al., 1990). The average concentrations of trace gases for the wintertime were: SO_2: $22 \pm 13 \, \mu g \, m^{-3}$; NO_2: $195 \pm 124 \, ppb$; CO: $3.1 \pm 1.9 \, ppm$.

The concentrations obtained for the carbonaceous fraction of the fine particulate matter added to the inorganic composition estimated, based on the stoichiometric ratios of the different compounds from Tables 1 and 2, allowed the checking of the mass balance closure of the fine particulate matter in wintertime and summertime in the region of São Paulo. The two

Table 1

Descriptive statistics of the fine and coarse mode particulate matter during the wintertime sampling period, from 10 July to 10 September in 1997 in the São Paulo metropolitan area

PM$_{2.5}$ aerosol ($d_p < 2.5 \mu$m)				Coarse mode aerosol ($2.5 < d_p < 10 \mu$m)			
Specie	Mean (ng m^{-3})	σ^a (ng m^{-3})	Number of samples	Specie	Mean (ng m^{-3})	σ (ng m^{-3})	Number of samples
PM$_{2.5}$[b]	30.2[b]	16.1[b]	181	CPM[b]	46.1[b]	38.1[b]	177
Black carbon[b]	7.6[b]	3.7[b]	181	—	—	—	—
Organic carbon[b]	15.8[b]	8.3[b]	57	—	—	—	—
Al	437	282	179	Al	1521	1212	177
Si	511	288	179	Si	2269	1726	177
P	14.3	4.9	25	P	25	14	114
S	1510	1166	179	S	733	580	177
Cl	52	35	78	Cl	250	279	177
K	407	252	179	K	486	433	177
Ca	146	93	179	Ca	1196	864	177
Ti	31	24	179	Ti	217	165	177
V	11.7	6.5	179	V	12	12	177
Cr	9.6	3.7	9	Cr	24	15	51
Mn	12.6	8.1	179	Mn	32	23	177
Fe	532	273	179	Fe	1981	1426	177
Ni	3.9	2.8	179	Ni	5.8	6.2	177
Cu	19	11	179	Cu	44	44	177
Zn	126	107	179	Zn	189	234	177
Se	3.0	2.6	123	Se	3.0	3.4	86
Br	14.3	6.2	65	Br	24	14	27
Rb	4.6	2.5	84	Rb	7.6	4.9	106
Sr	2.4	1.0	72	Sr	8.5	6.2	177
Zr	4.1	2.1	28	Zr	12	15	101
Pb	42	34	179	Pb	38	45	177

[a] σ is the standard deviation of the concentration distribution.
[b] Concentrations in (μg m^{-3}).

seasons have a very similar mass balance distribution. The OC mean concentrations of 15.8 and 5.3 μg m^{-3} in winter and summer, respectively constituted a fraction of (40 ± 16% winter; 35 ± 14% summer) of PM$_{2.5}$ in the metropolitan area of São Paulo. The BC mean concentration of 7.6–4.1 μg m^{-3} in winter and summertime, respectively represented 21 ± 4% in winter and 28 ± 10% in summer of PM$_{2.5}$ Considering that there is sufficient ammonia in the urban atmosphere we could assume that all sulfate could be in the form of ammonium sulfate ([NH$_4$]$_2$SO$_4$) (Andrade et al., 1994; Sweet and Gatz, 1998). The [NH$_4$]$_2$SO$_4$ was estimated by the sulfur concentration obtained by PIXE analyses assuming a conversion factor of 4.12. The ammonium sulfate mean concentrations was 6.2 and 5.1 μg m^{-3} estimated in winter and summertime periods representing 20 ± 10% in winter and 31 ± 11% in summer of PM$_{2.5}$. The crustal material was estimated by the sum of the oxides: Al $\times$ 1.89, Si $\times$ 2.14, Ca $\times$ 2.50, K $\times$ 1.20 and Fe $\times$ 1.43 and it added 3.6 and 1.0 μg m^{-3} representing 12 ± 2% in winter and 9 ± 2%, in summer of PM$_{2.5}$. The sum of these components adds up to 93 ± 18% in winter and 103 ± 20% in summer of the PM$_{2.5}$. Artaxo et al. (1999b) obtained for Santiago de Chile downtown an

