MORPHOLOGY AND SOLUTES CONTENT OF ATMOSPHERIC PARTICLES IN AN URBAN AND A NATURAL AREA OF SÃO PAULO STATE, BRAZIL

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Abstract. The objectives of this work were to characterize and compare the chemical composition of the water-soluble fraction of the PM_{10} particles (Dp $< 10\,\mu$m) in two sites: one inside the Metropolitan Area of São Paulo (MASP) and another, 250 km apart, inside the State Park of Serra do Mar (CUNHA) part of the Atlantic Forest Reserve, both located in São Paulo State, Brazil. The atmospheric particles were collected during dry and wet season. The morphologic parameters of the particles were characterized for the different size fractions of the collected material. In the aqueous extract of the particulate fine fraction the major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, NH_4^+, SO_4^{2-}) and trace elements (Al, Mn, Fe, Pb, Cd, Zn, Ti, Ni, Cu, Co, Ba) were determined. The morphological characteristics of the particles collected within the MASP are typical of polluted environment while in CUNHA there is no evidence of this type of contribution. Regarding the solute concentrations it was observed that the most abundant major ions and trace elements were K^+, Ca^{2+}, Na^+, Cl^- and Pb for CUNHA and NO_3^-, SO_4^{2-}, NH_4^+ and Mn, Ni, Pb, Co, Cd and Ba for MASP. These differences are associated with the different sources of the particles. In the urban area they are predominantly of pollution origin, mainly from vehicle emissions, and road dust suspension, while in the State Park they are mainly of biogenic, terrigenous and oceanic origins. For these reasons the CUNHA region can be considered to be a regional reference site for studies concerning eventual disturbances in the Cunha background site, derived from transported pollution.

Keywords: Atlantic Forest, PM_{10}, major ions, soluble fraction, trace elements, urban pollution

1. Introduction

The Metropolitan Area of São Paulo (MASP) with 17 million inhabitants has a high industrial activity and a fleet of about 7 million vehicles which lead to atmospheric pollution problems. Although in the last two decades the institutions responsible for the pollution control have taken actions to control industrial as well as vehicular emissions, the MASP is yet facing serious problems of atmospheric pollution, mainly during winter i.e. dry season, which is usually enhanced by the presence

of low altitude atmospheric inversion layer. The airborne particulate matter is an important carrier of diverse materials such as soil dusts, pollen, ashes and chemicals, such as heavy metals, nitrogen, sulfur oxides and hydrocarbons that can be transported to other regions.

In the Brazilian territory the particulate matter over the Amazon region has been intensively studied since the 70's due to the alarming problem of the biomass burning (Orsini *et al.*, 1982; Yamasoe *et al.*, 2000). Also, some studies in natural and rural areas (Orsini *et al.*, 1986) showed that soil and ocean derived particles were the main sources of the airborne particles. Concerning the urban areas it was pointed out that industries and fossil fuels combustion were the main sources of atmospheric fine particles (Orsini *et al.*, 1984; Sanchez-Ccoyllo and Andrade, 2002). However, studies regarding the soluble fraction of the fine particles are unknown for the MASP region. This type of study is important because it is the soluble fraction of the fine particles that determines the toxicity potential of particles since this fraction is furthermore prone to be absorbed by the pulmonary tissues (Adamson *et al.*, 1999). Beyond that, the soluble fraction of atmospheric particulate matter is an easily fraction removed by rainfall (Vautz *et al.*, 2003; Rocha *et al.*, 2003; Fornaro *et al.*, 2003). In order to evaluate the anthropogenic contribution in the airborne particulate matter of the MASP area, we also need a reference site with prevailing natural emissions, reduced anthropogenic influence and similar climate. Most of the studies in natural areas concerning atmospheric chemistry were done in the Amazon region which has distinct climatic and emissions characteristics from the Atlantic Forest region where the MASP is inserted. Therefore, besides the necessity of a reference site for atmospheric chemistry studies the knowledge of the particulate matter soluble fraction chemistry is important to subsidy studies on impacts on human health and on the vegetation within the considered region. To achieve these goals the chemical composition of the soluble fraction of the PM_{10} particles (Dp $< 10\,\mu$m) was characterized in two sites: one inside the Metropolitan Area of São Paulo (MASP) and another, 250 km apart, inside the State Park of Serra do Mar (CUNHA) part of the Atlantic Forest Reserve, both located in São Paulo State, Brazil.

2. Sampling Sites

The sites were selected based upon to their geographic position, sampling facilities and atmospheric characteristics (Figure 1). The urban site is one of the largest urban centers in the world while the regional reference site is located in a State Park area of the Atlantic Forest in the southeastern portion of São Paulo State.

