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CHEMICAL COMPOSITION OF ATMOSPHERIC PARTICULATE MATTER SOLUBLE FRACTION AND METEOROLOGICAL VARIABLES IN SÃO PAULO STATE, BRAZIL

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ABSTRACT

The objective of this work was to characterize and compare the chemical composition of the PM_{10} soluble fraction in relation to meteorological variables such as wind direction and air masses backward trajectories. The PM_{10} was collected during winter of 1999 in two contrasting sites: the São Paulo city and the State Park of Serra do Mar (Cunha) inside the Atlantic Forest Reserve. The aqueous extracts of PM_{10} were analyzed by Ion Chromatography for major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}) and by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for trace elements (Al, Mn, Fe, Pb, Zn, etc.). In São Paulo, the dominant chemical species were SO_4^{2-}, NO_3^-, NH_4^+, Zn, Fe, Al, Ba, Cu, Pb, Mn and Ni while in Cunha, Na^+, K^+, Cl^-, SO_4^{2-}, Zn and Ni were dominant. The chemical composition related to the wind direction during sampling reflected short-range influence due to soil occupation and anthropic activities.
Keywords: atmospheric particulate matter, chemical composition, soluble fraction, backward air mass trajectories.

RESUMO: COMPOSIÇÃO QUÍMICA DA FRAÇÃO SOLÚVEL DO MATERIAL PARTICULADO ATMOSFÉRICO E VARIÁVEIS METEOROLÓGICAS NO ESTADO DE SÃO PAULO, BRASIL
Este trabalho teve como objetivo a caracterização e a comparação da composição química da fração solúvel do PM_{10}, com variáveis meteorológicas, tais como, direção do vento e trajetórias de massas de ar. O PM_{10} foi coletado durante o inverno de 1999 em dois locais contrastantes: na cidade de São Paulo e no Parque Estadual da Serra do Mar (Cunha), Reserva de Mata Atlântica. Os extratos aquosos do PM_{10} foram analisados por Cromatografia de Íons para quantificação dos íons maiores (Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}) e por ICP-MS para quantificação dos elementos traço (Al, Mn, Fe, Pb, Zn, etc.). As espécies químicas que predominaram foram SO_4^{2-}, NO_3^-, NH_4^+, Zn, Fe, Al, Ba, Cu, Pb, Mn e Ni em São Paulo, e Na^+, K^+, Cl^-, SO_4^{2-}, Zn e Ni em Cunha. A composição química relacionada com a direção do vento que prevaleceu durante a amostragem, refletiu um transporte de curta escala influenciado pela ocupação do solo e as atividades antrópicas.
Palavras-chave: material particulado atmosférico, composição química, fração solúvel, trajetórias de massas de ar.

1. INTRODUCTION

The São Paulo State is located in the Southeastern Region of Brazil and it has the largest Brazilian demographic density and economic development (agriculture, industry and services) which lead to a large alteration of its natural environment (CETESB, 2006). The Metropolitan Area of São Paulo (MASP) has 8051 km^2, and about 17 million inhabitants being the fourth larger urban agglomeration of the world. It includes approximately 2000 thousand industries and 7.4 millions of vehicles representing 40% of the Brazilian fleet therefore, being atmospheric pollution problems of great concern (CETESB, 2008).

The air quality in the MASP was ensured by the CETESB's (Company of Technology of Ambient Sanitation) through monitoring program implemented in the years 70´s. The CETESB reports indicate that the MASP atmosphere is prone to the accumulation of atmospheric particles, including fine and inhalable particles, due to its geographic localization, its climate and its economic activities. The air quality standard for PM_{10} (airborne particles having an aerodynamically diameter smaller than 10μm) in the MASP is 150 $\mu g.m^{-3}$ (24h average) and 50 $\mu g.m^{-3}$ (annual standard). Due to pollution control programs the annual average concentrations in the MASP decreased from 75 $\mu g.m^{-3}$ in 1982 to 50 $\mu g.m^{-3}$ in 1999 indicating that the control programs are efficient (CETESB, 2001).

Epidemiologic studies pointed out that days with unfavorable conditions for pollutant dispersion and thus high pollutant concentrations have serious effect on human health. The PM_{10} is a good indicator of the morbidity due to poor air quality, because it includes fine particles that can deeply penetrate into the lungs interfering into the pulmonary functions and therefore increasing the risks of respiratory diseases (Böhm et al., 1989; Saldiva et al., 1992, 1995; Souza et al., 1998; Braga et al., 2001). Epidemiologic studies concerning the children mortality carried out in São Paulo city (Lichtenfels et al., 1992; Lin et al., 1999) showed that the number of respiratory emergencies was mainly related to high level of inhalable particulate matter.

Elementary chemical composition of the total atmospheric aerosol is being widely investigated since the years 80 as well as its water-soluble chemicals composition since that represents a great portion of the total mass particles (Wang et al., 2003; Almeida et al., 2005). In addition, Adamson et al (1999) suggested that the soluble fraction of the atmospheric particulate matter is the most hazardous component concerning its toxicity potential because it is the one more efficiently adsorbed by the human body. According to Fernandez-Espinosa (2002) V, Ni, Co and Mn are metals present predominantly in the more soluble and exchanging fraction of aerosols. Voutsa and Samara (2002), in a similar study, highlighted that Cu, Ni, Mn and Zn are metal present in urban particulate matter in their more soluble forms.

Works conducted in the State of São Paulo (Tavares et al., 1983; Vieira et al., 1988; Forti et al., 1990) have determined the chemical composition of the aqueous extracts of particulate matter. These studies, however, mainly focused on the evaluation of the fraction susceptible of being removed by rainfall and transferred to the soil surface. There is, thus, a lack of knowledge regarding the water-soluble inhalable fraction.

