Water-Soluble Ions and Trace Metals in Airborne Particles Over Urban Areas of the State of São Paulo, Brazil: Influences of Local Sources and Long Range Transport

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Abstract The atmosphere over Brazilian cities is influenced by a variety of emissions sources. In this study, aerosol collection and back-trajectory analysis were used to determine the influence of local and remote sources. Aerosols were collected at three locations within the state of São Paulo: one megacity and two cities in which sugar cane burning in the surroundings is observed. We quantified the major water-soluble inorganic ions and trace metals. As expected, vehicle emissions influenced the atmosphere of the megacity heavily, and sugar cane burning influenced that of the other locations. During the period of this experiment the back-trajectory analysis revealed that air masses are transported into the state from the northeast of Brazil, where biomass burning occurs. Multivariate statistical analysis revealed that the two principal components account for 48.5% of the total data variance. We conclude that local sources have a strong impact on the concentrations of particulate matter and pollutants. Remote sources also contribute to the concentrations of aerosol pollutants.

Capsule: Brazil is the largest user of alternative fuels, like alcohol and natural gas, and is developing the implementation of bio-diesel for heavy duty fleet in a large scale. These different fuels can impact negatively the air quality in a way not yet understood. Data presented here is not only of local interest, but can supply information regarding the impact of different fuels, biomass burning and air transport in the atmospheric chemistry.

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1 Introduction

Airborne particles reduce visibility and diminish the intensity of the solar radiation reaching the surface of our planet. In addition, these particles influence the chemical characteristics of the atmospheric environment and have an effect on human health. Furthermore, these particles play an important role in regulating the natural water cycle. In clouds, water droplets and ice crystals form on these particles, which act as cloud condensation nuclei (Seinfeld and Pandis 1998).

Airborne particulate matter includes organic and inorganic compounds, both of which can be harmful to human health. These substances are released into the atmosphere anthropogenically during the combustion of fossil fuels and wood, as well as from industrial processes and during waste incineration. Natural sources of emission include volcanoes, erosion, forest fires, oceans and biogenic emissions (Allen et al. 2001). Studies of organic compounds in the atmosphere over Brazilian cities have confirmed the carcinogenic potential of such particulate matter (Sato et al. 1995). Trace metals in particulate matter have also been found to affect human health in urban cities worldwide (Carvalho-Oliveira et al. 2005). In various studies using extracts of particulate matter collected in urban centers, the mutagenic effects of such pollution have been demonstrated (Sorensen et al. 2003; Claxton et al. 2004). In addition, epidemiological studies have associated airborne particulate matter with impaired lung and heart function, as well as with higher mortality rates (Fang et al. 2000; Wilson et al. 2006).

The composition of aerosol particles in the atmosphere over Brazilian cities is unique, since it is strongly influenced by alcohol-fueled motor vehicle emissions and by emissions from a variety of other sources, including the burning of gasoline, diesel and biomass, as well as by industrial emissions (Vasconcellos et al. 2005). In the tropics, biogeochemical cycles of the trace elements can be influenced by emissions from biomass burning.

The city of São Paulo is the capital of the state bearing the same name, and the Metropolitan Area of São Paulo (MASP) is the largest industrialized region in Latin America. Currently, there are approximately 18 million people and 7.8 million vehicles in the area (CETESB 2005). The principal sources of pollutants are light- and heavy-duty vehicles, which are responsible for 40% of the total emission of particulate matter smaller than 10 μm in diameter (PM_{10}) into the atmosphere (Miranda et al. 2002). The main sources of fine aerosol particles (smaller than 2.5 μm) emitted in the urban area have been identified as resuspension of soil dust, industrial emissions, motor vehicles, oil combustion, garbage incineration and vegetation (Sanchez-Ccoyllo and Andrade 2002; Castanho and Artaxo 2001; Andrade et al. 1994). Concentrations of O_3, CO and PM_{10} have been shown to be influenced by sources in air masses transported from other locations, as well by local sources of pollution (Sanchez-Ccoyllo et al. 2006a). For example, in the state of São Paulo, which is the largest sugar cane producing region in the world, the burning of sugar cane fields results in the annual release of particles and gases into the atmosphere from May to November (Rocha et al. 2003). Recent studies have been conducted in sugar cane burning areas in order to determine the predominant ions in wet deposition (Lara et al. 2001) and in aerosols (Allen et al. 2004).

In the present study, aerosol samples were collected in a megacity and in two cities whose atmospheres are influenced by vehicular emission that is the most important source in the urban areas, sugar cane burning, industrial activities, and air-mass transport, analyzing the major water-soluble inorganic ions and trace metals identified therein.