The urban site (point 1, Figure 1) is located within the MASP (23°32′52″S; 46°38′07″W). Mean altitude is 800 m and the sampling site is about 45 km from seashore. The climate of the region is predominantly tropical humid with marked rainy (summer) and dry (winter) seasons. The mean monthly temperature during
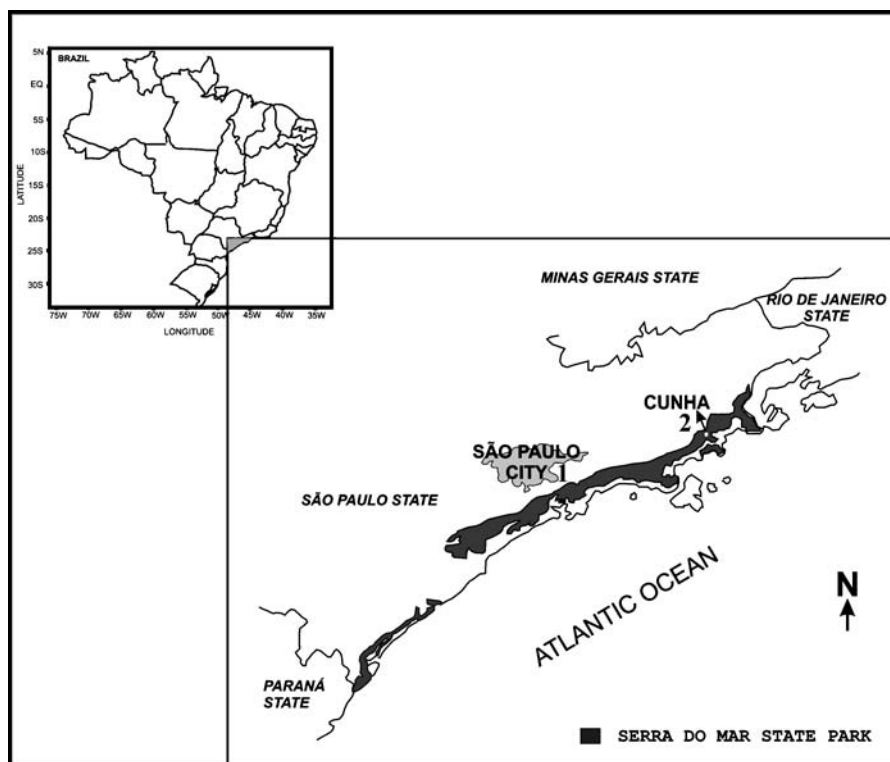
Figure 1. Localization of the sampling sites: São Paulo City-MASP (1) and CUNHA (2).

summer (from December to February) is 24 °C and during winter (from June to August) is 16 °C with an annual rainfall of 1500 mm. The dominant winds are S, SE and NW with mean speed of 3.5 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, when the latter are mainly associated with continental breeze during summer nightly convection (Bicudo *et al.*, 2002).

The regional reference area (point 2, Figure 1) is located in the Cunha-Indaiá Nucleo Reserve (CUNHA) (23°14′05″S; 45°01′16″W) within the Serra do Mar State Park. The Reserve has an area of 2,854 ha. It is situated within the Atlantic Forest that is a protected biome (UNESCO, 1998), and is covered with primary forest on the hill tops and secondary forest on abandoned pastures. Mean altitude is 1050 m and distance from seashore is about 25 km. The climate is typically tropical humid of altitude, which is affected by topography and proximity of the ocean. The dominant winds come from Southeast sector, blowing from the ocean toward the Serra do Mar, producing high rainfall (Cicco and Fujieda, 1992). Annual rainfall distribution varies between 2000 and 2500 mm and is characterized by a wet (September until March) and a dry (April until August) seasons. The mean

annual temperature is 16.5 °C. 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. Material and Methods

The suspended particles were collected in both sites during the winter (dry season, July 1999) and the summer (wet season, January and February 2000). Simultaneous sampling in both sites was not possible, because only one set of equipment was available. Two different samplers were simultaneously used to collect the particulate matter.

The high volume cascade impactor (HiVol: Sierra High Volume 235) consisted of 6 stages of anodized aluminum plates as collection supports. The HiVol was operated at $68 \, \text{m}^3 \, \text{h}^{-1}$ and the collected particles were separated in the following granulometric fractions, corresponding to stages 1 to 6: $>7.2 \, \mu\text{m}$, $7.2 \, \mu\text{m} - 3 \, \mu\text{m}$, $3 \, \mu\text{m} - 1.5 \, \mu\text{m}$, $1.5 \, \mu\text{m} - 0.95 \, \mu\text{m}$, $0.95 \, \mu\text{m} - 0.49 \, \mu\text{m}$ and $<0.49 \, \mu\text{m}$. Aluminum foils were used as substratum for the impacting particles because they allow a better observation of the collected material by Scanning Electron Microscopy (SEM). This type of sampler allowed adequate samples for crystallographic characterization of the different fractions. We checked that aluminum foils did not affect the results of the chemical analysis by studying blanks samples.