The comparison of the atmospheric particulate concentrations and chemistry with meteorological parameters can lead to the determination of its local and regional sources and consequently, giving a more comprehensive data set. Air mass trajectory analyses have been used to help identify the origin and location of pollutant sources or precursors which are transported across long distances (Buchanan et al., 2002; Yaaqub et al., 1991; Cobourn and Hubbard, 1999; Stunder, 1996; Stohl et al., 1995). Some authors have studied the pattern of temporal and spatial associations between the particulate matter concentration and the meteorological parameters in São Paulo city among them Andrade et al. (1994) which identified sources of PM_{10} relating it with meteorological parameters such as large-scale synoptic systems showing that sea breeze influences on the São Paulo city atmosphere. The sea breeze intensity had a positive correlation with industrial sources and a negative one with soil sources. Castanho and Artaxo (2001) also related the variations of PM_{10} concentrations with synoptic systems of low or high pressure and showed that meteorological conditions presented a significant influence on the pollutant dispersion or accumulation processes through the boundary layer height variation. Only a few works, however, have associated the chemical composition of the particulate matter with the local and regional meteorological conditions. Sánchez-Ccoyllo and Andrade (2002) studied the behavior of total trace elements concentrations in the particulate matter with the prevailing meteorological synoptic condition and showed a decrease of pollutants concentrations during cold front condition and higher concentrations during South Atlantic Subtropical High and Polar High synoptic conditions. Recently, a similar association has also been done with O_3, CO and PM_{10} concentrations in the MASP by Sánchez-Ccoyllo et al. (2006).

In the present study, the variations of chemical compositions of the atmospheric particulate matter soluble fraction were related with the direction of local winds distributed by sectors, as well as with the air masses backward trajectories. For that, we compared two contrasting areas of the State of São Paulo: a strict urban area (São Paulo city) and a natural forest (State Park of Serra do Mar), considered as a poorly anthropized reference.

2. SAMPLING SITES

The sampling sites were selected due to their sampling facilities and atmospheric characteristics (Figure 1). The urban site was situated in the center of the MASP area, when the natural site was located in a relatively well-protected area of the Atlantic Forest.

2.1 Urban area

The urban sampling site of the MASP (23°32'52"S; 46°38'07"W) was located at the gardens of the University of São Paulo Medical School (herein named FM), close to the São Paulo City Center where the traffic is intense and 45 km apart from the seashore. According the *Köppen climate classification* São Paulo has a *humid subtropical climate*. The climate of Sao Paulo is mild throughout the year, with average maximum temperatures ranging between 27°C in February and 22°C in July and average minimum ranging between 21°C in February and 12°C in July (DCA-IAG-USP, 2009). The monthly mean temperatures are 24°C during summer (from December to February) and 16°C during winter (from June to August). The rainy season begins in October and ends in March; Rainfall is abundant, amounting to an annual average of 1,500 millimetres. It is especially common in the warmer months (from December to February), and somewhat scant between June and August.The dominant winds are S, SE and NW with mean speed of 2.5 m.s^{-1}. The two former are associated with cold fronts crossing the area during the coldest months or with marine breeze circulation during summer daily convection and winter , when the latter are mainly associated with continental breeze during summer nightly convection (Bicudo et al., 2002; Freitas, 2003).

In this region the altitude varies between 700 and 800 m above of sea level and most of the area is surrounded by topographical units with around 1100 m altitude. Its topographical complexity associated with the ocean proximity and the intense urbanization make the MASP climate strongly influenced by the differentiated heating conditions between day and night and between summer and winter. During the coldest months, this region is under anticyclonic influence (high pressure) but frequently crossed by low convective activity frontal systems. The anticyclonic periods are characterized by a clear sky, low wind speeds, and a large atmospheric stability due to intense descending air movements. Thermal inversion that is unfavorable to pollutant dispersion frequently occurs at this time of the year resulting in the most polluted days of the year.

2.2 Natural area

The Cunha-Indaiá Nucleo Reserve (23°14’05”S; 45°01’16”W) covers an area of 2,854 ha located in the Northern portion of the São Paulo State, 250 km from the MASP, within the Serra do Mar State Park (Figure 1). The mean altitude from sea level is 1050 m and the distance to the seashore is 25 km. The landscape consists of hills with steep slopes and narrow flat-bottomed valleys. Most of hill tops are covered with primary forest, the slopes with secondary forest on abandoned pastures or croplands and the alluvial valley bottom with bamboo forest. The whole area is within the Atlantic Forest protected biome (UNESCO, 1998). The climate is typically tropical humid of altitude, affected by the topography and the proximity of the ocean. The dominant winds come from Southeast sector blowing from the ocean toward the Serra do Mar producing high rainfall. The annual rainfall distribution varies between 2000 and 2500 mm and is characterized by a wet season from September until March and a dry season from April until August. Around 71% of the annual rainfall occurs during the wet period (spring/summer), giving a mean monthly rainfall higher than 400 mm. The mean monthly rainfall during the dry season (autumn/winter) is lower than 100 mm. During June, July or August the mean monthly rainfall can be as low as 50 mm. The mean annual temperature is 16.5°C and the mean annual relative humidity is 80% (Cicco et al., 1989). As for the urban site, the dominant winds are SE and NW, the former being associated with cold fronts or with marine breeze circulation and the latter are mainly associated with continental breeze.

3. MATERIALS AND METHODS

3.1 Sampling instrumentation and periods

The airborne particulate matter was collected in both sites during winter, in July 1999 with sampling intervals of 24 h. The sampling was not simultaneous for the two different sites because of the unique set of equipment. Sampling has been done in Cunha from July, 1st until 10th, 1999, totalizing 9 samples and in São Paulo city, from July 17th until 31st, 1999, totalizing 14 samples. Sampling was conducted using a dichotomic sampler with a Stacked Unit Filter (SFU) consisting of a polycarbonate filters holder separating the collected material in two size fractions and fully characterized by Hopke et al. (1997). For the study only PM_{10} (which includes coarse and fine fractions) was considered in order to obtain enough particulate mass for chemical analysis.