ammonium sulfate estimative of 16% and crustal material of 4.8% of PM$_{2.5}$ that are a very low fraction compared to São Paulo city. Miranda et al. (1998) obtained higher fractions for ammonium sulfates, of 46–75% in Mexico City and crustal material of 6–13%. Chow et al. (1996) reported similar abundance for total carbon (organic + black carbon) in PM$_{2.5}$ (40–60%) in Central California. The same study reported the nitrate, sulfate and ammonium concentrations constituted 25–30% of the PM$_{2.5}$, and crustal material was estimated at 15–35% of the PM$_{2.5}$. Sweet and Gatz (1998) obtained that ammonium sulfate constituted 35–48% of the fine mass at Illinois and crustal material 6–12% of the PM$_{2.5}$. The coarse fraction of the particulate matter was estimated to be constituted by 30 ± 5% of crustal material, and 7 ± 3% ammonium sulfate. The carbonaceous fraction was not measured in the coarse fraction.

3.1. The quantitative source apportionment by absolute principal factor analysis

The absolute principal factor analysis was performed with the elemental data set of the fine and coarse particulate matter for the winter and summer periods.

Table 2
Descriptive statistics of the particulate matter and gases measured in summertime from 16 January to 6 March in 1998 in the São Paulo metropolitan area

PM$_{2.5}$ aerosol ($d_p < 2.5 \mu$m)				Coarse mode aerosol ($2.5 < d_p < 10 \mu$m)			
Specie	Mean (ng m^{-3})	σ^a (ng m^{-3})	Number of samples	Specie	Mean (ng m^{-3})	$\sigma^{(1)}$ (ng m^{-3})	Number of samples
PM$_{2.5}$[b]	15.0[b]	7.5[b]	48	CPM[b]	18.9[b]	10.0[b]	47
Black carbon[b]	4.1[b]	1.7[b]	48	—	—	—	—
Organic carbon[b]	5.3[b]	2.0[b]	26	—	—	—	—
Al	—	—	—	Al	513	279	47
Si	179	99	48	Si	903	465	47
P	—	—	—	P	22.1	9.2	47
S	1238	979	48	S	435	254	47
Cl	—	—	—	Cl	47	24	47
K	119	56	48	K	204	112	47
Ca	68	26	48	Ca	519	233	47
Ti	14.7	8.0	48	Ti	79	41	47
V	8.9	3.3	48	V	8.0	5.1	47
Cr	—	—	—	Cr	4.2	2.7	39
Mn	6.7	4.7	48	Mn	15.2	7.3	47
Fe	179	79	48	Fe	674	325	47
Ni	3.1	1.5	48	Ni	5.1	3.3	47
Cu	5.4	4.2	48	Cu	10.2	8.4	47
Zn	51	32	48	Zn	94	67	47
Br	—	—	—	Br	3.6	3.4	17
Sr	—	—	—	Sr	3.6	1.8	47
Zr	—	—	—	Zr	3.3	2.0	34
Pb	23	15	48	Pb	16	10	47

[a] Concentrations in (μg m^{-3}).
[b] σ is the standard deviation of the concentration distribution.

Elemental concentrations obtained through PIXE analysis are available for 20 elements, but only variables that were measured above the detection limit in all the samples were included in the analysis, to avoid problems with estimation of missing values. The BC and OC have a very strong correlation between each other, and only BC was included in the factor model because it is critical to the identification of the vehicle sources, in particular diesel emissions.