The PM_{10} sampler is constituted by a stacked filter unit (SFU), a vacuum pump with a flow rate of $0.96 \, \text{m}^3 \, \text{h}^{-1}$, a filter holder, a volume-meter and an inlet. The inlet has an aerodynamic design that allows the sampling of particles with aerodynamic diameter smaller than $10 \, \mu\text{m}$. This sampler was fully characterized in Hopke *et al.* (1997). PM_{10} fraction was collected using Nuclepore polycarbonate membranes with 47-mm diameter and $0.4 \, \mu\text{m}$ pore size. This sampler was employed to obtain samples for chemical characterization of the water-soluble fraction.

For this study, one sample is constituted by the particles impacted on a substratum (aluminum foil or membrane) during a sampling time interval as described in Table I. The relatively low number of samples is due to limitations imposed by the sampling technique and the equipment availability. This was not, however, a constraint to achieve our objectives since the PM_{10} sampling and the HiVol sampling can complement each other.

The soluble fraction of the atmospheric particulate matter was obtained from the aqueous solution extract of the collected particles. This solution was obtained by immersing each sample in deionized water (conductivity $18 \, \text{M}\Omega$ and pH $= 5.6$, at equilibrium with atmospheric CO_2) submitted to ultrasound by thirty minutes to accelerate the solubilization (Forti and Moreira-Nordemann, 1989). A volume of 50 ml of water was used for the CUNHA samples. For the MASP samples the volume of water was higher, 75 ml, due to higher quantities of particles on the samples. The aqueous solution was furthermore filtered using a Millipore membrane

TABLE I

Sampling conditions

Sampler	Sampling period	Fraction size (μm)	Time interval (h)	Number of samples	Type of analysis
HiVol	Winter	>7.2	12	Winter	SEM:
	MASP: 17–30 July 1999	7.2-3		MASP 180	8 winter and 12
	CUNHA: 1–11 July 1999	3-1.5		CUNHA 120	summer samples
	Summer	1.5-0.95		Summer	for each site
	MASP[a]: 2–4 Feb 2000	0.95-0.49		MASP 36	XRD:
	CUNHA: 4–14 Jan 2000	<0.49		CUNHA 142	10 winter samples for each site (other samples for other purposes)
SFU		PM_{10}	24	Winter	Aqueous extracts: all samples
				MASP 14	
				CUNHA 9	
				Summer	
				MASP 3	
				CUNHA 9	

[a]Short sampling interval due to a fire in a nearby building damaging the equipment.

filter with 0.22 μm pore diameter. One aliquot was stored for anion analysis. A second aliquot of 25 ml was stored in polypropylene bottle for metal analysis after acidification with 250 μL of ultra-pure nitric acid. Finally a third aliquot was stored in a polypropylene bottle for cation analysis after acidification with sulfuric acid (Appelo and Postma, 1993). The extracts were stored at 4 °C until analysis.

The major dissolved ions (NH_4^+, Ca^{2+}, Na^+, 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 United Kingdom Centre for Ecology and Hydrology-Hydrochemistry Laboratory (Robson and Neal, 1997). The trace elements were determined by Induced Coupled Plasma with Mass Spectroscopy (ICP-MS) by the Actlabs Laboratory in Canada.

A Scanning Electron Microscope (SEM: JEOL JSM-5600- LV) connected to an X-ray Energy Dispersion Spectrometer (NORAN) was employed for the morphological and semi-quantitative chemical characterization of the atmospheric particles. This technique allows the definition of the particles with respect to their size

and morphology as well as the identification of other properties such as particles association or aggregation (Buseck and Bradley, 1982; Zou and Hooper, 1997).

Mineralogical characterization of the particles was performed by X-Ray powder diffraction with a Philips PW3710 diffractometer. Copper $K\alpha$ radiation was used energized to 40 kV and 40 mA. The divergence slit was $1°$ and integration time of 1 s. The 2θ angles were scanned continuously from 3 to $69°$. No crushing was necessary due to the small size of the atmospheric particles. As the X-Ray powder diffraction method is not destructive, the same samples have been used for SEM studies.