This study, in which samples collected in 2003 were analyzed, is part of a larger project to quantify and qualify air pollutants in urban areas whose atmospheres are influenced by multiple emission sources. All samples were collected during winter when sugarcane burning, high vehicular emissions and air-mass transport result in deterioration of air quality. Sanchez-Ccoyllo et al. (2006a), show that, during the winter dry season, air-mass back trajectories in MASP originated from four quadrants: northeast (32%), southeast (12%), southwest (19%) and northwest (37%). They showed a transport of O_3 precursors and O_3 from the northeast region, which is associated with agricultural activities involving biomass burning. For particulate matter, the main contribution to particulate concentration seems to come from local sources.

2 Materials and Methods

2.1 Experimental

2.1.1 Characteristics of Sampling Sites

Samples were collected in the MASP, which features urban as well as industrial areas, and in two cities, also within the state of São Paulo. The urban and industrial site was at West region of the city (SPA). The other two sites represent areas where sugar cane is routinely burned at the countryside surrounding the cities, Araraquara (ARQ) and Piracicaba (PRB; Fig. 1). These three sampling sites were chosen in order to compare the pollutant concentrations at different locations and to investigate the transport of smoke arriving in SPA. Every year in the dry season, sugarcane burning and pollution events are observed in these sites (Allen et al. 2004; Rocha et al. 2003; Sanchez-Ccoyllo et al. 2006b). The agricultural burning in Central Brazil and in the São Paulo State occurs in the dry season (May to November) as shown in the Fig. 2 (Allen et al. 2004). In this figure is presented the number of total fires in July 2003 in São Paulo State calculated by Instituto Nacional de Pesquisas Espaciais (INPE) based on data from NOAA-12N.

The SPA collection site is at approximately 800 m above sea level. This is an area that is potentially impacted by various types of sources. It is located in a green area, within approximately 2 km of a major highway carrying relatively heavy traffic consisting of gasohol-, diesel-, and ethanol-fueled vehicles. The PM_{10} sampler (a HI-VOL sampler with inlet for PM_{10}) was placed in an open area on the roof of the Department of Atmospheric Sciences, located on the campus of the University of São Paulo, ~20 m above ground level.

The second collection site, which was located in the city of Araraquara and designated the ARQ site, is 300 km from the SPA. The city has a population of over 190 000 inhabitants and a vehicle fleet of 56,000 (52,000 light-duty vehicles, 3,000 heavy-duty vehicles and 1,000 buses). Large areas are dedicated to agriculture. At the ARQ site, samples were collected on the campus of São Paulo State University, which is in an urban area completely surrounded by sugar cane plantations. A high-volume PM_{10} sampler was located at a height of 4 m and at a distance of 50 m from a highway with heavy traffic. Samples were collected during the sugarcane burning period.

The third site, located in the city of Piracicaba and designated the PRB site, is an urban site and is 200 km from the SPA. The city has 300,000 inhabitants and a vehicle fleet of over 100,000 (97,000 light-duty vehicles, 1,200 heavy-duty vehicles and 1500 buses). The principal activities are agriculture (sugarcane, coffee, orange) and the presence of more than 5,000 industries (metallurgical and mechanical processes). Samples of total suspended particulate (TSP, particles smaller than 100 μm in diameter) were collected on the campus of the Luiz de Queiroz Advanced School of Agriculture. The sampler was positioned in an open area (1.4 m high) in which the influences of sugar cane burning were observed in the surroundings (~500 m).

2.1.2 Sampling Procedure

Filters were weighted gravimetrically (humidity <50%) before and after sampling. Samples were collected at the SPA, ARQ and PRB sites during the

Fig. 1 Sampling sites in the state of São Paulo part (**a**) and satellite image indicating the urban areas (*in pink*) and vegetated areas (*in green*; **b**)
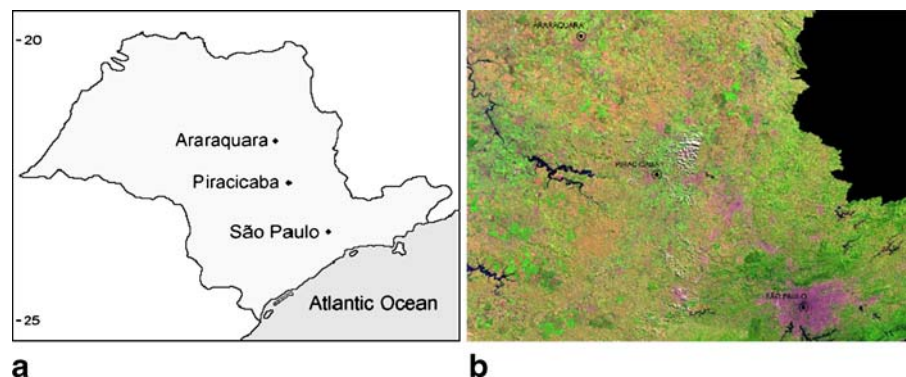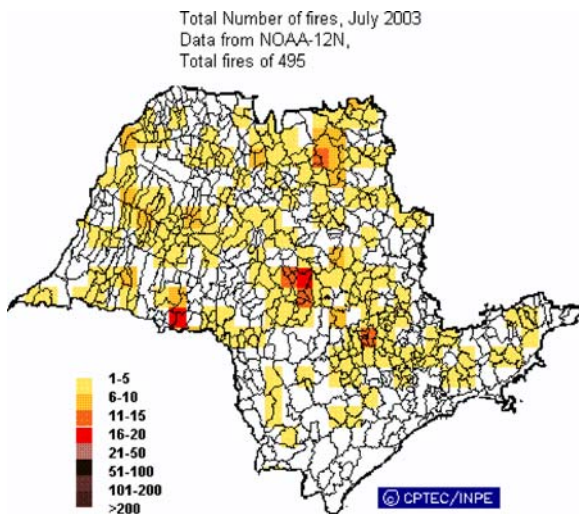
Fig. 2 Number of total fires in July 2003 in Brazil, calculated by Instituto Nacional de Pesquisas Espaciais (INPE) based on data from NOAA-12N