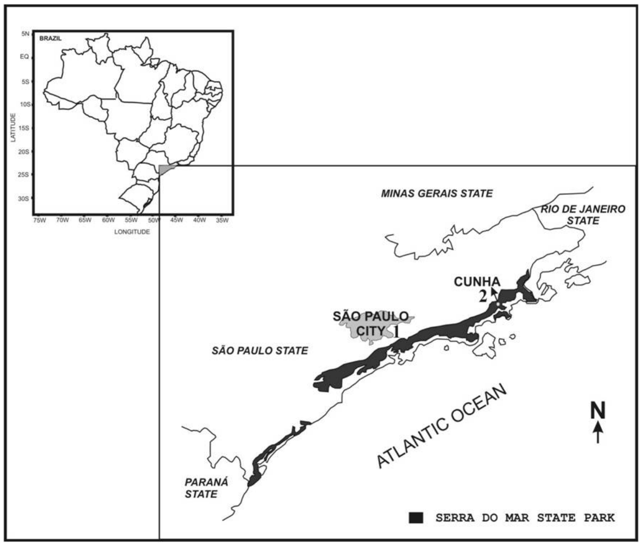

Figure 1 - Localization of the sampling sites.

3.2 Chemical composition analysis

The total amount of particles deposited on the filters was determined gravimetrically weighing the filter before and after sampling. The weighting were done using standard protocol which is to keep the charged filters in a dry box (dessicator) for 24 h and then proceed to weight them until samples reach constant weight. The aqueous solution extracts of particles was obtained by immersing each sampling filter in deionized water (conductivity 18 MΩ and pH= 5.6) submitted to ultrasound during thirty minutes to accelerate the solubilization (Forti and Moreira-Nordemann, 1989). It was used a volume of 50 ml of water for the Cunha samples and 75 ml for the São Paulo samples, due to the higher quantities of particles on the latter. The aqueous extracts were subsequently filtered with 0.22 µm Millipore membrane filters; such a pore size was chosen to eliminate microorganisms and fungi seeds. One aliquot was stored without preservation for anion analysis. A second aliquot of 25 ml was stored in polypropylene bottle for metals analysis after acidification with 1% in volume of supra-pure nitric acid. Finally, a third aliquot was stored in polypropylene bottle for cation analysis after acidification with sulphuric acid (Appelo and Postma, 1993). The extracts were stored at 4°C until the analysis took place.

The major dissolved ions (NH_4^+, Ca^{2+}, Na^{2+}, K^+, Mg^{2+}, Cl^-, SO_4^{2-} and NO_3^-) were analyzed by Liquid Ion Chromatography (DIONEX DX500). For the cations a Dionex-CS12 column was used with methanosulfonic acid as eluent. For the anions a Dionex-AS4A column was used with carbonate/bicarbonate as eluent. The precision of the analysis was better than 10% and the accuracy was checked against standards from the Centre for Ecology and Hydrology – CEH/U.K. Trebs et al. (2004) also give an overview of the most common sampling methods for the collection of inorganic gas and aerosol species and their chemical analytical methods. The trace elements (Al, Ti, V, Mn, Fe, Zn, Ni, Cu, Pb, Co, Cd, Ba) were determined by Induced Coupled Plasma with Mass Spectroscopy (ICP-MS) by the Actlabs laboratory in Canada.

3.3 Meteorological data analysis

The meteorological data concerning air temperature, relative humidity, precipitation and wind direction and speed during the sampling periods were obtained from the Meteorological Station of the Institute of Astronomy, Geophysics and Atmospheric Sciences of the São Paulo University for the urban sampling and from the Meteorological Station of the Forest Institute of São Paulo for the Cunha sampling.

During July 1999, five frontal systems reached the region (Climanálise, 1999) and nine thermal inversions occurrences have been detected at less than 200 m height in the RMSP (CETESB, 2001)

For the São Paulo urban site, the mean temperature was 17.4° C and the mean relative humidity was 80.6% during the sampling period and the total rainfall was 1.2 mm and the mean wind speed was 1.4 $m.s^{-1}$ coming predominantly from N-NE and SE directions.

For the Cunha site, the mean temperature was 13.5° C and the relative humidity was 94.5% for the sampling period and the total rainfall was 37 mm and the mean wind speed was 1.3 $m.s^{-1}$ coming predominantly from NE-ENE and SE-ESE sectors for the same period.

The backward trajectories of the air masses corresponding to the sampling days were computed using a 3-D cinematic trajectory model developed at the University of São Paulo herein named USPTM (Freitas et al., 1996; Freitas et al., 2000; Longo et al., 1999). The air mass back-trajectories were calculated using the zonal, meridional and vertical wind velocity. More details can be obtained in Sánchez-Ccoyllo et al. (2006).

For the integration of the trajectory the following equation was used:

$$\frac{dr}{dt} = v(r(t)) \qquad (1)$$

with t being time, r the position vector, and v the wind vector.

The iterative scheme of Pettersen (1940) was used with the following equations:

$$r_1 = r_0 + \Delta t v(r_0, t)$$
$$r_n = r_0 + \frac{\Delta t}{2}[v(r_0, t) + v(r_{n-1}, t + \Delta t) \qquad (2)$$

where Δt is the integration time step, x_0 is the initial position vector and x_1 and x_n are the position vectors at interactions 1 and n respectively.

The wind vector (v) for the trajectory calculations was numerically generated by the Regional Atmospheric Modeling System (RAMS) version 4.3 (Pielke et al., 1992; Cotton et al. 2003).