4. Results and Discussion

4.1. CHARACTERIZATION OF ATMOSPHERIC PARTICLES BY SCANNING ELECTRON MICROSCOPY (SEM).

4.1.1. *CUNHA – Winter*

SEM micrographs of CUNHA-winter samples displayed dominantly large soil dust and biogenic particles in the first stages of the HiVol. Representative soil dust particles are shown in Figure 2a. They are mainly composed of silicates dominated by alumino-silicates, with diameter between 5–10 μm, presenting angular and irregular shapes, which is characteristic of natural sources. These soil dust particles were referred as kaolinite $[Al_2Si_2O_5(OH)_4]$, which is the dominant soil mineral in the area. The alumino-silicates identified in sheets or fragments with high K peak in the obtained spectrum of the samples were associated with illite $[K_xAl_2Si_{(4-x)}Al_xO_{10}(OH_2)]$, muscovite $[KAl_2AlSi_3O_{10}(OH)_2]$ and orthoclase $[KAlSi_3O_8]$ particles and the ones with high Na and Ca peak are probably plagioclase feldspars $[(Na,Ca)Al(Si,Al)Si_2O_8]$. Some particles with high peak of Mg and K suggest the presence of biotite $[K(Mg, Fe)_3(Al, Fe)Si_3O_{10}(OH)_2]$.

The biogenic particles, such as pollen or fungi which are not always distinguishable by scanning electron microscopy shown in Figure 2b, were abundant in the first stages, and they were also found in significant amount in lower stages, which indicates that these particles can bounce from one stage to the next due to their difference in density. Their morphology varies from spherical to oval and they may be covered or not with alveolus or thorns, as well as shriveled ball shapes.

In the lower stages where the finer granulometric fractions were collected, various types of salt particles (isolated or clusters) were observed. Cube shaped NaCl particles had sizes between 2 and 10 μm (Figure 2c). The presence of mineral particles in the lower stages was also attributed to bouncing between stages.

In Figure 2d S- and Ca-containing particles are interpreted to relate to anhydrite $[CaSO_4]$ and gypsum $[CaSO_4 \cdot 2H_2O]$. They occur as isolated or efflorescence rods. Particles with high S, Ca and Na content denote the presence of glauberite
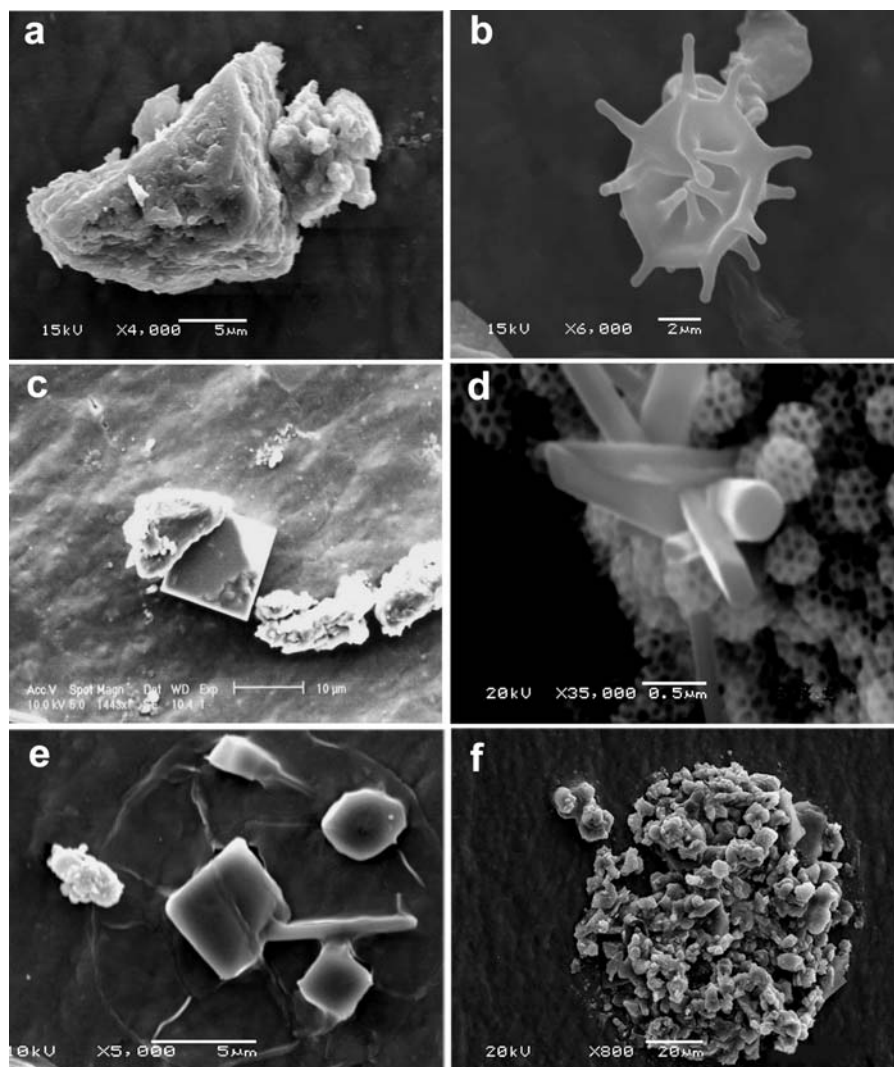
Figure 2. SEM micrographs of atmospheric particles collected in CUNHA. (a) Fragment of terrigenous particle of alumino-silicate; (b) Biogenic particle; (c) Cubic halite crystal (NaCl); (d) Gypsum rosette together with brochosomes; (e) Salt cubes from evaporated sea salt water drops; (f) Cluster of different kinds of particles.