The factor-loading matrix after VARIMAX rotation for the fine fraction of particulate matter sampled during wintertime (142 samples) is shown in Table 3. The last column shows the values of the communalities, that express the amount of data variability that was explained by the 6 retained factors. The communalities are higher than 0.8 for all the variables, indicating the adequacy of the 6 factors solution, and the 6 factors explained 91% of the total variance of the data set. The first factor for the wintertime analysis shown in Table 3 is loaded with Al, Si, Ti, Ca and Fe, representing fine mode soil dust aerosol. The second factor is associated with the motor vehicles emissions, with high loadings for Cu and BC. The BC is associated with emissions of diesel vehicles (Puri et al., 1996), and Cu is associated with the ethanol fuel used in São Paulo that is mixed

with gasoline at a rate of 22% in volume. The fine mass has a significant loading in this traffic-related factor. The third factor has significant loadings for sulfur, the fine particle mass and potassium, representing mostly sulfate aerosol. The fourth factor has significant loadings for V and Ni, representing residual oil combustion. The fifth factor is loaded with Zn, Pb, S, Ni and Mn, representing industrial emissions, mostly non-ferrous smelters. The last factor is loaded with Ca, Mn and Fe and consists of a second soil dust component. In the wintertime analysis the soil dust appeared in two factors, probably because they are related to different atmospheric or resuspension process or different types of soil.

The factor analysis for the summertime fine mode aerosol samples is shown in Table 4. Five factors were retained, and they explain 91% of the data variability. Communalities are higher than 86% for all elements. The first factor is the fine mode soil dust component, with Ca, Si, Ti, Fe and K. The second factor is associated with Zn, Mn, Pb, Fe, Ni and S, representing an industry emissions component. The third factor has high loadings for sulfur and the fine mass concentration, representing sulfates. The fourth factor has high loadings for Cu and BC, representing the transport sector emissions. The fifth factor is loaded with V and

Table 3
VARIMAX rotated factor loading matrix for the elemental, $PM_{2.5}$ and black carbon concentrations of the fine particulate matter sampled in wintertime from 10 July to 10 September 1997 in São Paulo city[a]

Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communalities
	Soil dust 1	Motor vehicles	Sulfates	Oil combustion	Industry	Soil dust 2	
Al	0.94	0.11	0.12	—	—	—	0.92
Si	0.89	0.20	—	—	—	0.21	0.88
Ti	0.76	—	0.19	—		0.51	0.89
Cu	0.22	0.88	—	0.15	0.20	0.23	0.94
Bc	0.23	0.80	0.31	0.27	0.22	—	0.91
S	—	—	0.75	0.33	0.43	0.22	0.91
$PM_{2.5}$	0.24	0.47	0.70	0.28	0.29	0.21	0.97
K	0.43	0.29	0.68	0.33	—	0.15	0.87
V	—	0.29	0.29	0.86	0.16	—	0.94
Ni	—	0.18	0.25	0.81	0.43	—	0.93
Zn	—	0.35	0.22	0.33	0.80	—	0.92
Pb	—	0.56	0.36	0.35	0.60	—	0.93
Ca	0.58	0.12	0.17	—	—	0.67	0.83
Mn	0.23	0.17	0.33	0.27	0.55	0.58	0.90
Fe	0.52	0.45	0.23	0.21	0.16	0.56	0.91
Variance (%)	21.8	17.2	14.6	14.2	12.8	10.6	91.1

[a] Only factor loadings larger than 0.1 are shown.