The output of USPTM model was the daily trajectory endpoints indicating the locations (Latitude-Longitude pairs) and height of the air parcel. The chosen arrival elevation was 100 m above the surface (900 m above sea level-ASL) which was below the mean inversion layer and is generally considered as the most representative of the air masses (Lin et al., 2001).

4. RESULTS AND DISCUSSION

4.1 Particulate matter concentration

PM_{10} concentrations showed a large variation between the two sampling sites. In the urban area, the mean concentration was 62.7 ± 26.3 $\mu g.m^{-3}$ with a maximum of 108 $\mu g.m^{-3}$ and a minimum of 31.6 $\mu g.m^{-3}$. In Cunha, the mean concentration was 41.2 ± 12.2 $\mu g.m^{-3}$ with a maximum of 62.1 $\mu g.m^{-3}$ and a minimum of 24.1 $\mu g.m^{-3}$. As expected, the higher concentrations found in the urban site contrast with the lower ones found in the natural area.

The variation of daily concentrations of particulate matter is presented in Figure 2. It can be noted that the mean value concentration was higher than the annual quality standard of 50 $\mu g.m^{-3}$ defined by the World Health Organization (WHO) in 64% of the sampling period in the urban area whereas in Cunha, it occurred only on two days during the sampling period. However, considering the national air quality standard for 24h, the particulate matter concentrations in both sites were under the limit value of 150 $\mu g.m^{-3}$. In Cunha, the highest particulate matter concentration occur on July, 3rd probably associated with particular atmospheric conditions since the temperature (18.5ºC) and wind speed (7.04 $m.s^{-1}$) were the highest of the period sampling, the relative humidity (69.7%) was the lowest of the period sampling and this day was also characterized by no precipitation.

In the São Paulo urban site, thermal inversion episodes occurred during most of the days that presented high particulate matter concentration (July, 19th, 23rd, 24th, 26th and 29th). During these days, it was observed rising temperatures with a maximum at July, 20th (21.4 °C). It has also been observed that higher PM concentrations occurred on Mondays (July, 19th and 26th) which traduce the traffic influence impact in this sampling site. During sampling periods, the rainy events were generally associated with a pre-frontal situation or the passage of a cold front.

4.2 Chemical composition of the particulate matter soluble fraction

The mean and standard deviation values for the concentrations of the chemical species analyzed in the soluble fraction of the particulate matter (PM_{10} fraction) are presented in the Table 1. In São Paulo the water-extractable predominant species were SO_4^{2-}, NO_3^-, NH_4^+ for major species and Zn, Fe, Al, Ba, Cu, Pb, Mn and Ni for trace metals. In Cunha, the predominant species were Na^+, K^+, Cl^-, SO_4^{2-}, and Zn and Ni, respectively.

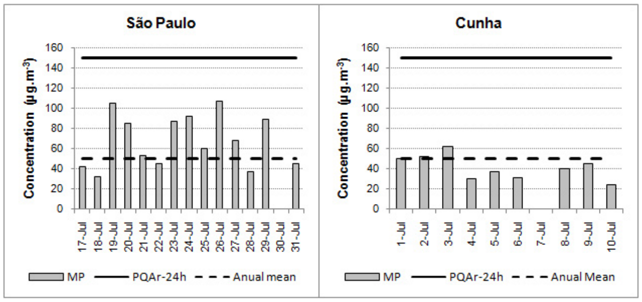

Figure 2 – Variation of daily particulate matter concentrations and comparison with the national Air Quality Standard PQAr-24h (150 $\mu g.m^{-3}$) and PQAr-24h (50 $\mu g.m^{-3}$) according to WHO Air Quality Guidelines.

For Cunha, the water-extractable species with the highest concentrations were Cl^-, K^+, Na^+ and SO_4^{2-} accounting for about 21%, 23%, 33% and 16%, respectively. The variation of daily concentrations for chemical species analyzed in the particulate matter aqueous extracts is showed in the graph of Figure 3. From this figure, it can be observed that higher concentrations of NH_4^+, K^+, Cl^-, SO_4^{2-}, Cu, Pb, Co and V occurred on July, 4th and 10th whereas highest concentrations of Ca^{2+} have been observed only on July, 4th and for Mg^{2+}, NO_3^-, Al, Mn, Ni, Ba and Sr on July, 10th. During the latests days (July, 9th and 10th) of period sampling, a group of tourists visited the site and stay for few days. Exhausts emissions promoted by heavy vehicles and vegetation burning may have affected the sampling results, which may be associated with higher concentrations of Zn and Ni for these days. On July, 3rd, most of the metals species also presented high concentrations, principally for Mn, Ni, Pb, Cd, Co, Ba, Rb and Sr. On this day, the wind velocity was the highest of the period sampling (2.87 $m.s^{-1}$) with gusts of 7.0 $m.s^{-1}$ and relative humidity was low (69.7%) suggesting that dust re-suspension contribution may be higher since most of these elements have terrigenous origin or are adsorbed on terrigeous particles or co-precipitated with Fe, Mn, Al oxides and hydroxides and clay minerals as evidenciated by Scanning Electron Microscopy in other study (Bourotte et al., 2006).

On July, 5th, precipitation event (29 mm) lowered concentrations for most of the analyzed species, except for Zn that presented the highest concentration on this day, which has not been explained. During more stable atmospheric conditions (Subtropical High and Polar High synoptic conditions), Na^+, K^+, Mg^{2+} and Cl^- concentrations were higher (July, 1st, 2nd, 6th, 9th and 10th).

Although the temporal variation of species concentrations is irregular, covarying pattern may suggest similar processes or sources for these species.