$[Na_2Ca(SO_4)_2]$. These salts are of marine origin and their presence in CUNHA is explained by the proximity of the sampling location to the coast (Tem Brink *et al.*, 1980; Zhou and Tazaki, 1996). Together with the identified gypsum rosette in Figure 2d, the Buckyball-looking hollow structures are brochosomes, produced by leafhoppers (Cicadelliae) to serve as an efficient water-repellent protective surface coating (Wittmaack, 2005).

4.1.2. *CUNHA – Summer*

The CUNHA summer samples present the same diversity of particles as the ones observed during the winter. During the summer the particles are almost the same that those observed during the winter, however, they are often found associated in clusters whose diameter is in the range 25–40 μm (Figure 2f). The soil dust particles are smaller and less angular than those observed during winter. Biogenic particles are still abundant, but occur mainly in the second stage of the HiVol (7.2–3 μm). Salt particles present dissolution features (Figure 2e) and sulfate particles were less abundant during this season.

4.1.3. *MASP*

The SEM studies showed that no well defined differences exist between winter and summer for the MASP-site. Most particles were found in the lower stages being related to the finer granulometric fractions (<1.5 μm), in both seasons. Typical particles represented by a spongy irregular shape are shown in Figure 3a and 3b as an example, which corresponds to a cluster association of smaller particles (<0.5 μm). These particles are rich in C, S and sometimes Fe, Cu and Zn. Such particles typically originate from incomplete combustion of fossil fuel, largely diesel as already observed by Mamane *et al*. (1986), Zou and Hooper (1997) and Piña *et al*. (2000).

In the first stages were found clusters as large as 25 μm (Figure 3c) associating salt, mineral and carbon-rich particles. They are related to the association of salts, soil dust and fly-ash. Spherical particles ($\leq$5 μm) of iron (Figure 3d) and titanium oxides (Figure 3e) were identified in the finer stages. They were observed isolated or associated with spongy particles (Figure 3f). Their origin mainly relates to combustion processes from industries and metallurgical activities (Lichtman and Mroczkowski, 1985; Mamane *et al*., 1986; Rojas and Van Grieken, 1992; Piña *et al*., 2000).

The irregular shaped Fe and Fe-Ti bearing particles of diameter larger than 5 μm can be related to oxides of crustal origin such as goethite [FeOOH], hematite [Fe$_2$O$_3$], or ilmenite [FeTiO$_3$]. The Ti bearing particles of irregular shape can be related to an anthropogenic (paints, metallurgy) as well as a crustal origin (anatase [TiO$_2$]).

