Composition of PM$_{2.5}$ and PM$_{10}$ Collected at Urban Sites in Brazil

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ABSTRACT

Atmospheric particulate matter samples (PM$_{2.5}$ and PM$_{10}$) were collected at urban sites (São Paulo, SPA; Piracicaba, PRB) in São Paulo State, Brazil. In order to characterize the chemical composition of particulate matter, several chemical components were analyzed from the samples, and among these were inorganic and organic anions, monosaccharide anhydrides, and organic and elemental carbon. Long-range transport of the particulate matter while sugar cane was being burned contributed to an increase in PM$_{2.5}$ and PM$_{10}$ concentrations at the SPA site. Sulphate, nitrate, ammonium, elemental carbon and particulate organic material (POM) were major components of the total PM$_{2.5}$ and PM$_{2.5–10}$. The contribution of POM to PM$_{2.5}$ at PRB was 29%, similar to the results found for the winter season at the SPA site.

The Cl$^-$/Na$^+$ ratio at the SPA site for PM$_{2.5}$ was different from that at the other site, with chloride depletion indicating several sources beyond sea salt. The occurrence of levoglucosan and its correlations with potassium confirm the contribution of local biomass burning (at PRB) and long-range transported particles at SPA. OC/EC ratios and the correlation coefficients indicated secondary formation of OC at both sites.

Keywords: Air composition; OC/EC; Levoglucosan; Sugarcane burning; Air pollution.

INTRODUCTION

Aerosol chemical characterization is important in atmospheric chemistry studies to increase the understanding of the effects of aerosol composition on human health, visibility, cloud-aerosol dynamics and air quality (Martins *et al.*, 2009; Alves *et al.*, 2011).

Brazilian cities adopted air quality standards only for PM$_{10}$ and discussion has been developed to reduce particulate matter emissions.

São Paulo is the largest city in the country and has experienced the increasing of vehicles due to the current economic expansion. Almost 85% of all new light duty vehicles are flexible fuelled vehicles. The heavy duty vehicles that are on average more than ten years old contribute to urban ultrafine particles, which are linked to adverse respiratory problems (Nel *et al.*, 2006). Previous studies in São Paulo, showed health effects, mainly during episodes of sugarcane burning in surrounding regions of the city (Carvalho-Oliveira *et al.*, 2005; Umbuzeiro *et al.*, 2008).

The determination of molecular markers is important to get information on specific emission sources and some species are presented here. Potassium has been used as a tracer of biomass combustion, whereas magnesium and calcium as dust tracers. Sugar alcohols, mono- and disaccharide, and monosaccharide anhydrides comprise an important fraction of water soluble organic carbon in atmospheric aerosols. Levoglucosan is a major organic component of fine smoke particulate matter emitted from biomass burning and it has been used as marker (Zhang *et al.*, 2008; Iinuma *et al.*, 2009). It is accompanied by minor quantities of isomers, namely mannosan and galactosan.

Other compounds can be useful to study the main pollution sources. Elemental carbon (EC), emitted directly into atmosphere as a result of fossil fuel or biomass burning, is the principal light-absorbing component in the atmosphere and it has a warming effect on climate (Jacobson, 2002; Niemi *et al.*, 2009). Organic carbon (OC) is an effective light scattered and it may contribute significantly to both visibility degradation and the direct and indirect aerosol climatic forcing.

Besides, carboxylic acids are ubiquitous and have been a target of interest in the chemical characterization of the atmosphere because they are considered to be one of the classes of organic compounds detected in a variety of environments in many regions in the world (Souza *et al.*,

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1999; Wang *et al.*, 2007).

In this work particulate matter samples ($PM_{2.5}$ and PM_{10}) were collected at urban and sites in São Paulo State, Brazil. The chemical composition of particulate matter is reported. Several chemical components were analyzed among these inorganic, organic anions, monosaccharide anhydrides and organic and elemental carbon.

MATERIAL AND METHODS

Site Description

The measurements were made in two cities. The first one, in São Paulo city, an urban and industrial site (SPA, 23°33' 34''S and 46°44'01''W) which is impacted by different type of emission sources. This city is the largest industrialized region in Latin America (chemical, petrochemical and pharmaceutical industries). The measurement site was approximately 2 km far from a major highway with dense vehicular traffic. São Paulo Metropolitan Area has over 19 million inhabitants and a fleet of over 7 million vehicles.

The second measurement site was located in Piracicaba city (PRB, 22°42'20''S and 47°38'27''W). It is an urban area 200 km far from SPA. The city has over 360,000 inhabitants and a vehicle fleet of over 185,000. The principal activities are agricultural (sugarcane, coffee, orange) and industrial. Biomass burning has been the largest factor affecting the local air quality (Allen *et al.*, 2004; Vasconcellos *et al.*, 2007).