Table 4
VARIMAX rotated factor loading matrix for the elemental, $PM_{2.5}$ and black carbon concentrations of the fine particulate matter sampled in summertime from 16 January to 6 March 1998 in São Paulo[a]

Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communalities
	Soil dust	Industry	Sulfates	Motor vehicle	Oil combustion	
Ca	0.89	—	—	—	0.27	0.87
Si	0.86	0.27	0.11	—	—	0.83
Ti	0.82	0.14	0.39	0.25	0.17	0.93
Fe	0.59	0.57	0.45	0.16	0.20	0.94
Zn	0.13	0.79	0.35	0.33	0.26	0.94
Mn	0.44	0.77	0.17	0.19	—	0.86
Pb	—	0.75	0.41	0.34	0.21	0.89
S	0.16	0.46	0.81	—	0.22	0.94
$PM_{2.5}$	0.36	0.36	0.71	0.40	0.25	0.99
K	0.48	0.32	0.51	0.35	0.42	0.89
Cu	—	0.39	—	0.84	0.20	0.90
Bc	0.16	0.15	0.38	0.83	0.12	0.90
V	0.26	—	0.15	0.18	0.92	0.97
Ni	0.23	0.47	0.32	0.17	0.72	0.93
Variance (%)	23.5	21.8	17.0	15.0	14.0	91.3

[a] Only factor loadings large than 0.1 are shown.

Ni, representing residual oil combustion. The factor structure obtained in both seasons had a very good agreement although they had been carried out in two different sites in the city and in different seasons.

In order to study the relationship between the aerosol sources identified by factor analysis and trace gas concentrations a correlation analysis was performed between the factor scores and the trace gas concentrations. Table 5 shows the correlation matrix between the factor scores and the corresponding data for CO, NO_2, SO_2, and OC concentrations. It can be noticed that the factor identified as motor vehicle is significantly

correlated with CO, NO_2 and the OC, which are mostly vehicles emissions. This confirms the identification of the source by the factor model. It also shows a statistically significant correlation of these trace gases with the soil dust source, indicating the important contribution of the traffic in the soil dust resuspension. OC also correlates with the soil dust factor, but the highest association is with the motor vehicle factor. The reason of the correlation of SO_2 with the second soil dust factor is not clear.

In order to quantify the relative importance of each identified aerosol source in the fine fraction, the absolute principal factor analysis was used to derive absolute elemental source profiles. These source profiles for the fine fraction are shown in Table 6 for the winter time analysis and in Table 7 for the summertime. The soil dust elemental source profile obtained in this study had a good agreement with the results obtained before by Andrade et al. (1994) in a similar study in São Paulo. The elemental profile is also similar to soil dust source profile results in other urban regions such as in California (Seinfeld and Pandis, 1998), and in Santiago de Chile (Artaxo et al., 1999b). The motor vehicle elemental source profile was similar to the profile obtained by Watson et al. (1994) that comprises an average of diesel-fueled and gasoline-fueled vehicle exhaust. The profile obtained by APFA in Santiago de Chile (Artaxo et al., 1999b) presented higher Pb concentrations due to the use of this constituent in the gasoline in the region of Santiago. The oil combustion factor presented some differences between São Paulo and Santiago source profile obtained by APFA, maybe because of the differences in the compositions of the fuel used in these cities. The elemental sources profiles obtained for São Paulo shows good agreement between the winter and summer analysis.

In terms of apportioning of the $PM_{2.5}$, the traffic source represented 28% and 24% of the fine aerosol for winter and summer, respectively. Resuspended soil dust accounted for 25% and 30% of $PM_{2.5}$. The oil combustion source represented 18% and 21%, sulfates explained 23% and 17% and finally industrial emissions contributed with 5% and 6% of $PM_{2.5}$. The model explained 97–99% of the fine mode mass concentration.

Table 5
Correlation coefficients between factor scores identified by the APFA procedure in wintertime and the concentrations of CO, NO_2 and SO_2 and organic carbon obtained by the carbon monitor in the same period[a]

Fine particulate sources	Gaseous species			Carbon monitor
	CO	NO_x	SO_2	Organic carbon
Soil dust 1	0.35	0.33	0.58	0.56
Motor vehicle	0.80	0.75	0.43	0.71
Sulfates	—	−0.24	—	−0.17
Oil combustion	—	—	—	—
Industry	—	—	—	—
Soil dust 2	—	—	0.35	—

[a] Only statistically significant (within 95% confidence interval) correlation coefficients are shown.