Well defined salt particles or clusters with rounded ridges and large size (10 μm) were also observed. Sulfate clusters have a small size (between 5 and 10 μm) and display efflorescence features or occur as little rods with more or less rectangular shape. The Na and S bearing particles (Figure 3h) have a marine origin component; however, weathering processes from the building surfaces also produce a significant amount of S bearing particles containing Ca and Na (gypsum) which are the result of acid reactions of SO$_2$ with the calcareous or concrete building material in moist conditions (Ausset *et al*., 1994; Marinoni *et al*., 2003). Besides, particles of crustal origin are also present. Another important source of S bearing particles is the gas-particle conversion reactions in the atmosphere that
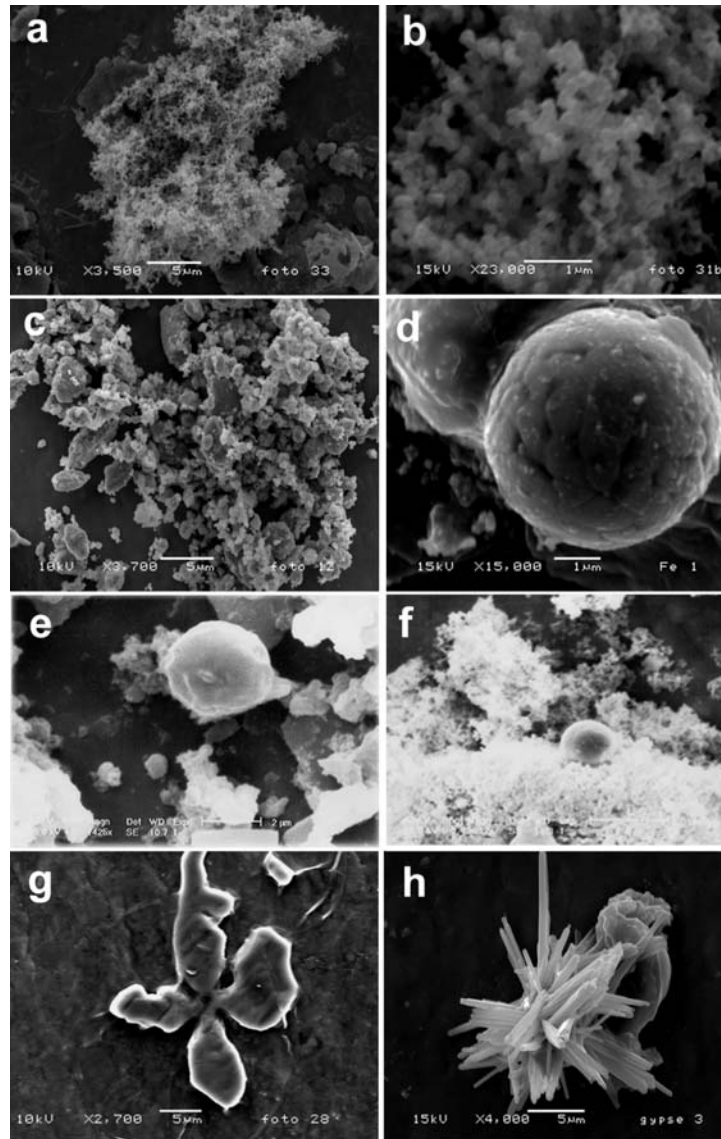
Figure 3. SEM micrographs of atmospheric particles collected in MASP. (a) Smooth spongy anthropogenic particle; (b) Detail of Figure 3a. particle; (c) cluster of particles; (d) spheroid particle of iron; (e) spheroid particle of titanium oxide; (f) spheroid particle of iron onto a spongy particle; (g) NaCl particle showing a "flower" shape; (h) sulfate particle with presence of Na and Ca.

are derived from combustion processes. Although this process produces small particles (nm), they can form larger particles through coagulation and clustering or they can be adsorbed and react on the surface of other larger particles (McMurry and Wilson, 1983; Querol *et al.*, 1998).

However, no defined seasonality has been observed, although some aspects may be associated with one or another period. For instance, during summer marine and soil dust particles appeared in clusters which were attributed to the combination of seawater drops with the soil dust grains. Also, it was observed that the sea salt particles had "ball" or "flower" shapes (Figure 3g) which indicated a process of salt precipitation following the evaporation of sea spray after the impaction with the collector substratum, whereby the observed rounded halo around the particle may correspond to the shape of the initial drop (Storms *et al.*, 1984).

4.1.4. *Comparison between CUNHA and MASP*

In CUNHA, no particles of anthropogenic origin were identified. The silicates and biogenic particles were less abundant in MASP than in CUNHA, however their morphology was similar. A significant presence of sea salt particles in the CUNHA samples compared with MASP was observed. The presence of likely anthropogenic $CaSO_4$ bearing particles in the MASP samples prevailed over the ones observed for CUNHA, particularly during the summer.

To complement these observations, a mineralogical characterization by X-Ray powder diffraction (XRD) of the atmospheric particles was done utilizing a subset of samples for MASP and CUNHA (Table I). The identified minerals were almost the same, for both sites. The prevailing identified silicate minerals were kaolinite, quartz and talc $[Mg_3Si_4O_{10}(OH)_2]$ derived from terrigeneous particles and the sulfate minerals such as anhydrite and glauberite from marine sources. Other minerals identified in small quantities were gibbsite $[Al(OH)_3]$, carbonates as nitro calcite $[Ca(NO_3)_2 \cdot 4H_2O]$ and some dolomite $[(Ca,Mg)(CO_3)_2]$, fluorite $[CaF_2]$ and monazite $[LaPO_4]$.

4.2. Aqueous solution chemistry of the fine particles

Some statistical parameters of the aqueous extracts from the samples collected in MASP and CUNHA, respectively, are given in Table II. The prevailing chemicals in the aqueous extracts were SO_4^{2-}, NO_3^-, NH_4^+, Zn, Fe, Al, Ba, Cu, Pb, Mn and Ni for the MASP site and Na^+, K^+, Cl^-, SO_4^{2-}, Zn, Ni, and Al for the CUNHA site. The variation in concentration for a given element during a given sampling campaign was high. The mean values, however, showed coherent seasonal variation and variation between sampling sites.