Most of Na^+ and Cl^-, and a fraction of the SO_4^{2-}, are coming from sea-salts aerosols transported by sea breeze. Typically, Na is used as a reference to determine the sea-salt component in aerosol particles since the water-soluble Na is assumed to originate solely from seawater, whereby the Cl to Na mass ratio in marine aerosol is 1.7 (Cauer, 1951; Chesselet et al., 1972). In Cunha, the Cl/Na ratio is 1.6, which indicates a marine contribution for Na and Cl due to the high frequency of sea breeze blowing landward during this season. Potassium can be attributed to continental sources as the K/Na ratio (1.13) also showed higher value than seawater K/Na ratio (0.036). According to Calloway et al. (1989), significant sources of

Table 1 - Chemical composition of PM10 aqueous extract collected in São Paulo and Cunha during winter 1999. (Std.: standard deviation).

	São Paulo		Cunha			São Paulo		Cunha	
Species	Mean	Std.	Mean	Std.	Species	Mean	Std.	Mean	Std.
	$\mu g.m^{-3}$					$ng.m^{-3}$			
Na^+	1.68	2.59	8.71	10.3	Al	54.3	41.1	39.6	99.7
NH_4^+	1.93	1.18	1.19	1.16	Ti	2.07	1.42	0.96	2.88
K^+	0.47	0.33	9.80	6.80	V	6.00	2.60	1.20	2.80
Mg^{2+}	0.15	0.09	0.08	0.07	Mn	18.9	10.4	7.70	7.20
Ca^{2+}	0.97	0.53	0.75	0.73	Fe	97.0	49.3	nd*	nd
Cl^-	0.98	0.76	13.6	8.55	Zn	118	95.6	221	282
NO_3^-	2.79	2.14	1.61	4.33	Ni	18.1	16.8	55.3	47.1
SO_4^{2-}	4.98	1.92	5.59	1.64	Cu	29.3	45.7	4.00	4.60
					Pb	16.6	8.8	13.2	5.80
					Co	1.10	0.95	0.20	0.30
					Cd	2.10	1.30	0.50	0.30
					Ba	46.9	19.3	6.90	10.6

*nd= not detected

terrestrial K^+ are biogenic, such as fertilizers, pollens and wood or biomass. After combustion processes, the K released in the atmosphere can associate with anions to form soluble salts. K can thus be used as a tracer of biomass burning (Echalar et al., 1995; Artaxo et al., 1990) and the association between K and Cl during biomass combustion was also showed by Sequeira and Lai (1998) and Allen et al. (2004). Biomass burning in fireplaces is also able to produce K, S or Zn-bearing particles (Artaxo et al., 1990; Echalar et al., 1995). Combustion processes produce small particles after gas-particle conversion, so that the associated K or S is able to be easily water-extracted.

In the urban area, the water-extractable concentrations were higher than in Cunha, except for Na^+, K^+, Cl^-, SO_4^{2-}, V, Fe and Cd. The water-extractable predominant species were SO_4^{2-}, NO_3^-, NH_4^+ for major species accounting for about 38%, 19% and 14% of the total water soluble mass, respectively. Known sources of Na and Cl in urban atmosphere are sea salt (Thurston and Spengler, 1985), crustal aerosols and motor vehicle emissions, the latter for Cl only (Ondov et al., 1982; Kitto, 1993). The Cl/Na mass ratio is 0.58 in the urban area, lower than in Cunha, denoting a lower contribution from marine sources for the urban area. The lower values for Na and Cl also reflect different losses during transport due to differences in atmospheric conditions. The lower value for K is due to a smaller vegetation production in the urban area. However, although some combustion processes can be detected locally, transport processes from regions where biomass burning is a common practice have to be considered when looking for the K sources in the urban area (Allen et al., 2004; Freitas et al., 2005). Beyond that, according to Ooki et al. (2002), K may act as a tracer of anthropic sodium. The K/Na ratio (0.28) is higher than the sea water ratio, which reinforces the hypothesis that a significant part of K is of anthropic origin. According to Kasahara et al. (1990), K is an indicator of waste incinerators in the urban atmosphere and in a study carried on waste incinerators emissions of Philadelphia, Mamane (1988) showed that NaCl and KCl were the predominant compounds. Part of K, Mg and Ca can also have a common origin which is the re-suspension of soil dust particles as it has been previously reported in studies about the chemical composition of rainwater in the city of São Paulo (Forti et al., 1990). Regarding Mg, the Mg/Na mean ratio in Cunha and in São Paulo city was lower than sea water Mg/Na ratio (0.12), indicating that a significant part of Mg comes from local terrestrial sources. Ca also showed higher values than the reference seawater value for both the study areas indicating sources other than marine. Most of the water-extractable trace metals had concentrations in the urban area more than 2 or 3 times higher than in Cunha. Ba and Pb are typically produced by anthropogenic activities such as motor vehicle emissions (Ondov et al., 1982; Johnson, 1988). Relevant sources of Mn, Zn, Cd, Cu, Co and Cr are industrial activities (Kowalczyk et al., 1982; Mészáros et al., 1997). In the urban area, Andrade et al. (1994) associated Mn, Zn and Pb with foundries and metal processing industries and Ni with residual oil burning and diesel fuel combustion. Metallic particles as produced from foundries, however, are poorly soluble. The water-extractable concentrations here observed were more likely to be related to non-metallic species adsorbed on particles.

The variation of daily concentrations for chemical species analyzed in the particulate matter aqueous extracts is showed in the graph of Figure 4.