July 15–29, 2003 period (n=45 samples). At the PRB site, TSP samples were collected at 1.13 m^3/min. The samplers used to collect particles at the SPA and ARQ sites were each equipped with a size-selective inlet (Andersen) for the collection of particles smaller than 10 μm and a sensing device for measuring the flow rate through the filter. All samples were collected for 24-h periods on quartz fiber filters.

2.1.3 Analysis

After sampling, one-fourth of the filter was extracted in order to identify water-soluble ions. This was achieved by adding 15 ml of ultra pure deionized water to a conical flask containing the filter samples, ultrasonicating the samples at 60°C for 1 h, adding 5 ml of ultra pure deionized water and passing the solution an Autovial filter containing a polytetrafluoro-ethylene membrane with a pore size of 0.45 μm (Whatman plc, Middlesex, UK). The filter extracts were analyzed for Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, F$^-$, Cl$^-$, NO$_3^-$, PO$_4^{3-}$, SO$_4^{2-}$, NH$_4^+$ using the Ion Chromatography (IC) System (Metrohm AG, Herisau, Switzerland), which consists of a 750 Auto Sampler, a 733 IC Analytical Separation System, a 732 IC Detector, a 709 IC Pump and a 752 Pump Unit, and according to the protocol described by Sathrugnan and Balasubramanian (2005).

Another one-fourth of the filter was extracted in order to analyze metals using the MLS1200 MEGA Microwave Digestion System (Milestone, Monroe, CT, USA). The procedures described by Swami et al. (2001) were followed, although some modifications were made in order to achieve maximum recovery efficiencies.

A part of the filter was extracted and analyzed for total metals. The extraction solvents, made up of reagent-grade mixtures, 4 ml of nitric acid, 2 ml of hydrogen peroxide, and 0.2 ml of hydrofluoric acid, were added to the filter samples and processed in the microwave digestion systems for 5 min at 250 W, 5 min at 400 W, and 2 min at 600 W. The extracts were analyzed by use of the ICPMS. These filter extracts were analyzed in triplicate for Al, Co, Cr, Cu, Fe, Mn, Pb, Zn, Cd, Ni, Ti and V using the ELAN 6100 Inductive Coupled Plasma Mass Spectrometer (Perkin Elmer, Norwalk, CT, USA). Filter blanks were also analyzed for anions and metals, and the values were subtracted from the sample results. This methodology allows the total metal concentrations to be determined.

2.1.4 Meteorological and Air Quality Conditions

State of São Paulo presents a tropical climate, with the dry season occurring during the winter months, according to data from climatological stations provided by the National Institute of Meteorology (INMET). In the summer months (December through February), average monthly temperatures reach up to 23°C, compared with 16°C in the winter months (June through August). The rainy season typically begins in late November and ends in April, and the average annual precipitation is approximately 1,500 mm. The local circulation is driven by southeast and northeast winds, which are primarily associated with the Atlantic Ocean breeze. In winter, polar air masses often arrive accompanied by cold fronts that can intensify the circulation driven by the southeast wind. Prior to the arrival of the frontal systems, the wind blows from the northwest, bringing warmer, drier air from continental areas, which is characteristic of the air mass transport from these regions (Montero et al. 2001; Sanchez-Ccoyllo et al. 2006b).

No rain episodes were observed during the sampling period and all of the sampling days were typical winter days (average temperature, 18°C). During this period, thermal inversion episodes were recorded under sunny conditions. Meteorological data used in this study were as

follows: temporal variations in temperature; relative humidity; wind velocity; solar radiation; and precipitation volume. These data were provided by the Department of Atmospheric Sciences of the University of São Paulo.