Sampling of $PM_{2.5}$ and PM_{10}

PM_{10} samples were collected with a high-volume sampler (flow rate at 1.13 m^3/min) and a cyclone device collected $PM_{2.5}$ operating at 34 L/min, both for 24-h periods. Quartz fiber filters (20 cm × 25 cm) were pre-heated at 800°C for 8 h before sampling. After sampling the filters were wrapped in aluminum foil and kept at 5°C during storage. $PM_{2.5–10}$ fractions have been obtained by subtracting the $PM_{2.5}$ from the PM_{10} results.

At the SPA site, the samplers were placed in an open area on the roof of the Department of Atmospheric Sciences, located at the University of São Paulo, ~20 m above ground level. Samples were carried out during dry and cold season in 2008 (SPA, August 7th to 28th, PM_{10} and $PM_{2.5}$). The samplers were located in another campus of the University of São Paulo (Piracicaba City) at a height of 1.4 m in an open area. Samples were collected in the beginning of the wet and hot season in 2008 (PRB, November 10th to 18th, PM_{10} and $PM_{2.5}$). Precipitation was observed only on November 14th (0.2 mm).

During the sampling period at SPA, 2990 fires were observed in the São Paulo State, and back trajectories showed air masses coming predominantly from the sugarcane region (Vasconcellos *et al.*, 2010).

Chemical Analyses

The filters were weighed before and after sampling. After mass determination, they were cut with steel punchers (1 cm^2 pieces) for analysis of water-soluble ions, organic carbon (OC), elemental carbon (EC) and monosaccharide anhydrides.

For determination of the soluble ions (Cl^-, NO_3^-, SO_4^{2-}, oxalate, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}) the sample aliquots were extracted in 10 mL ultrapure water (18MΩ cm) and shaken for 15 min. The analyses were done using two ion chromatographs (ICS 2000 system, Dionex) simultaneously: cation and anions analyses were made using CG12A/CS12A (4 mm i.d. × 50 + 250 mm length) and AG11/AS11 (4 mm i.d. × 50 + 250 mm length) columns. Detection limit was 5.0 ng/mL for Mg^{+2} and Ca^{+2}, and others in the range 1.0 and 2.0 ng/mL.

The carbonaceous fraction (OC and EC) was determined with a thermal-optical transmission method (TOA; Sunset Laboratory Inc.). The instrument uses a two-phase thermal method (EUSAAR_2) to separate OC and EC (Viidanoja *et al.*, 2002). The optical correction was performed in order to separate pyrolysed organic carbon from elemental carbon. The uncertainty of the analyzer was estimated to be 10% for OC and 20% for EC.

Water soluble organics (acetate, formate, glyoxylate, malonate, maleate, succinate, malate, adipate, pinonate, pinate and azelate) and phosphate were determined by an ion chromatography (ICS 3000) using AG11/AS11 columns (2 mm i.d. × 50 + 250 mm length) coupled with a mass spectrometer. Carbon-13 labeled malonate (^{13}C-malonate) was used as an internal standard.

Concentrations of three monosaccharide anhydrides (levoglucosan, mannosan and galactosan) were measured using a high-performance anion-exchange chromatography analysis coupled with electrospray ionization to a quadrupole mass spectrometer (HPAEC/ESI-MS; Dionex ICS-3000 System and Dionex MSQ^{TM}). The complete procedure is described in Saarnio *et al.* (2010). The samples were extracted with 5 mL of deionized water with an internal standard (Carbon-13 labeled levoglucosan, Cambridge Isotope Laboratories Inc.) by 15 min of gentle rotation. The inject volume of 50 μL was used in analysis.

RESULTS AND DISCUSSION

Meteorological Data and Backward Trajectory Analysis

São Paulo State presents an upland tropical climate with a dry season during wintertime. During summer in the Southern hemisphere, from December to February, monthly average temperatures reach up to 23°C. In winter monthly average temperatures are around 16°C (from June to August). The prevailing wind directions are from southeast and northeast, mainly associated with the Atlantic Ocean breeze. Polar air masses associated with cold front systems arrives in São Paulo in the wintertime and they can intensify the circulation coming from southeast.

Meteorological conditions are presented in the Table 1. Backward trajectories (HYSPLIT model, 96-h and 500 m height) showed air masses coming predominantly from the sugarcane burning region during the sampling period (73% of the time) to SPA site (Vasconcellos *et al.*, 2010).

$PM_{2.5}$ and of $PM_{2.5–10}$ Concentrations
Concentrations of São Paulo Samples (SPA)

Table 1. Average values for meteorological conditions at the sites investigated.

	PRB	SPA
Temperature (°C)	23.4	18.6
Wind velocity (m/s)	2.8	1.4
Relative humidity (%)	69.9	71.8

The $PM_{2.5}$ mass concentrations for samples collected during dry and cold season, at SPA ranged from 17 to 83 $\mu g/m^3$ (average 47 $\mu g/m^3$). The $PM_{2.5–10}$ mass concentration ranged from 13 to 39 $\mu g/m^3$ at SPA (average 17 $\mu g/m^3$).