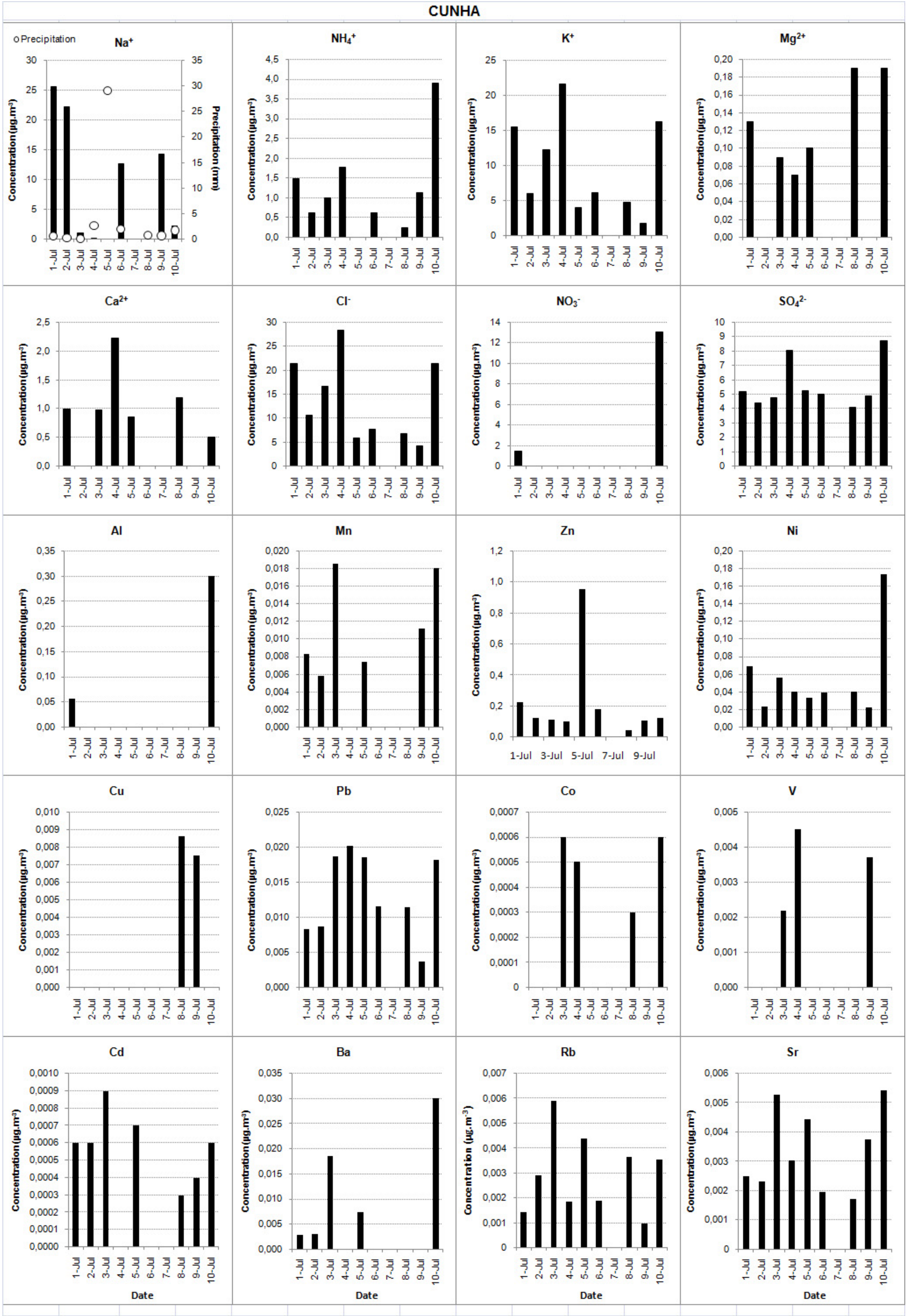

Figure 3 - Variation of daily concentrations of chemical species analyzed in aqueous extracts of particulate matter collected in Cunha area.

Figure 4 – Variation of daily concentrations of chemical species analyzed in aqueous extracts of particulate matter collected in São Paulo area.

From this figure it can be observed that for most of the chemical species, the highest concentrations occurred during July 19th, 23rd, 24th, 26th and 29th. Thermal inversion epidodes have been registered during these days. Due to the atmospheric stability promoted by synoptic situations of low wind velocities and relative humidity, the gas-particle conversion processes may be accentuated and affect principally sulfate, ammonium and nitrate and most of metals species. However, the lowest concentrations for most of the analyzed chemical species were observed during rainfall events, higher wind velocity periods, higher relative humidity and frontal system occurrence, observed on July, 18th, 20th to 22nd, 31st.

For both the study areas, sulfate is one of the dominant specie in the particulate fraction. The strong correlation between NH_4^+ and SO_4^{2-} (r=0.85 in Cunha and r= 0.87 in the urban area) reinforces that these species have a secondary origin due to the atmospheric gas-to-particle conversion processes. As it is highlighted by Hazi et al. (2003), the oxidation of SO_2 into sulfuric acid and sulfate salts through gas/particle phase oxidation is a rapid process under high relative humidity conditions and in the presence of some metals. Sulfuric acid can further react with ambient ammonia (NH_3) to produce NH_4HSO_4 and $(NH_4)_2SO_4$. Since SO_2 and NO_x are precursors to H_2SO_4 and HNO_3, respectively, both SO_4^{2-} and NO_3^- concentrations should have similar pattern as it is illustrated by the strong correlation between SO_4^{2-} and NO_3^- in São Paulo (r=0.77). Anthropic sources such as vehicular emissions, fossil fuel combustion and industrial activities are the main responsible sources for sulfur emissions in the urban atmosphere. Particulate nitrate originates from nitrous oxides conversion in nitric acid which can react with sodium chloride or ammonium chloride (Clase and Gysels, 1998; Harrison et al., 2000). High concentrations of NH_4^+ may be also due to a lesser thermal volatilization ratio of ammonium chloride and nitrate chloride and a higher frequency of atmospheric calm conditions during winter (Wang and Shooter, 2001).

The temporal variation of chemical species concentrations is affected by factors such as wind direction, precipitation frequency, changes in source emissions intensity and the residence time of particulate matter that depend on particle size. In order to appreciate the daily concentration species variation, meteorological factors such as prevailing wind direction and backward trajectories have been considered.