During the sampling period, 96-h back trajectories were calculated (Sanchez-Ccoyllo et al. 2006a,b) for July 16 to July 31, showing the air masses that were transported from areas influenced by industrial (Minas Gerais and São Paulo States) and agricultural activities (Fig. 3). In Fig. 3 are shown the more frequent directions for the back-trajectories related to the four quadrants of wind (northeast, southeast, southwest and northwest). 43% of the trajectories are identified with northwest direction of the wind, 33% with wind coming from northeast direction, 14% with southwest and 9% with southeast. During this month occurred many biomass burning in the Central part of São Paulo State, resulted from accidental fires and human activities as already shown in Fig. 2. The air quality in MASP during this sampling period was characterized by average PM_{10} concentrations of $70 \pm 50 \ \mu g/m^3$.

2.1.5 Chemometrics Analysis

Principal component based methods can be used to reduce the number of variables of data sets, substituting them with a smaller number of factors or principal components that facilitate graphical analysis and help lead to a better understanding of the problem being investigated.

Principal components are obtained by diagonalizing the correlation matrix, Y^tY, of an experimental data matrix, Y. Y consists of n rows, one for each sample, and p columns, one for each water-soluble ion and trace metal with element values being the concentrations determined for these species. On diagonalizing Y^tY a small number of principal components are selected that are capable of describing a large portion of the data variance. Ideally the variance of the selected components describes signal whereas that of the discarded components pertain to noise. For the principal component model

$$Y = TP^t + \varepsilon$$

where the product of score and loading matrices, T and P^t, are expected to contain useful information and ε, the noise. The loading matrix contains elements that are correlation coefficients between the principal components and the original variables. A graph of these loading indicates which of the investigated variables are correlated with each other. The score matrix contains information about the samples and its graph can be used to determine similarities among samples based on their concentration values for all the elements investigated.
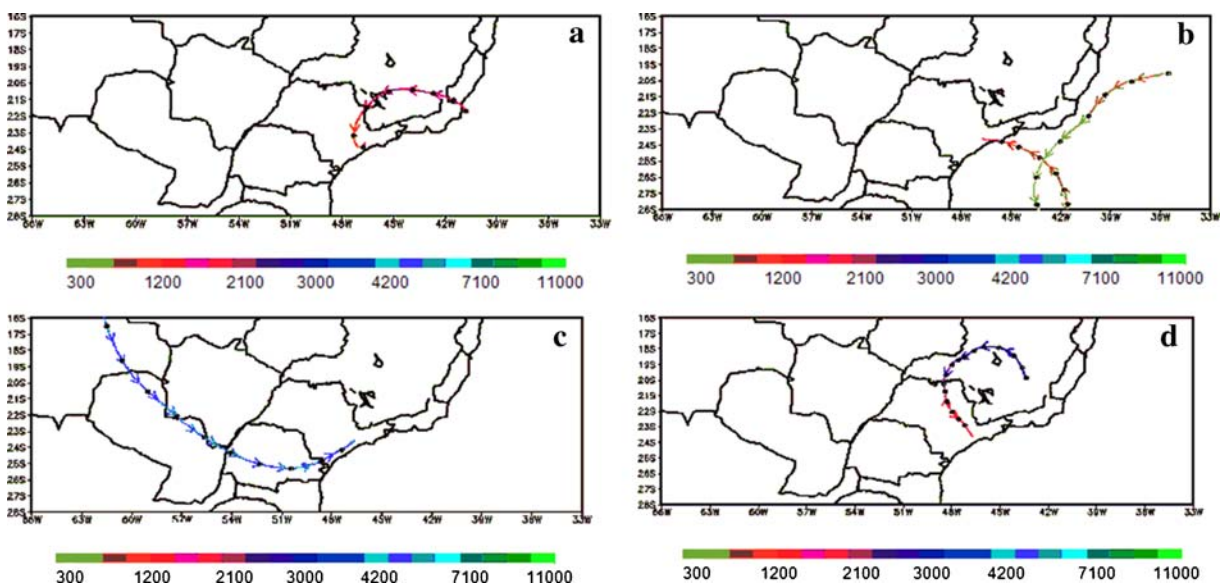

Fig. 3 Examples of Back trajectories calculated for the period, **a** from NE direction, **b** from SE direction, **c** from SW direction and **d** from NW direction

The principal component calculation was carried out using the Statistica for Windows software (Statistica 1999).

3 Results

Concentrations of water-soluble inorganic ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, NH_4^+) and trace metals (Al, Co, Cr, Cu, Fe, Mn, Pb, Zn, Cd, Ni, Ti, V) are presented in Table 1. We found that NO_2^- was present in only 6 samples (average concentration, 0.01 $\mu g\ m^{-3}$).