The highest $PM_{2.5}$ concentration was found on August 18th (83 $\mu g/m^3$) when the lowest relative humidity (57%) and the hottest day (21°C) of this campaign were observed. Sugarcane burning period (May–October) has effects on PM concentrations (Allen *et al.*, 2004). During this sampling period, air masses from biomass burning areas circulated over the sea and over the biggest industrial park of the state (Cubatão, city with chemical, pharmaceutical, petrochemical, steel, fertilizers, among others activities) prior to arriving to the measurement site (Vasconcellos *et al.* 2010).

The high particulate matter concentration and the influence of the industrial complex have been studied by Allen *et al.* (2009).

The higher concentration of coarse particulate was obtained on August 28th at SPA (39 $\mu g/m^3$). This can be attributed to sea salt particles contribution transported, high concentration of sodium (310 ng/m^3) and chloride (635 ng/m^3) were also found on that day. High concentration of calcium (373 ng/m^3) was found probably originated from the resuspension of soil and civil construction.

Both $PM_{2.5}$ and PM_{10} mass concentration measured in this work and in other studies are showed in the Table 2. The results of the current study showed higher concentrations of $PM_{2.5}$ at SPA site (winter) than those found in the same season in Ghent (25 $\mu g/m^3$) and in Barcelona (26 $\mu g/m^3$). In the summer the concentrations were comparable (Ghent, 12 $\mu g/m^3$; Barcelona, 16 $\mu g/m^3$). PM_{10} mass concentration was higher at SPA in the winter than other sites. The variation is associated with geographical and meteorological different and local emission sources, and influences for long range transport of air masses. During the sampling campaign in São Paulo, sugar cane burning smoke from neighbor cities may have led to the increased particulate matter concentration.

Concentrations of Piracicaba Samples (PRB)

At PRB site the $PM_{2.5}$ mass concentration ranged from 6 to 26 $\mu g/m^3$ (average 18 $\mu g/m^3$) and $PM_{2.5–10}$ from 9 to 29 $\mu g/m^3$ (average 19 $\mu g/m^3$) in 2008, when sugarcane burning events were scarce. $PM_{2.5}$ levels were comparable with those found in European sites (from 12 to 26 $\mu g/m^3$) in different seasons.

Chemical Composition

The average mass concentrations and the results of the relative contribution of different components for both the $PM_{2.5}$ and $PM_{2.5–10}$ are shown in Table 3.

São Paulo Site (SPA)

The concentrations of the carbonaceous species at SPA site for fine particles were between 0.8 to 11 $\mu gC/m^3$ (av. 6.6 $\mu gC/m^3$) for EC and 5.5 to 15 $\mu gC/m^3$ (av.10 $\mu gC/m^3$) for OC (Table 3). The level of contribution relative EC obtained was 14% and the one of in the particulate organic matter (POM) was 26% for $PM_{2.5}$ during the sampling period (Fig. 1).

The organic carbon (OC) originates from both direct emissions of particles and atmospheric transformation of organic gases. Secondary OC is generated by the condensation of low vapor pressure products (Chow *et al.*, 1996; Chen *et al.*, 2003). In order to convert the measured amount of carbon to the total particulate organic matter, the organic carbon mass was multiplied to the factor 1.2 that is an estimate of the average molecular weight per carbon weight for the organic aerosol (Huang *et al.*, 2005).

The contribution of OC mass higher than EC, in the fine particulate shows influences of local vehicular traffic. However, the relative contribution of EC at São Paulo indicates that there was influence of particles coming from the incomplete biomass burning.

Oxalate was the most abundant organic ion in $PM_{2.5}$. The average concentration obtained during dry and cold season at SPA was 243 ng/m^3 (range 167–364 ng/m^3). Oxalate presents different sources, although it is often associated with combustion processes and secondary reactions. The average concentrations of other organic components were low (below detection limit).

The average concentration of levoglucosan was also measured at SPA site (284 ng/m^3). For mannosan and galactosan at SPA the average concentrations were 22 and 16 ng/m^3 in $PM_{2.5}$. The presence of levoglucosan in urban

Table 2. Average concentrations of $PM_{2.5}$ and PM_{10} ($\mu g/m^3$) measured at various sampling sites and this work.

| References	Site	Sampling period	$PM_{2.5}$	PM_{10}
This work	São Paulo, Brazil	Winter, 18–28/Aug. 2008	47	64
	Piracicaba, Brazil	Spring, 10–18/ Nov. 2008	18	35
Viana *et al.*, 2007	Ghent, Belgium	Summer, 6/10–7/16/04	12	20
	Ghent, Belgium	Winter, 1/10–2/14/05	25	29
	Barcelona, Spain	Summer, 7/27–9/1/04	16	30
	Barcelona, Spain	Winter, 11/16–12/16/04	26	34
Yin and Harrison, 2008	Bristol Road, UK	5/16–11/20/05	16	27
	Birmingham, UK	5/18/04–5/11/05	16	24
	Churchill Pumping Station, UK	11/22/05–5/22/06	14	19

Table 3. Mean concentration (range) of the chemical species to $PM_{2.5}$ e $PM_{2.5-10}$ (ng/m^3) at sites studied.