4.3 Meteorology influence on chemical composition

The atmospheric particulate matter concentrations and its chemical composition may depend upon the wind dynamic of the studied area. The mean concentrations values give little information about the contribution of the diverse emission sources and transport trajectories. It is more relevant to look for the relations between the concentrations and the wind prevailing direction. Similarities in concentration patterns of given chemical specie can be attributed to a common emission source or a common factor such as the local meteorology.

The backward trajectories calculated for each sampling day are given in Figure 5. For Cunha (Figure 5a), 100% of air masses originated from the ocean. For São Paulo city (Figure 5b), around 40% of air mass trajectories had a continental origin (Freitas et al., 1996) and 60% originated from the ocean. However, trajectories originated from the ocean were closer to the coast for São Paulo city than for Cunha. The chemical composition of the particulate matter reflected these differences since, as already mentioned, the prevailing species in Cunha were Na^+, K^+, Cl^- and SO_4^{2-}, for major ions, and NO_3^-, SO_4^{2-} in São Paulo with lower concentrations of Na^+ and NH_4^+. Moreover, the more significant contribution of trace metals in São Paulo city than in Cunha reflected the continental origin component of the air masses during the sampling period.

The prevailing winds in Cunha were from SE and NE sectors, representing 25% of the total sampling period. In São Paulo city, the prevailing winds of SE and NE sectors represented about 14% of the sampling period. The mean concentrations of PM_{10} and chemical species for the two sampling sites as a function of the wind prevailing direction are presented in the wind roses of Figures 6 and 7, for major ions and trace metals, respectively.

The wind roses were based on hourly wind direction mean according to the method of Harrison and Williams (1982). The mean concentration was calculated from the following equation:

$$C_i^d = \{(S c_i h_i^d) / (S h_i^d)\} \qquad (3)$$

where C_i^d is the mean chemical specie´s concentration during the sampling period i for wind in sector d, c_i is the chemical specie´s concentration obtained during the sampling period i and h_i^d is the number of hours during the sampling period i for which wind was in the sector d.

For the particulate matter collected in Cunha, although the mean concentrations did not presented a well defined prevailing direction, it can be observed that PM_{10} concentrations were slightly higher for NE and ESE wind sectors. In São Paulo city, higher concentrations were observed during low wind days, which suggest that the influence of local source emissions is more intense than transport once they are associated with thermal inversions and reduction of vertical diffusion. High concentrations were also observed for winds in the first quadrant (N-E), which indicates a transport from these directions during the sampling period.

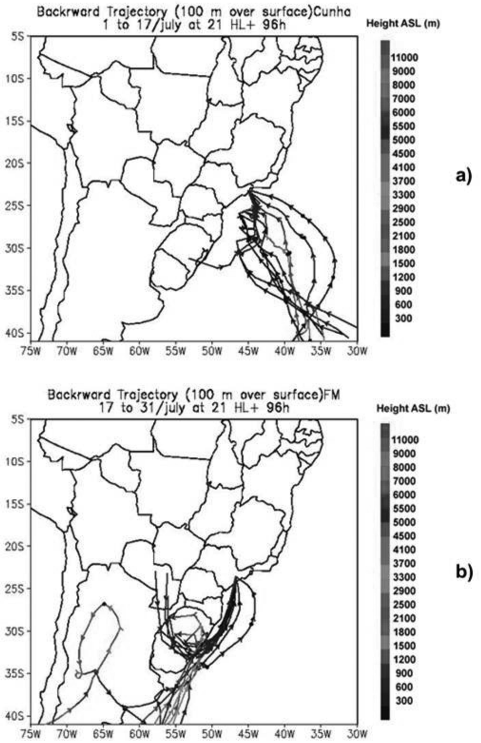

Figure 5 - Calculated backward air mass trajectories arriving in Cunha (a) and São Paulo (b) sampling sites at 900 m above sea level for the winter 1999 sampling period. The vertical scale indicates the height above sea level in meters.

The influence of wind direction upon a chemical specie concentration depends on the chemical specie for Cunha. There is a clear prevailing direction in ESE sector for Cl^-, Na^+, K^+ and NO_3^-. It was not observed a clear prevailing wind direction for SO_4^{2-} and NH_4^+ however, the concentrations were slightly higher for southeastern winds. For winds in E and ESE sectors the Mg^{2+} concentrations were higher and Ca^{2+} presented higher concentrations for winds in E-SE sector.

Concerning the trace metals it has been observed a clear prevailing direction for Ti and Mn suggesting a common source for these elements in the NE sector and that the sources for Zn, Pb and V are likely in the SW, WSW and SE sectors, respectively. For Co and Ba no prevailing direction was observed. The sectors in E, WSW and NE, and ESSE presented higher concentrations for Cu, Cd and Ni, respectively.

Regarding the MASP the comparison between the wind direction and chemical concentrations indicates that it is possible to associate the chemical species concentrations with a prevailing wind direction. Na^+ showed higher concentrations during low wind day's conditions and for winds in SSE sector, which can be related to incoming sea breeze and Mg^{2+} and Ca^{2+} had higher concentrations during low wind days and for winds in ENE sector. A clear prevailing wind direction has been observed for K^+ (NNE), Cl^- (ENE), SO_4^{2-} (E, ENE), NO_3^- (E, NNE) and NH_4^+ (E, NNE), which suggests a dominant source and perhaps a common emission source for these elements. Most of the considered trace metals such as Mn, Ni, Pb, Co, Cd, Ba and Cu, showed higher concentrations during low wind days, suggesting a higher contribution of local emission sources than of transport for these elements. High concentrations were also underlined for all elements in the first quadrant, between N and E sectors: NE direction for Ti, Mn, Ni, Co and Cd, NNE direction for V, Fe, Cu, ENE direction for Ba and E direction for Al, Zn and Pb. This suggests that a prevailing and common emission source in this direction may also exist. A high number of industries are localized in the northeastern region of the MASP, which can be associated with an anthropic origin for these elements. Andrade et al. (1994) have shown a correlation between industrial sources and winds in NE sector as well as for winds in SE sector (sea breeze). Sources associated with combustion processes and soil dusts re-suspension has shown no correlation with sea breeze. Transport associated with agricultural activities involving biomass burning from the