To determine the principal sources of the elements found in the aerosols, enrichment factors (EFs) were calculated related to the soil resuspension source. These calculations incorporate a reference metal, which is an indicator of a specific source. In this

case, the reference metal was Ti. This element appeared to be the best indicator of crustal material because other elements analyzed, for instance silicon and iron have another sources. The ratio of the concentration of each element to the concentration of Ti was calculated for the mean value, for each sample and for each of the three sites. The mean EF for each site is presented in Fig. 4 for the elements with dust soil origin.

It is important to point out that the quantification of the biomass contribution depends on the identification of a tracer. In this analysis excess-K was considered as a tracer for biomass burning.

Principal component analysis was helpful for understanding the emission sources. The score graph of these two principal components is shown in Fig. 5, and its corresponding loading graph is shown in Fig. 6.

Table 1 Average concentrations and standard deviations for water-soluble inorganic ions and trace metals

	SPA site (average ± SD)	ARQ site (average ± SD)	PRB site (average ± SD)
Water-soluble ions ($\mu g\ m^{-3}$)			
Na^+	0.55±0.13 (n=13)	0.34±0.08 (n=13)	0.43±0.12 (n=12)
K^+	0.72±0.36 (n=13)	1.59±0.43 (n=13)	1.23±0.61 (n=12)
Ca^{2+}	1.13±0.59 (n=13)	0.73±0.10 (n=13)	1.76±0.52 (n=12)
Mg^{2+}	0.12±0.04 (n=13)	0.26±0.04 (n=13)	0.51±0.19 (n=12)
F^-	0.05±0.03 (n=12)	0.07±0.02 (n=13)	0.11±0.05 (n=12)
Cl^-	1.21±0.77 (n=13)	0.20±0.09 (n=13)	0.48±0.11 (n=12)
NO_3^-	4.17±2.05 (n=13)	1.95±0.42 (n=13)	10.98±6.47 (n=12)
PO_4^{3-}	0.03±0.01 (n=13)	0.21±0.06 (n=13)	0.12±0.05 (n=12)
SO_4^{2-}	5.21±2.41 (n=13)	4.12±1.14 (n=13)	3.62±1.49 (n=12)
NH_4^+	1.35±1.08 (n=13)	0.80±0.47 (n=13)	0.80±0.57 (n=12)
Total	14.53	10.27	20.03
Trace metals ($\mu g\ m^{-3}$)			
Al	1.57±1.30 (n=12)	2.83±0.53 (n=13)	3.36±1.07 (n=12)
Co	0.01±0.01 (n=8)	n/a	0.01±0.01 (n=8)
Cr	0.01±0 (n=6)	0.01±0.01 (n=9)	n/a
Cu	0.08±0.15 (n=11)	0.14±0.07 (n=13)	0.27±0.11 (n=12)
Fe	1.86±1.10 (n=13)	2.83±0.62 (n=13)	3.66±1.05 (n=12)
Mn	0.03±0.02 (n=13)	0.04±0.01 (n=13)	0.07±0.02 (n=12)
Pb	0.01±0 (n=3)	0.01±0.01 (n=12)	0.01±0 (n=10)
Zn	0.24±0.09 (n=13)	0.06±0.01 (n=13)	0.04±0.03 (n=11)
Cd	0.01±0 (n=1)	0.01±0.02 (n=4)	0.01±0 (n=1)
Ni	0.01±0.01 (n=12)	0.03±0.02 (n=12)	0.01±0 (n=11)
Ti	0.57±0.08 (n=13)	0.24±0.08 (n=13)	0.64±0.14 (n=12)
V	0.01±0.01 (n=13)	0.03±0.02 (n=13)	0.01±0 (n=5)
Total	4.42	6.43	8.08

n/a Below detection limit

Fig. 4 Enrichment factors calculated for the sites studied
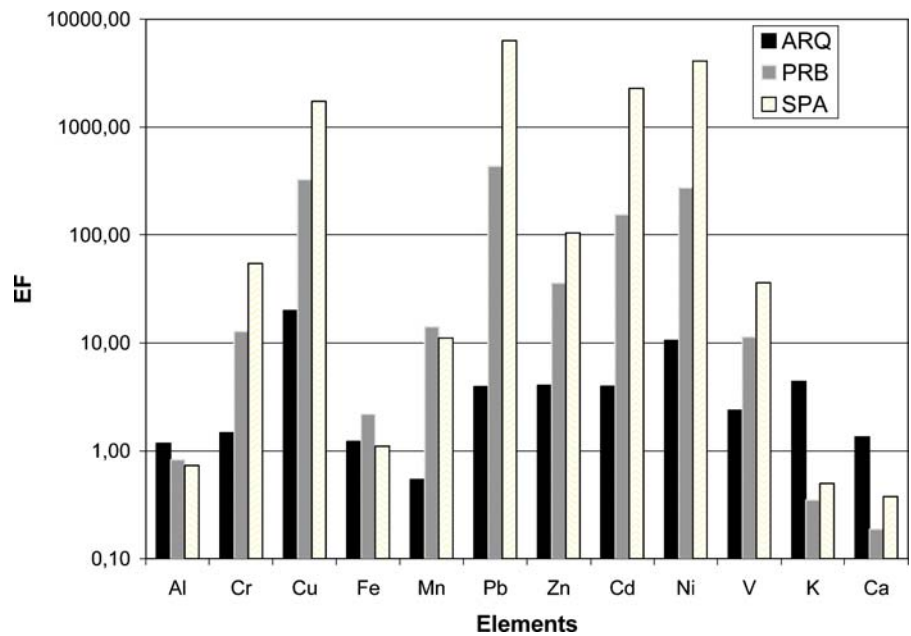
4 Discussions