	PRB, spring	SPA, winter
$PM_{2.5}$	**18 (6–26)**	**47 (17–83)**
PO_4^{3-}	44 (24–69)	30 (8.9–49)
Cl^-	49 (< dl–85)	267 (34–553)
SO_4^{2-}	1782 (692–3273)	3348 (1076–6590)
Nss- SO_4^{2-}	1764 (685–3244)	3312 (1039–6546)
NO_3^-	497 (235–742)	2079 (859–4661)
Acetate	9.3 (3.5–13)	3.7 (< dl–5.1)
Formate	16 (1.7–37)	21 (6.7–47)
Oxalate	141 (67–231)	243 (167–364)
Glyoxylate	5.1 (< dl–11)	11 (5.4–20)
Malonate	28 (12–49)	33 (16–46)
Maleate	1.8 (0.7–2.7)	1.3 (0.5–2.8)
Succinate	18 (7.9–35)	37 (22–51)
Malate	30 (15–56)	36 (21–59)
Adipic	3.9 (1.5–6.1)	7.8 (2.4–11)
Pinonic	0.3 (< dl–5.3)	93 (< dl–206)
Pinic	3.8 (< dl–6.6)	2.3 (< dl–4.4)
Azelaic	2.7 (0.2–5.3)	11 (2.8–34)
Na^+	71 (27–121)	148 (49–230)
NH_4^+	648 (204–1417)	1508 (573–2643)
K^+	357 (261–514)	529 (314–793)
Nss-K^+	355 (260–512)	524 (312–786)
Mg^{2+}	38 (17–67)	31 (11–66)
Nss-Mg^{2+}	30 (14–58)	14 (0–48)
Ca^{2+}	233 (156–319)	233 (113–373)
Nss-Ca^{2+}	230 (155–316)	227 (111–364)
Levoglucosan	66 (23–140)	284 (37–453)
Mannosan	2.0 (< dl–4.8)	22 (2.1–36)
Galactosan	3.6 (< dl–7.9)	16 (4.6–28)
OC (µg/m^3)	4.4 (2.8–6.9)	10 (5.5–15)
EC (µg/m^3)	1.7 (1.1–2.6)	6.6 (0.8–11)
$PM_{2.5-10}$	**19 (9–29)**	**27 (13–39)**
PO_4^{3-}	15 (0.4–42)	25 (7.4–37)
Cl^-	100 (1.9–495)	763 (273–1433)
SO_4^{2-}	564 (14–1554)	1384 (656–2627)
Nss- SO_4^{2-}	535 (14–1535)	1298 (604–2572)
NO_3^-	247 (70–560)	2076 (1240–3828)
Acetate	3.9 (0.0–16)	42.4 (29–53)
Formate	1.8 (0.0–9)	72 (26–108)
Oxalate	13 (0.0–25)	46 (22–104)
Succinate	5.3 (0.0–16)	23 (0.0–50)
Na^+	118 (0.2–393)	349 (185–780)
NH_4^+	670 (106–1838)	817 (173–2551)
K^+	106 (71–141)	170 (56–356)
Nss-K^+	101 (69–137)	157 (41–345)
Mg^{2+}	57 (0.1–104)	115 (53–153)
Nss-Mg^{2+}	43 (0.03–84)	73 (23–106)
Ca^{2+}	101 (1.1–237)	817 (416–1089)
Nss-Ca^{2+}	96 (1.1–234)	804 (400–1077)
Levoglucosan	32 (10–60)	78 (27–152)
Mannosan	6.5 (< dl–12)	6.9 (< dl–21)
Galactosan	4.3 (1.4–7.7)	6.0 (< dl–16)
OC (µg/m^3)	0.9 (0.0–1.8)	na
EC (µg/m^3)	0.8 (0.1–1.8)	na

areas is attributed to long range transport of air masses.

SO_4^{2-}, NO_3^- and NH_4^+ were the dominant inorganic species in both fraction size (Fig. 2). The contribution of sulphate in $PM_{2.5}$ at SPA was 7%, of nitrate was 4% and of ammonium was 3%. The average concentration in fine particulate of SO_4^{2-} and NO_3^- and NH_4^+ were 3.3 µg/m^3, 2.1 µg/m^3 and 1.5 µg/m^3 respectively.