Table 6
Absolute aerosol source apportionment for the elemental, $PM_{2.5}$ and black carbon concentrations of the fine particulate matter sampled in wintertime from 10 July to 10 September 1997 in São Paulo[a]

($ng\,m^{-3}$)	Factor 1 Soil dust 1	Factor 2 Vehicle traffic	Factor 3 Sulfates	Factor 4 Oil combustion	Factor 5 Industry	Factor 6 Soil dust 2	Concentration Model/measured
$PM_{2.5}$[b]	5.9	8.5	7.0	5.6	1.5	1.6	1.01
Bc[b]	1.5	3.4	0.75	1.4	0.27	—	1.03
Al	378	40.7	21.5	—	5.7	−6.4	0.99
Si	372	69	—	36.0	5.5	25.4	1.01
S	—	86	557	520	162	140	1.03
K	139	70	102	87	—	12.2	0.99
Ca	85	15.8	11.1	—	—	30.4	1.03
Ti	24.7	—	2.5	—	−0.92	5.5	0.98
V	0.80	2.2	1.2	6.8	0.34	0.23	1.01
Mn	3.0	1.6	1.7	2.6	1.4	2.3	1.00
Fe	207	131	38.8	66.8	14.2	73	1.00
Ni	−0.21	0.53	0.42	2.6	0.38	0.08	1.00
Cu	3.8	11.1	—	2.0	0.74	1.2	1.02
Zn	—	39.8	14.3	41.3	27.4	3.5	1.00
Pb	−2.7	19.6	7.1	13.1	6.5	−0.73	0.98

[a] $PM_{2.5}$: fine mode particulate matter; BC: black carbon.
[b] Concentration in ($\mu g\,m^{-3}$).

Table 7
Absolute aerosol source apportionment for the elemental, $PM_{2.5}$ and black carbon concentrations of the fine particulate matter sampled in summertime from 16 January to 6 March 1998 in São Paulo[a]

($ng\,m^{-3}$)	Factor 1 Soil dust	Factor 2 Industry	Factor 3 Sulfates	Factor 4 Vehicles traffic	Factor 5 Oil combustion	Model/measured[b]
$PM_{2.5}$[c]	4.6	0.89	2.5	3.6	3.2	0.98
Bc[c]	0.89	0.10	0.34	1.9	0.75	0.96
Si	140	9.1	—	—	—	0.83
S	279	144	370	—	371	0.94
K	42.1	5.8	13.1	21.6	35.7	0.99
Ca	42.7	—	—	3.9	17.5	0.95
Ti	9.9	0.35	1.4	1.9	1.3	1.01
V	1.9	0.07	0.28	0.92	5.5	0.97
Mn	3.6	1.2	0.39	1.2	—	0.96
Fe	85.7	15.1	17.5	19.7	36.0	0.97
Ni	0.55	0.22	0.22	0.30	1.8	0.99
Cu	—	0.51	—	3.9	0.93	0.99
Zn	8.3	8.3	5.5	13.0	15.1	0.98
Pb	—	3.7	3.0	6.8	6.5	0.88

[a] $PM_{2.5}$: fine mode particulate matter; BC: black carbon.
[b] The last column shows the ratio of the modeled concentration with the actual measurements.
[c] Concentration in ($\mu g\,m^{-3}$).