The PM$_{10}$ samples collected at the SPA site presented higher concentrations of water-soluble ions (14.53 µg m^{-3}) than did those collected at the ARQ site (10.27 µg m^{-3}). In the SPA samples, SO$_4^{2-}$ (5.21 µg m^{-3}), NO$_3^-$ (4.17 µg m^{-3}) and NH$_4^+$ (1.35 µg m^{-3}) were predominant. In the ARQ samples, higher concentrations of SO$_4^{2-}$ (4.12 µg m^{-3}), NO$_3^-$ (1.95 µg m^{-3}) and K$^+$ (1.59 µg m^{-3}) were observed (Table 1).

In the samples collected at the PRB site, the overall average TSP soluble ion concentration was 20.03 µg m^{-3}, and the most abundant species were NO$_3^-$ (10.98 µg m^{-3}), SO$_4^{2-}$ (3.62 µg m^{-3}) and Ca^{2+} (1.76 µg m^{-3}). Of the total water-soluble ions, NO$_3^-$ accounted for 54%.

The PRB samples presented NH$_4^+$ at a concentration of 0.8 µgm^{-3} in TSP and ARA at a concentration of 0.8 µgm^{-3} in PM$_{10}$. Bacterial metabolism in wastes from domestic animals, wild animals and humans results in the production of NH$_3$, which is also emitted during combustion processes and the production of fertilizer (Blume 1992).

It has been also suggested that the major sources of NH$_3$ gas, which promotes the formation of NH$_4$NO$_3$,
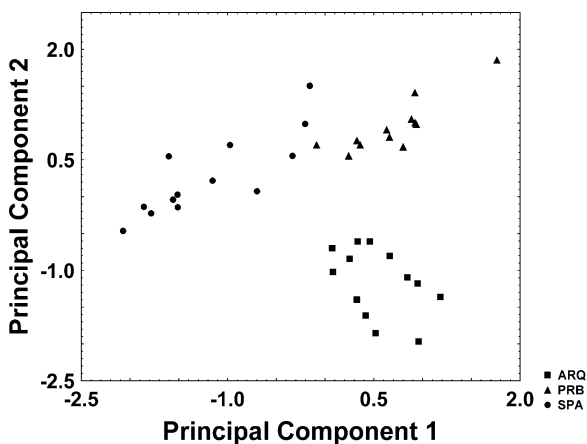

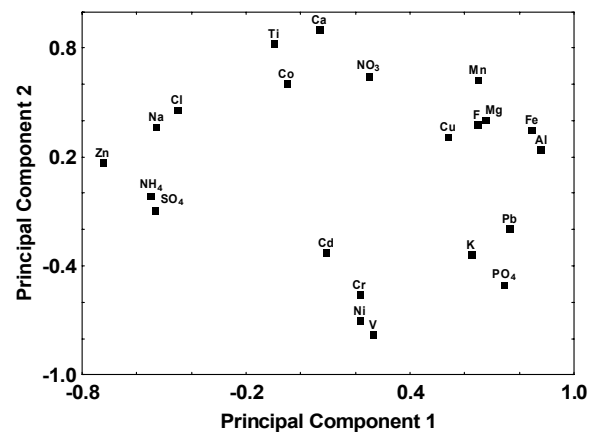**Fig. 5** Graph of the two principal components

Fig. 6 Factor loading graph of the two principal components

are local livestock and sugar cane burning (Jacobson 2002; Allen et al. 2004). The PRB site is within 500 m of a sugar cane field a dairy farm with herds of cattle.

Over 18 million people live in MASP, and not all domestic waste is sent to sewage treatment plants. This waste might be a factor contributing to the higher NH_4^+ level seen in the SPA samples (1.35 μg m^{-3}). Ammonium formation can be attributed to regional pollution due to human sewage. Other possibilities (sources of NH_3) include industrial and vehicular emissions, as well as long-range transported aerosol ammonium, but for São Paulo it is not available an estimative of the industrial and vehicular emission source of NH_3.