The high concentrations of sulfate and nitrate in the fine particles may indicate strong influence vehicle emissions, consistent with other studies (Vasconcellos *et al.*, 2007).
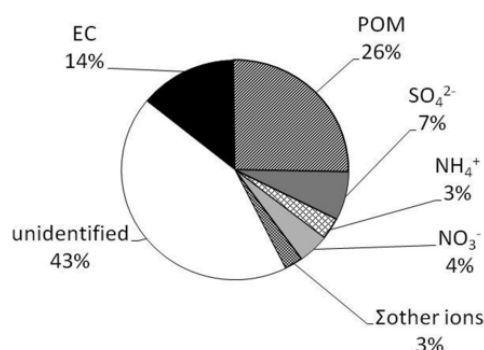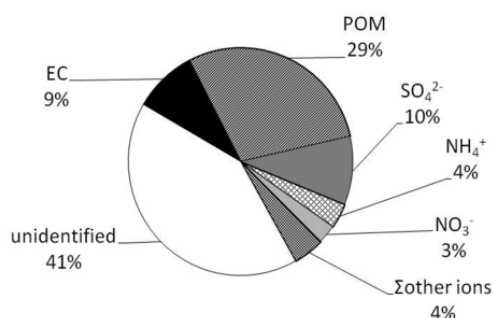
Fig. 1. Relative contribution of the chemical compounds on $PM_{2.5}$ at SPA and PRB sites.
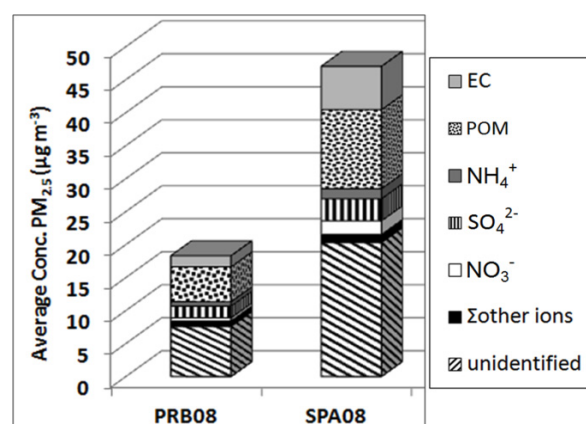
Fig. 2. The average concentration and distribution of chemical components on $PM_{2.5}$.

In $PM_{2.5-10}$, oxalate was the organic ions presented in higher concentrations. The average concentration during the cold and dry season at SPA was 817 ng/m³ (range 173 to 2551 ng/m³). For $PM_{2.5-10}$ samples, the average concentration of levoglucosan was 78 ng/m³ in the winter season. The average concentrations of mannosan and galactosan at SPA were 6.9 and 6.0 ng/m³ in $PM_{2.5-10}$. Of all water soluble ions analyzed, SO_4^{2-}, NO_3^- and NH_4^+ were the dominant compounds also found in $PM_{2.5-10}$.

The formation of nitrate and sulfate on coarse particles is an important way of removing the major gaseous pollutants (NO_x and SO_2) (Kai *et al.*, 2007). These secondary species presented in the particulate matter are markers of vehicular emissions in urban centers. The relative contribution of NO_3^- (31%) was higher than SO_4^{2-} (21%) in coarse particulate, indicating that in dry and cold periods, lower loss by volatilization of this specie takes place (Fig. 3).

The difference between the particulate matter concentration and the sum of components measured was attributed to unidentified compounds (trace metals and mineral compounds insoluble, for example). These accounted for 43% of the total analyzed samples from SPA site.

Piracicaba Site (PRB)

The contribution of POM to $PM_{2.5}$ at PRB (29%) was quite similar to the winter season at SPA (Fig. 2). However at PRB average concentration was 5.3 µg/m³, lower than that found at SPA (12 µg/m³) site, and EC and OC were 1.7 µgC/m³ and 4.4 µgC/m³, respectively. The ratio of OC/EC (ratio 3) found at PRB site was higher than at the urban center site (SPA, ratio 2). This may be explained by proximity of sample collection to agricultural regions and

biomass burning. It is consistent with results of Mkoma *et al.* (2009), found at rural sites.

The presence of oxalate (average 141 ng/m³) in Piracicaba can be attributed to different sources as biomass burning, vehicular and industrial emissions. A secondary route takes place through the production of photooxidation of cyclo-olefins in the presence of ozone (Wang *et al.*, 2007).

The average concentration of levoglucosan at PRB was 66 ng/m³ (range from 23 to 140 ng/m³). Although it is a region of biomass burning, samples were collected when there was a reduction of these fires, leading to a lower concentration of these markers. Similar to the data observed in the Amazon Basin region, levoglucosan concentrations are higher in dry season than in the wet one (Claeys *et al.*, 2010).

The relative contribution of sulphate to $PM_{2.5}$ at PRB was 10% and the contribution of ammonium was 4%. The contribution of the secondary component NO_3^- in $PM_{2.5}$ was 3%. The meteorological conditions such as temperature and humidity can contribute to the accumulation of sulfate in the atmosphere and higher volatilization of nitrate can occur (Kai *et al.*, 2007; Mkoma *et al.*, 2009).

POM, EC, sulphate, nitrate and ammonium were the major components in the mass balance of the total $PM_{2.5-10}$. At PRB site, the average concentrations of OC and EC were similar (0.9 and 0.8 µg/m³, respectively). The average contribution of EC was 4% and POM accounted to 6% in $PM_{2.5-10}$.