The source apportionment for the coarse mode fraction of particulate matter sampled in winter (177 samples) and summer (47 samples), respectively was also calculated. Both analyses presented high values of communalities (>0.7) for all elements and explained 90% of the variance of the data set. In the coarse fraction analysis basically three aerosol sources were identified for the winter and summertime samples. Soil dust, industrial emissions and marine aerosol were the main aerosol sources. In the summertime analysis a second soil dust component was identified with an unusual high loading for P, and it is not clear the reason for the presence of P in this factor. The coarse mode industrial component has high loading for Ni, S, V, Zn and Pb. The last factor in both analyses is loaded with Cl with some association to Zn, Pb and Cu. The Cl in previous analyses was associated with Na indicating the marine aerosol origin. Occasionally the sea breeze reach São Paulo, which is located about 60 km from the coast (Andrade et al., 1994). The air mass from the ocean to the sampling site is transported over industrial regions, a fact that could explain the loadings of Pb, Mn, Zn and other elements in this marine aerosol factor.

The absolute principal factor analysis was also applied to the coarse mode of the particulate matter, with a calculation of the absolute source profiles. The coarse mode resuspended soil dust accounted for 75% and 78% of the coarse aerosol mass in winter and summer, respectively. Industrial emissions contributed to 14% and 16% respectively and sea salt accounted for 11% and 6% of the coarse aerosol fraction in winter and summer, respectively.

The factor scores of the coarse mode were subject to correlation analysis between the fine and coarse factor scores achieved from APCA in winter. The results showed a statistically significant (within 95% confidence interval) correlation coefficient (0.7) between the fine and coarse soil dust factors indicating the same and local source of both factors. Also a statistically significant correlation (0.5) between the fine motor vehicle factor with the coarse mode soil factor. This indicates the clear relationship of the transportation activities and the resuspension of the coarse mode soil dust. It can be noticed a very good agreement with the identification of the sources for the winter and summertime field campaigns, in spite of the campaigns had been carried out in different sites in the city. This indicates that there is a rather homogeneous aerosol composition and impact around the downtown area and that there is no significant change in the structure of the aerosol source between summer and wintertime.

4. Conclusions

A complex system of air pollution sources and meteorological conditions modulates the levels of air pollution of the large metropolitan area of São Paulo, Brazil. High levels of air pollutants were measured during the winter and summertime. The methodologies used (the aerosol sampling using SFU and measurements of elemental composition by PIXE), coupled with the real time measurements of PM_{10}, carbonaceous aerosol and trace gases (CO, NO_2, SO_2), was essential to

assist in the identifications and quantification of the main air pollution sources. It was possible to quantify the contribution of the motor vehicles that is an important source of air pollution in several Latin American cities such as São Paulo, Santiago and Mexico City. The motor vehicle emissions represented 28% and 24% of the $PM_{2.5}$ for winter and summer, respectively. Resuspended soil dust accounted for 25% and 30%, and this factor is also related to vehicle traffic. The oil combustion source represented 18% and 21%. Sulfates accounts for 23% and 17% and finally industrial emissions contributed with 5% and 6% of $PM_{2.5}$, for winter and summer, respectively. The resuspended soil dust accounted for a large fraction (75–78%) of the coarse mode aerosol mass. The set of tools used in this study identified the responsibility of the motor vehicles for the direct emission of several gases and particulate pollutants and for the resuspension of soil dust. The results of APFA for the winter and summertime field campaigns, pointed that there is no significant change in the structure of the aerosol sources for both periods. The main difference between winter and summer periods is in the absolute concentration of the particulate mass that is significantly higher during the winter, when the conditions for dispersion of the pollutants are frequently more unfavorable. The meteorological conditions presented significant responsibility in the process of accumulation or dispersion of pollutants during the day through the variability of the boundary layer height. The movements of large-scale synoptic systems also are an important component of the air pollution pattern over the São Paulo metropolitan area. The analyses of the particulate mass balance showed that the OC ($40 \pm 16\%$) represent a large fraction of the fine particulate matter, followed by BC ($21 \pm 4\%$), sulfates ($20 \pm 10\%$) and the soil component ($12 \pm 2\%$). The sampling campaigns carried out in the winter and summer periods resulted in similar aerosol source apportionments despite the fact that they were carried out in two different sampling sites. This fact indicates the similarity of the aerosol sources in the urban area in São Paulo, and the robust characteristic of the methodologies used in this study.