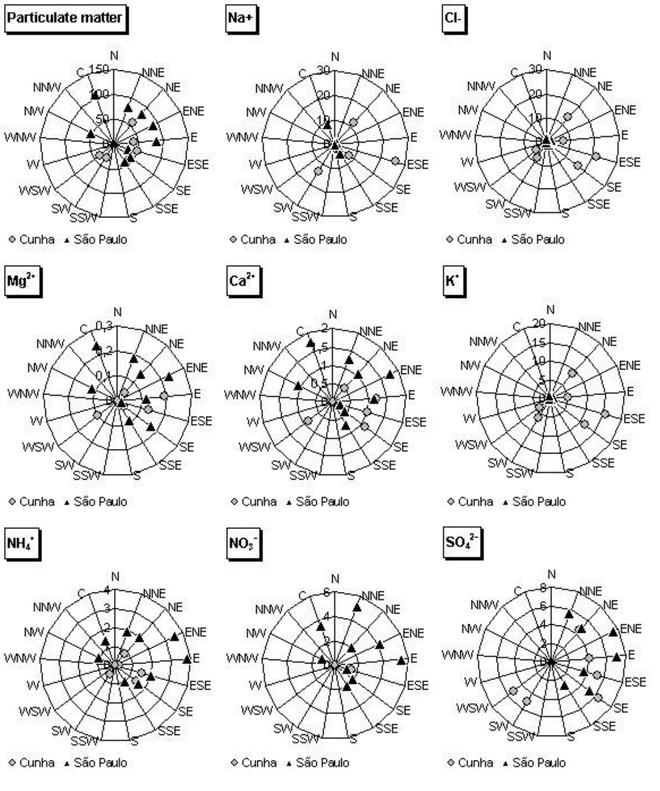

Figure 6 - Mean concentrations of atmospheric PM_{10} particulate matter ($\mu g.m^{-3}$), and Na^+, Cl^-, Mg^{2+}, K^+, Ca^{2+}, NH_4^+, NO_3^- and SO_4^{2-} species (in $\mu g.m^{-3}$), determined in aqueous extracts of samples collected in Cunha and São Paulo sampling sites, during winter 1999, as a function of prevailing wind direction.

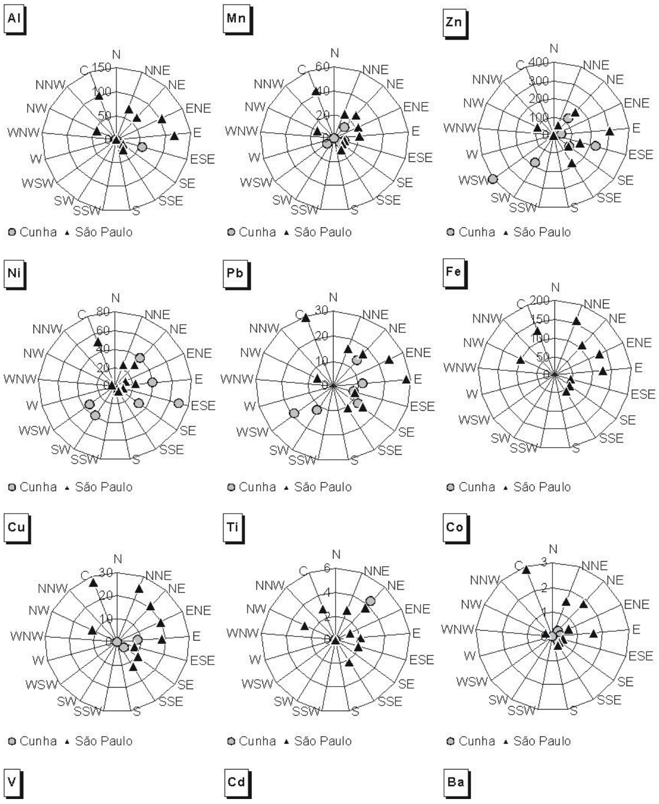

Figure 7 - Mean concentrations of trace metals (in ng.m^{-3}) determined in aqueous extracts of particulate matter collected in Cunha and São Paulo sampling sites, during winter 1999, as a function of prevailing wind direction.

northeast region of São Paulo State to the MASP has also been verified by Sánchez-Ccoyllo et al. (2006).

5. CONCLUSION

The chemical composition of the soluble fraction of the PM$_{10}$ was associated with air mass backward trajectories during sampling period and for each sampling site. The results reflect a distinct origin for air masses (ocean or continental origin) as well as an association between the mean concentrations of chemical species and wind direction which also showed that the wind direction influence on the chemical composition depends upon the studied area. Some chemical species were specific for continental (K^+, Ca^{2+}, NH_4^+) and marine (Na^+, Cl^-) air masses as well as tracers of anthropic activity (Co, Cu, Cd, Pb, Fe, V). Other originated both from natural and anthropic sources (SO_4^{2-}, NO_3^-, NH_4^+, Mg^{2+}, Al, Fe, Ti). The meteorological conditions associated with high concentrations of particulate matter and chemical species in the soluble fraction, thus susceptible to be hazardous for health, were the low wind days and the NNE to E prevailing wind directions. However, atmospheric wet deposition that promotes the transfer of pollutants must be also evaluated since it has significant consequences for local, as well as global modeling studies (Gonçalves et al., 2000).

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