For $PM_{2.5-10}$, the average concentration of levoglucosan at PRB was 32 ng/m³, and the average concentrations of mannosan (6.5 ng/m³) and galactosan (4.3 ng/m³) were higher than those found in the fine mode.
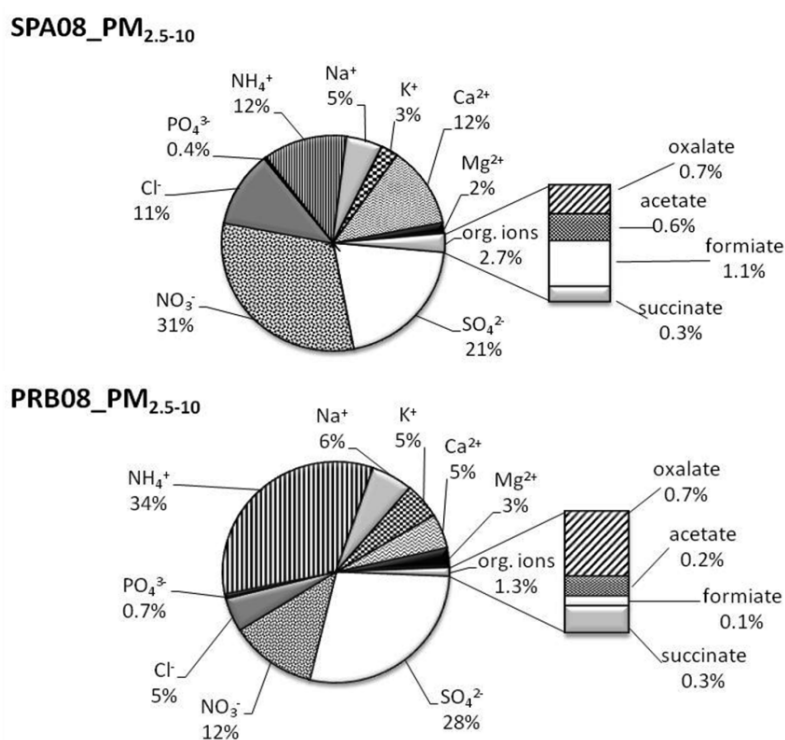

Fig. 3. The proportion of different organic and inorganic compounds in $PM_{2.5-10}$.

SO_4^{2-}, NO_3^- and NH_4^+ were also the dominant compounds for $PM_{2.5-10}$. The average concentration of SO_4^{2-} was 564 ng/m^3 and for NO_3^- 247 ng/m^3 at PRB. On average, the relative contribution of ammonium (7%) was highest than sulphate (6%) and NO_3^- (3%) for $PM_{2.5-10}$.

Fine-to-Coarse Ratio and Correlations between the Chemical Components

The relative amount of fine particles in the PM_{10} is expressed in the $PM_{2.5}$ to PM_{10} ratios (Fig. 4). $PM_{2.5}$ contributed on average 69% to PM_{10} at SPA. At SPA nss-SO_4^{2-}, NH_4^+, NO_3^- concentrations were higher in $PM_{2.5}$ than in $PM_{2.5-10}$ (Table 3) suggesting that fine particulate matter is more abundant in secondary species and contains lower concentrations of soil components.

The average $PM_{2.5}/PM_{10}$ ratio is 0.5 at PRB site, which indicates that, on average, half the total mass of the PM_{10} is attributed to the fine particles of the samples collected at this site. According to World Health Organization, the ratio of 0.5 is characteristic of the urban areas of developing countries and corresponds to the lower limit of the range found in urban areas of developed countries (0.5–0.8).

However, it was observed at PRB that some of the specific species were found predominantly in fine mode, such as phosphate (24–69 ng/m^3) that is associated with land use in agricultural activities. Also the higher mass concentration of nss-K$^+$ was found in fine fraction rather than in coarse at both sites and might be indicative of influence of biomass burning. In Piracicaba, emissions are associated with the sugar cane burning, and in São Paulo, its origin is attributed to input by transport of air masses, and the burning of urban waste. Conversely, at PRB site Na$^+$

(av. 118 ng/m^3) and nss-Mg^{2+} (av. 43 ng/m^3) concentrations were higher in $PM_{2.5-10}$ than in $PM_{2.5}$ that can be attributed to soil resuspension.

The correlation matrix (not shown) and diagnostic ratio (Table 4) were used to identify the relationship between mass and chemical components in both $PM_{2.5}$ and $PM_{2.5-10}$. Statistically good correlation was obtained between sulfate and nitrate in both $PM_{2.5}$ and $PM_{2.5-10}$ at PRB and SPA (R $\geq$ 0.7). SO_4^{2-} and NO_3^- species may have had similar formation and removal processes. SO_4^{2-}/NO_3^- ratios were higher during hot and wet periods (2.3 to 5.3) than cold and dry period (1.0–4.0) in $PM_{2.5}$. This may suggest that sulfate is more stable than nitrate during long-range transport (Abdalmogith and Harrison, 2006).