The water-extractable species correspond to high soluble chemicals, as Cl or Na, or to chemicals weakly adsorbed on the particles. The comparison of the obtained water-extractable species concentrations with the total elemental composition of the particulate matter found in the literature for MASP (Andrade *et al.*, 1994; Castanho and Artaxo, 2001) shows that Al, Ti, Mn, Fe and Pb are mostly found in the insoluble phase while the others such as Na, Cl, S, K, Ca, Zn and Ni are in the soluble phase. However, according to our results, a fraction of Al, Ti, Mn, Fe and Pb was also extractable in the soluble phase.

TABLE II

Chemical composition of the aqueous extract of the particulate matter collected in the MASP and CUNHA ($ng \cdot m^{-3}$)

	MASP				CUNHA			
	Summer		Winter		Summer		Winter	
	AM	STD	AM	STD	AM	STD	AM	STD
Species	$ng \cdot m^{-3}$				$ng \cdot m^{-3}$			
Na^+	nd	nd	1675	2585	1389	2199	8709	10266
NH_4^+	672	485	1934	1176	451	482	1191	1159
K^+	470	203	465	331	96.2	58.7	9799	6807
Mg^{2+}	143	60.7	152	89.3	18.3	19.9	85.0	75.5
Ca^{2+}	717	328	971	527	9.11	27.3	748	728.6
Cl^-	654	448	969	754	206	129	13448	8437
NO_3^-	319	315	2790	2135	26.4	54.3	1616	4331
SO_4^{2-}	3441	1640	4976	1912	1492	859	5594	1635
Al	6.70	11.6	54.3	41.1	nd	nd	39.6	99.7
Ti	0.99	1.54	2.07	1.42	0.78	0.78	0.96	2.88
Mn	6.10	2.30	18.9	10.4	3.00	2.70	7.70	7.20
Fe	63.9	15.0	97.0	49.3	nd	nd	nd	nd
Zn	81.9	76.7	118	95.6	17.5	6.80	221	282
Ni	4.20	1.00	18.1	16.8	1.30	0.20	55.3	47.1
Cu	9.40	2.90	29.3	45.7	3.40	1.75	4.00	4.60
Pb	10.3	5.50	16.6	8.80	2.00	1.20	13.2	5.80
Co	0.10	0.05	1.10	0.95	nd	nd	0.20	0.30
Cd	0.60	0.40	2.10	1.30	0.10	0.05	0.50	0.30
Ba	25.3	9.10	46.9	19.3	nd	nd	6.90	10.6

AM: arithmetic mean; STD: standard deviation.

The mean concentration values for most of the chemical species were higher during the winter than during the summer for both sites, mainly due to the lower rainfall. However, the high frequency of thermal inversion is also an important factor.

For CUNHA in winter, the water-extractable species with the highest concentrations were Cl^-, K^+, Na^+ and SO_4^{2-}. Most of Na^+ and Cl^-, and a fraction of the SO_4^{2-}, are coming from sea-salts aerosols transported by sea breeze, as explained later. According to Calloway *et al.* (1989), biogenic particles produced by the forest are a significant source of K. Biomass burning due to fireplaces was also able to produce K, S or Zn-bearing particles (Artaxo *et al.*, 1990; Echalar *et al.*, 1995). Such processes produce small particles by gas-particle conversion, so that the associated K or S is able to be easily water-extracted. The quite low values for Fe and Al, in spite of the presence of Al and Fe-bearing soil particles as determined in the

SEM study, indicates that such crustal minerals do not significantly contribute to the soluble fraction.

The water-extractable concentration in the MASP-winter samples were higher than in CUNHA, excepted for Na^+, K^+, Cl^-, SO_4^{2-}, Zn and Ni. The lower values for Na^+ and Cl^- reflect different losses during transport due to differences in atmospheric conditions. The lower value for K^+ is due to a smaller vegetative production in the urban area. Most of the water-extractable trace metals had concentrations in the MASP more than 2 or 3 times higher than in CUNHA. Ba and Pb in urban atmosphere 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 (Gordon, 1980; Kowalczyk *et al.*, 1982; Mészáros *et al.*, 1997). In the MASP, 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.

4.2.1. *Marine Contribution for Soluble Species*

Known sources of Na and Cl in urban atmosphere are sea salt (Thurston and Spengler, 1985), crustal aerosols and motor vehicle emissions (the latter only for Cl) (Ondov *et al.*, 1982; Kitto, 1993). 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 1.5 during winter, which indicates a marine contribution for Na and Cl due to the high frequency of sea breeze blowing landward during this season. During the summer, the Cl/Na ratio is quite low (0.14). This may indicate a low contribution from sea breezes; however, the discrepancy between the values suggests other processes such as a loss of gaseous Cl during the air masses transport (Johansen *et al.*, 1999; Sturges and Barrie, 1988).