Acknowledgements

References

Andrade, M.F., Orsini, C., Maenhaut, W., 1994. Relation between aerosol sources and meteorological parameters for inhalable atmospheric particles in São Paulo city, Brazil. Atmospheric Environment 28 (14), 2307–2315.

Artaxo, P., Castanho, A.D.A., 1998. Aerosol concentrations and source apportionment in the urban area of São Paulo, Brazil. IAEA (International Atomic Energy Agency), TEC DOC series.

Artaxo, P., Orsini, C., 1987. PIXE and receptor models applied to remote aerosol source apportionment in Brazil. Nuclear Instruments and Methods in Physics Research B 22, 259–263.

Artaxo, P., Castro, W.E., Freitas, M., Longo, K.M., 1995. Receptor modeling of atmospheric aerosols in the urban area of São Paulo. In: Applied Research on Air Pollution Using Nuclear-Related Analytical Techniques. IAEA (International Atomic Energy Agency). Publication NAHRES-26, 5–1, pp. 5–11.

Artaxo, P., Castanho, A.D.A., Yamasoe, M.A., Martins, J.V., Longo, K.M., 1999a. Analysis of atmospheric aerosols by PIXE: the importance of real time and complementary measurements. Nuclear Instruments and Methods in Physics Research B 150, 312–321.

Artaxo, P., Oyola, P., Martinez, R., 1999b. Aerosol composition and source apportionment in Santiago de Chile. Nuclear Instruments and Methods in Physics Research B 150, 409–416.

Ayers, G.P., Keywood, M.D., Gras, J.L., 1999. Teom vs manual gravimetric methods for determination of $PM_{2.5}$ aerosol mass concentration in urban Australia. Atmospheric Environment (Technical Note) 33 (22), 3717–3721.

Campbell, J.L., 1995. Instrumentation, fundamentals, and quantification. In: Johansson, S.E., Campbell, J.L., Malmqvist, K.G. (Eds.), Particle Induced X-ray Emission Spectrometry. Wiley, New York, pp. 19–99.

CETESB, 1998. Relatório de Operação Inverno 1997. Report CETESB, São Paulo, in Portuguese. Available at www.cetesb.sp.gov.br.

Chow, J.C., Watson, J.G., Lu, Z., 1996. Descriptive analysis of $PM_{2.5}$ and PM_{10} at regionally representative locations during SJVAQS/AUSPEX. Atmospheric Environment 30 (12), 2079–2112.

Hansen, A.D.A., Rosen, H., Novakov, T., 1984. The aethalometer—an instrument for the real-time measurement of optical absorption by aerosol particles. Science of the Total Environment 36, 191–196.

Henry, R.C., 1991. Multivariate receptor models. In: Hopke, P.K. (Ed.), Receptor Modeling for Air Quality Management. Elsevier, Amsterdam, pp. 117–147.

Hopke, P.K., 1991. Receptor Modeling for Air Quality Management. Elsevier, Amsterdam.

Hopke, P.K., Xie, Y., Raunema, T., Biegalski, S., Landsberger, S., Maenhaut, W., Artaxo, P., Cohen, D., 1997. Character-

ization of the gent stacked filter unit PM_{10} sampler. Aerosol Science and Technology 27, 726–735.

John, W., Hering, S., Reischl, Sasaki, G., 1983. Characteristics of nuclepore filters with large pore size, II, filtration properties. Atmospheric Environment 17, 373–382.

Macchione, M., Oliveira, A.P., Gallafrio, C.T., Muchão, F.P., Obara, M.T., Guimarães, E.T., Artaxo, P., King, M., Lorenzi-Filho, G., Junqueira, V.C.B., Saldiva, P.H.N., 1999. Acute effects of inhalable particles on the frog palate mucociliary epithelium. Environmental Health Perspectives 107 (10), 829–833.