The average SO_4^{2-}/NO_3^- ratio were about three times higher at PRB (2.3) in the spring than at SPA (0.7) in the winter season, in $PM_{2.5-10}$. The volatilization of nitrate in the aerosol has been reported in the literature and the winds bringing sulphate derived from sea salt can increase these ratios (Yin and Harrison, 2008; Rastogi and Sarin, 2009).

Ammonia reacts with acids present in the atmosphere mainly in the fraction $\geq$ 2.5 μm to form compounds of ammonium. The ammonium is primarily associated with sulfate aerosol, and ammonium nitrate is unstable at higher temperature (Maenhaut *et al.*, 2008). The highest correlation coefficient was obtained between sulfate and ammonium (r = 1.0). The average NO_3^-/NH_4^+ ratio was higher at SPA for both $PM_{2.5}$ (1.4) and $PM_{2.5-10}$ (4.0) than for PRB, 0.9 and 0.4 (Table 4). The concentration of nitrate increased in relation to ammonium in dry and low temperatures periods confirming the nitrate stability in cold season and loss in the warm season.
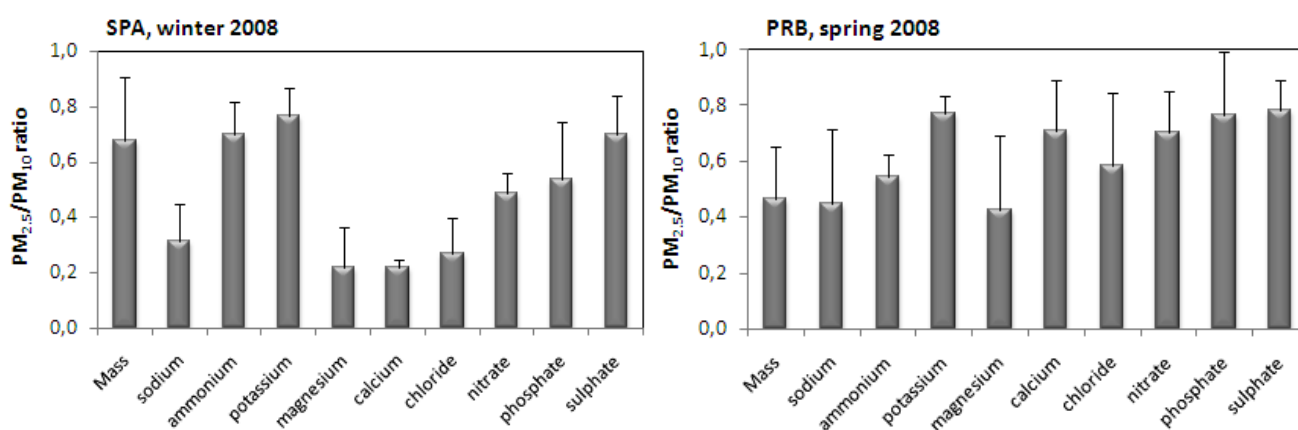

Fig. 4. Ratios of $PM_{2.5}$ to PM_{10} mass and chemical components at SPA and PRB sites.

Table 4. Average diagnostic ratios among different inorganic and organic components.

	PRB ($PM_{2.5}$)	R	PRB ($PM_{2.5-10}$)	R	SPA ($PM_{2.5}$)	R	SPA ($PM_{2.5-10}$)	R
SO_4^{2-}/NO_3^-	3.6 ± 1.0	0.7	2.3 ± 1.2	0.9	1.8 ± 1.0	0.8	0.7 ± 0.2	0.8
SO_4^{2-}/NH_4^+	2.9 ± 0.4	1.0	1.0 ± 0.7	1.0	2.2 ± 0.4	0.2	2.6 ± 1.7	1.0
NO_3^-/NH_4^+	0.9 ± 0.3	0.7	0.4 ± 0.2	0.8	1.4 ± 0.5	0.3	4.0 ± 2.3	0.3
Cl^-/Na^+	0.9 ± 0.5	0.1	2.0 ± 3.7	1.0	1.8 ± 0.9	0.6	2.3 ± 1.3	0.4
K^+/Levog.	7.2 ± 4.3	0.6	5.1 ± 4.1	0.1	3.1 ± 2.6	0.1	2.5 ± 1.2	0.1
OC/EC	2.7 ± 0.4	0.8	6.0 ± 11.9	0.1	2.3 ± 2.1	0.8	nd	nd

Cl^-/Na^+ ratio higher than 1.8 indicates sea salt contribution (Fu *et al.*, 2004). Chlorine depletion can occur by interaction with acidic species and aging by atmospheric transport (Yao *et al.*, 2003; Mkoma *et al.*, 2009).