The abundance of SO_4^{2-} (5.21 μg m^{-3}) and NO_3^- (4.17 μg m^{-3}) at the SPA site confirms the strong influences of vehicle emissions. São Paulo government environmental agency states that vehicles are responsible for 97% of CO emissions, 97% of HC, 96% of NO_x, 40% of PM and 42% of SO_x emissions (CETESB 2006). Other studies based on receptor modeling concluded stated that the main source of pollutants in the Metropolitan Area of São Paulo is the vehicular emission (Castanho and Artaxo 2001; Ynoue and Andrade 2004).

Another ion found at a high concentration in the SPA samples was Cl$^-$ (1.21 μg m^{-3}). Sulfuric and nitric acids condensing on coarse and fine mode sea-spray drops can displace chloride to the gas phase. Sea-spray acidification is most severe in coastal regions near pollution sources. The SPA site is 80 km from the Atlantic Ocean, and the marine influence might contribute Cl$^-$ ions to its atmosphere. However, the high concentration of these ions suggests another local source. Burning of solid wastes and biomass is commonly observed on small properties and at landfills. Many people still use on-site disposal methods such as backyard burning to dispose of their domestic waste. The ARQ samples also presented an abundance of SO_4^{2-} (4.12 μg m^{-3}) and NO_3^- (1.95 μg m^{-3}). These secondary pollutants can also originate from the burning of sugar cane (Allen et al. 2001). In addition to biomass burning, other sources, such as vehicle emissions and industries, are considered.

The average K$^+$ concentration was 1.59 μg m^{-3} in ARQ samples and 1.23 μg m^{-3} in PRB samples. These two sites both suffer from the influences of sugar cane burning. It has been suggested that water-soluble

potassium is a tracer for wood smoke in receptor models (Simoneit 2002). Fresh wood smoke contains K$^+$, Ca^{2+}, Mg^{2+}, Na$^+$, NH_4^+, Cl$^-$, NO_3^- and SO_4^{2-} (Jacobson 2002). The results of various studies in the literature (Mouli et al. 2003; Graham et al. 2004; Jacobson 2002) indicate that there are other sources of potassium ion emissions: soil dust; sea spray; and fossil fuel combustion for energy and for industrial processes.

In the PRB samples, Ca^{2+}, Mg^{2+} and Cl$^-$ were found in abundance (1.76 μg m^{-3}, 0.51 μg m^{-3} and 0.48 μg m^{-3}, respectively). Soil has been considered the main source, although foundry activities can emit high quantities of Ca^{2+}, and biomass burning can produce Ca^{2+} and Cl$^-$ (Yamasoe et al. 2000). A previous study of rainwater composition at the PRB site demonstrated that industry has an influence on the concentrations of NO_3^- and SO_4^{2-} (Lara et al. 2001). At PRB site the concentrations of nitrate are seen to be much larger in PRB than in the other sites. Finlayson-Pitts and Pitts (2000) reports that higher concentrations of NO_3^- can be found in the coarse particles.

The ARQ samples presented higher trace metal total concentrations (6.43 μg m^{-3}) than did the SPA samples (4.42 μg m^{-3}). The PRB samples presented 8.08 μg m^{-3} of trace metal concentration in the TSP.

Aerosols from all three sites presented the same predominant soil compounds: Fe, Al and Ti. In the ARQ samples, the elements V and Ni were abundant and were strongly correlated ($R^2=0.89$). It is likely that these elements originated from the burning of diesel and residual oil (Miranda et al. 2002).

Correlations between some species are presented in the Table 2. A strong correlation ($R^2=0.9$) was found between Ca, Fe and Al in the SPA samples. These compounds exist as crustal elements. In SPA and PRB samples, a strong correlation ($R^2=0.9$) was also found for Pb and Mn, suggesting anthropogenic sources (metal processing industries) in addition to soil resuspension.

Table 2 Correlations between some species at the sites

Correlations/sites	SPA site	ARQ site	PRB site
V×Ni	0.50	0.73	–
Fe×Ti	0.61	0.89	0.89
Ti×Al	0.67	0.89	0.89
Fe×Al	0.97	0.96	0.98
Pb×Mn	0.90	0.25	0.90

Comparing our results with those of other studies in the literature, the metal concentrations found in our study were much lower than those found for samples collected in rural remote areas of Pakistan (Ghauri et al. 2001), particularly for Fe (3950 ng m^{-3}), Al (8043 ng m^{-3}), Ti (439 ng m^{-3}) and Zn (122 ng m^{-3}). In contrast, Chester et al. (2000), in their analysis of metal concentrations in samples collected at urban and rural sites in the UK, reported values that were considerably lower (Fe, 340 ng m^{-3}; Al, 317 ng m^{-3}; Zn, 36 ng m^{-3}; etc.) than those found in the present study. These discrepancies can be attributed to differences in soil composition and other factor s as grain size, humidity, precipitation and wind speed.