The Cl to Na mass ratio in the MASP (0.58) during the winter is lower than in CUNHA (1.5), denoting a lower contribution from marine sources for MASP. The Cl/Na ratio was not determined in the MASP during summer. The Cl value was higher than in Cunha, which likely indicates anthropic Cl emission.

In order to examine the marine contribution to aerosol chemical composition, an attempt was made to estimate the non sea salt (NSS) and the sea salt (SS) fractions of SO_4^{2-}. Assuming that the continental contribution for atmospheric Na is negligible, the following expressions (Mihalopoulos *et al.*, 1997) were used:

$$NSS\text{-}SO_4^{2-} = \left(SO_4^{2-}\right)_{measured} - \left(SO_4^{2-}/Na^+\right)_{seawater} \times (Na^+)_{measured}$$
$$SS\text{-}SO_4^{2-} = \left(SO_4^{2-}\right)_{measured} - NSS\text{-}SO_4^{2-}$$

where, $SO_4^{2-}/Na^+ = 0.252$ (Millero and Sohn, 1992; Riley and Chester, 1971).
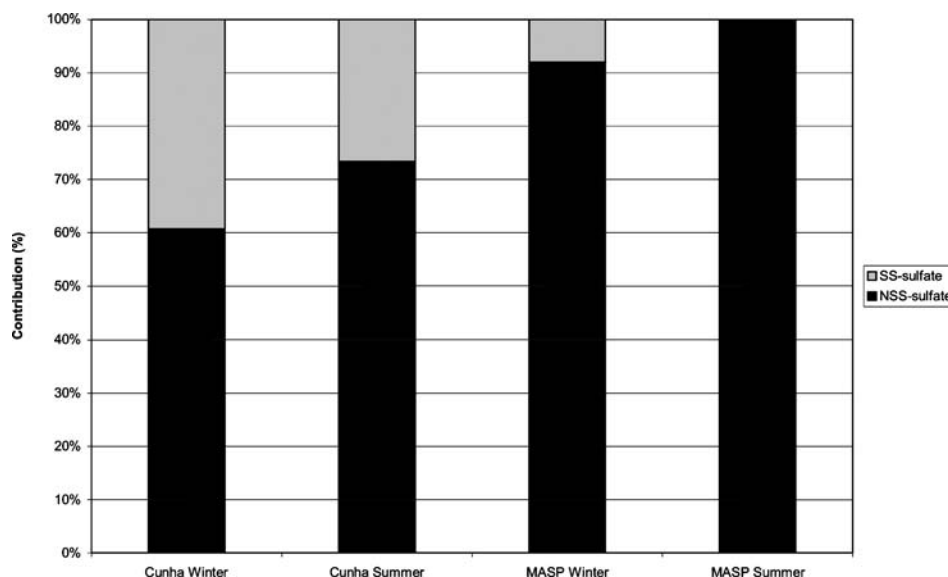
Figure 4. Calculated non sea salt sulfate (NSS-SO_4^{2-}) and sea salt sulfate (SS-SO_4^{2-}) fractions in ng m^{-3}, for each site and sampling period.

The non sea salt (NSS-SO_4^{2-}) and the sea salt (SS-SO_4^{2-}) fraction values are presented in Figure 4. From this figure it is observed that in CUNHA 39% and 24% of sulfate comes from the ocean during winter and summer, respectively. In the MASP 8% of sulfate is derived from sea-salt during winter while in the summer period the sea-salt sulfate fraction is negligible.

5. Conclusion

The SEM observations showed no significant differences between winter and summer for the particles morphology, for both sites. For CUNHA the identified particles have morphological characteristics of biogenic, soil and marine natural sources. The salt particles were mainly found as isolated or in clusters particles. For the MASP the silicate and biogenic particles were less abundant and anthropogenic particles were dominant in the smaller fraction. Shapes characteristic of industrial and vehicular sources were identified for metal-bearing particles.

The water-extractable fraction of chemicals significantly differed from the usual concentrations of the corresponding elements in bulk aerosol particles. In CUNHA, the chemistry of the water extract was mainly controlled by marine (Na$^+$, Cl$^-$ and about 30% of the SO_4^{2-}) and biomass (K$^+$, SO_4^{2-}, Zn) sources. In the MASP, most of the water-extractable species relate to human activity. Significant amounts of Fe, Zn, Cu, Pb and Ba were found in the aqueous extracts. Most of the SO_4^{2-} was anthropogenic.

Since significant amount of aerosols from anthropogenic sources as well as particles with anthropogenic morphology characteristics were not been detected in the CUNHA region, it is suggested that this area can be considered as a reference site for atmospheric pollution studies in the domain of the Atlantic Forest.

Acknowledgments

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