The Cl^-/Na^+ ratio at SPA site in $PM_{2.5}$ was 1.8 and 2.3 in $PM_{2.5-10}$. The correlation matrix in $PM_{2.5}$ (r = 0.6) and $PM_{2.5-10}$ (r = 0.4) suggests source similarity and possibly from sea salt.

Furthermore, at PRB site Cl^-/Na^+ ratios were 0.9 and 2.0 in $PM_{2.5}$ and $PM_{2.5-10}$, respectively, and only coarse fraction was obtained a significant correlation (r = 1.0), suggesting that both in coarse fraction were originated by the same source. Cl^- has also other sources such coal burning (Abdalmogith and Harrison, 2006) and, especially in developing countries, burning of solid waste and biomass on small properties (Vasconcellos *et al.*, 2007).

At SPA site, in fine particles, the correlation between K^+ and Cl^- was 0.7 and between K^+ and Na^+ was 0.6. Chlorine, sodium and potassium correlation in the fine particulate, suggested that these species were originated from biomass burning. Ca^{2+} and Mg^{2+} are dust tracers and presented good correlation in $PM_{2.5}$ and coarse fraction (0.8 and 0.9, respectively) only at PRB site. The correlation Na^+ and Ca^{2+} and between Na^+ and Mg^{2+} were also high (0.8 and 0.7) in $PM_{2.5}$ at this site. Ca^{2+} and Mg^{2+} highly correlated with Na^+ in both coarse and fine particles mode suggest the contribution of resuspended soil and long-range atmospheric transport (Kawamura *et al.*, 2007).

The K^+/levoglucosan ratios found at PRB (7.2) was higher than at SPA site (3.1) in $PM_{2.5}$. These values obtained were comparable with those reported by Caseiro *et al.* (2009) for agricultural (7.4) and forest fires (1.8–8.7). The region of Piracicaba presents large agricultural activities besides the sugarcane burning. Biomass burning is a major source of potassium but can be also originated from fossil fuel burning, biogenic origin and soil dust. The correlation between levoglucosan and K^+ and between oxalate, OC and Cl^- found in this study (0.5–0.9), enhance the contribution of biomass burning often observed at this region and long transport affecting SPA site.

The oxalate correlation with SO_4^{2-}, NO_3^- and NH_4^+ in the $PM_{2.5}$ samples collected at SPA (r = 0.6) indicated secondary aerosol formation and contribution of vehicle emissions.

Previous studies in São Paulo indicated that the vehicular emission might be the major primary source of acetate, whereas formate appeared to be formed through photochemical reactions during the daytime, mainly in gas-phase (Souza *et al.*, 1999; Montero *et al.* 2001).

The ratio formate-to-acetate indicates the formation and main emission source of these species in atmospheric aerosol. These ratios at SPA site indicated the contribution of photochemical activity and *in situ* formation in all sampling period in both fractions (range 1–28) suggesting that the sources and formation processes are similar.

Measurements of total OC and EC are needed to assess the relative and absolute contribution of carbonaceous species to atmospheric aerosols, and to provide a basis for the determination of mass balance for organic compounds

(Viidanoja *et al.*, 2002). The average ratios of OC/EC at sites investigated were > 2 (from 2.3 to 2.8) and the correlation coefficients were good (from 0.6 to 0.8) in $PM_{2.5}$. Secondary formation of OC seems to contribute to the organics fraction (Wang *et al.*, 2006; Miyazaki *et al.*, 2009). Moreover, these results might suggest that either both are derived from the same emission sources or different ones but continuous (Rastogi and Sarin, 2009).

Previous studies confirm that fossil-fuel combustion emits predominantly EC and presents anthropogenic and biogenic sources and proportions of OC highly variable (Pöschl, 2005).

CONCLUSIONS

Long-range transport of the particulate matter during sugar cane burning period contributed to the increase of $PM_{2.5}$ and PM_{10} concentrations of the samples collected at SPA.

Meteorological conditions influenced the concentration levels of sulfate and nitrate in coarse particles at SPA site. Besides, $PM_{2.5}$ concentration was also influenced by humidity and temperature.

Sulphate, nitrate, ammonium, elemental carbon and particulate organic material were major components of the total $PM_{2.5}$ and $PM_{2.5-10}$.

The presence, correlation and ratio between SO_4^{2-} and NO_3^- in the fine particulate, indicates strong influence of vehicle emissions for $PM_{2.5}$ and $PM_{2.5-10}$ and the stability of nitrate.

The high correlation between SO_4^{2-}, NO_3^-, and NH_4^+ confirms the *in situ* secondary formation of these species. Cl^-/Na^+ ratio at SPA site in $PM_{2.5}$ was different from the other sites where chloride depletion can indicate several sources beyond sea salt.

The occurrence of levoglucosan and its correlations with potassium confirm the contribution of local biomass burning (at PRB) and long-range transported particles at SPA. OC/EC ratios and the correlation coefficients indicated secondary formation of OC at sites.

Further studies are necessary for better understanding of atmospheric chemistry of species emitted by different emissions sources including the combustion of alternative fuel.

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