Meyer, M., Lijek, J., Ono, D., 1992. Continuous PM_{10} measurements in a wood smoke environment. In: Chow J.C., Ono, M. (Eds.), PM_{10} Standards and National Particulate Source Controls, Vol. 1. Air Waste Management Association, TR-22, pp. 24–38.

Miranda, J., Suárez, A.L., Gutiérrez, R.P., González, S., Lucio, O.G., Andrade, E., Morales, J.R., Sobarzo, M.J.A., 1998. A study of atmospheric aerosols from five sites in Mexico city using PIXE. Nuclear Instruments and Methods in Physics Research B 136–138, 970–974.

Orsini, C., Artaxo, P., Tabacniks, M., 1984. The São Paulo PIXE system and its use on a national monitoring air quality program. Nuclear Instruments and Methods in Physics Research 231, 462–465.

Orsini, C., Tabacniks, M., Artaxo, P., Andrade, M.F., Kerr, A.S., 1986. Characteristics of fine and coarse particles of natural and urban aerosols of Brazil. Atmospheric Environment 20, 2259–2269.

Puri, E.S.S., Hansson, H.C., Edner, H., 1996. Urban air pollution source apportionment using a combination of aerosol and gas monitoring techniques. Atmospheric Environment 30 (15), 2795–2809.

Reid, J.S., Hobbs, P.V., Liousse, C., Martins, J.V., Weiss, R.E., Eck, T.F., 1998. Comparison of techniques for measuring short-wave absorption and black carbon content of aerosol from biomass burning in Brazil. Journal of Geophysical Research 103 (D24), 32031–32040.

Rojas, C.M., Artaxo, P., Van Grieken, R., 1990. Aerosols in Santiago de Chile: a study using receptor modeling with X-ray fluorescence and single particle analysis. Atmospheric Environment 24B, 227–241.

Saldiva, P.H.N., Pope, C.A., Schwartz, J., Dockery, D.W., Lichtenfels, A.J., Salge, J.M., Barone, I., Bohm, G.M., 1995. Air pollution and mortality in elderly people: a time-series study in São Paulo, Brazil. Archives Environmental Health 50, 159–163.

Schwartz, J., 1994. Air pollution and daily mortality: a review and meta analysis. Environmental Research 64, 36–52.

Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics—from Air Pollution to Climate Change. New York, USA, Wiley.

Spektor, D., Hofmeister, V.A., Artaxo, P., Braga, J.A.P., Echalar, F., Nogueira, D.P., Hayes, G., Thurston, M., Lippmann, 1991. Effects of heavy industrial pollution on respiratory function in the children of Cubatão, Brazil: a preliminary report. Environmental Health Perspectives 94, 51–54.

Soutar, A., Watt, M., Cherrie, J.W., Seaton, A., 1999. Comparison between a personal PM_{10} sampling head and the tapered element oscillating microbalance (TEOM) system. Atmospheric Environment 33, 3373–4377.

Stull, R.B., 1991. An Introduction to Boundary Layer Meteorology. Kluwer Academic Publishers, Boston, pp. 2–26.

Sweet, C.W., Gatz, D.F., 1998. Short communication summary and analysis of available $PM_{2.5}$ measurements in Illinois. Atmospheric Environment 32 (6), 1129–1133.

Tabacniks, M., Orsini, C., Artaxo, P., 1987. PIXE analysis for air pollution source apportionment in urban areas of Brazil. Nuclear Instruments and Methods in Physics Research B 22, 315–318.

Thurston, G.D., Spengler, J.D., 1985. A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. Atmospheric Environment 19 (1), 9–25.

Watson, J.G., Chow, J.C., Lowenthal, D.H., Pritchett, L.C., Frazier, C.A., 1994. Differences in the carbon composition of source profiles for diesel and gasoline powered vehicles. Atmospheric Environment 28 (15), 2493–2505.