The elements that are primarily expected to be associated with soil resuspension (Al and Fe) presented enrichment factors near a value of 1 for all three sites. Elements such as Cu, Pb, Zn, Cd, Ni and V, which are associated with anthropogenic emissions, presented EF values higher than 1, and these values were even higher at the more urban site (SPA). Piracicaba also presented a high enrichment factor for these metals associated to metallurgical processes.

The trajectories are able to show that metal contribution at PRB site is from local origin as the ARQ site that is upwind from PRB didn't present higher EF for the anthropogenic metals.

The K$^+$ EF values followed a different pattern. In the ARQ samples, K$^+$ was not represented in the soil signature and was found at higher concentrations as a result of the sugar cane burning at that site.

The first principal component accounts for 29.5% of the data variance, distinguishing the ARQ and PRB samples from the SPA samples (Fig. 4). Compared to the SPA samples, the ARQ and PRB samples would be expected to have relatively high concentrations of those elements with positive loadings on the first principal components (K$^+$, PO$_4^{3-}$, Fe and Al) and lower concentrations of those with negative loadings (Zn, NH$_4^+$, SO$_4^{2-}$, Na$^+$ and Cl$^-$; Table 1).

The second principal component accounts for 20.3% of the total data variance and completely separates the PRB samples (high scores) from the ARQ samples (low scores). The SPA samples present intermediate scores for this component. The score and loading graphs show that the PRB samples would be expected to have relatively high concentrations of Mn, Ti, Ca^{2+} and NO$_3^-$ relative to the ARQ samples. The ARQ samples, however, would be expected to be relatively rich in Ni and V (Table 1) coming from diesel and residual oil burning.

This principal component analysis was complemented by a hierarchical cluster analysis, which confirmed the existence of the groupings of points shown in Fig. 6. This is important since the principal component graph in this figure explains only 68.8% of the total data variance and is therefore an approximate projection, whereas the cluster analysis uses exact interpoint distances.

The average concentrations of total particulate matter were comparable between the SPA and ARQ samples (68 µg m^{-3} vs. 76 µg m^{-3}). In a previous study involving the ARQ site, Magalhães et al. (2007) observed an average PM$_{10}$ concentration of 21 µ m^{-3} in the wet season (when there is no biomass burning), indicating that PM$_{10}$ are 3.6 times higher than the dry season concentrations observed in the present study.

Among the individual samples of particulate matter, total mass concentrations were higher in those collected at the ARQ site on July 20 (PM$_{10}$=144 µg m^{-3}), at the PRB site on July 21 and 22 (TSP=113 and 143 µg m^{-3}, respectively) and at the SPA site on the July 23 and 24 (PM$_{10}$=116 and 108 µg m^{-3}, respectively). The 96-h back trajectories calculated for July 20 showed air masses coming from Rio de Janeiro State into the SPA. Air masses arriving from the states of Rio de Janeiro and Minas Gerais had passed over areas in which industrial and agricultural activities influence the atmosphere. Within the state of São Paulo, air masses passed over industrial areas and sugar cane plantations before arriving in the SPA. At the ARQ site, the highest total concentrations of trace metals and PM$_{10}$ (9.0 µg m^{-3} and 144 µg m^{-3}, respectively) were found on July 20. The highest total metal concentration at the PRB and SPA sites were recorded on July 24 (11.80 and 8.81 µg m^{-3}, respectively). On July 21, when back trajectories showed air masses coming from the northwest of the state of São Paulo, crossing industrial and sugar cane burning areas before reaching the SPA, the highest ARQ sample metal concentration was recorded (9.02 µg m^{-3}).

5 Conclusions

The results obtained here have allowed tentative identification of some of the mechanisms that influence the concentrations of trace metals and water-soluble

ions in airborne particulate matter. Sugar cane burning and industrial activities are most strongly implicated, since the highest total concentrations of water-soluble ions and trace metals were found at the PRB site. In addition, the burning of solid waste and biomass on small properties and at landfills is probably responsible for the high Cl^- ion concentrations seen in the SPA site samples. Furthermore, the abundance of NO_3^-, SO_4^{2-} and K^+ at the ARQ site suggests that the atmosphere there was influenced by vehicular emissions and by emissions from biomass burning, and the presence of NO_3^-, SO_4^{2-} Fe, Al, Ca^{2+} and K^+ at the PRB site suggests that soil resuspension and sugar cane burning are strong influences. The strong correlation found between Pb and Mn suggests that the local atmosphere is influenced by industrial activities.

We conclude that local sources have a strong impact on the concentrations of particulate matter and pollutants. Remote sources also contribute to the concentrations of aerosol pollutants produced by fossil fuel combustion, soil resuspension and biomass burning.

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