Comparative study of the atmospheric chemical composition of three South American cities

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ABSTRACT

PM_{10} samples were collected in 2008 at three sites in South America in the framework of an international project (South American Emissions Megacities, and Climate; SAEMC). The concentration of metals, metalloids, ion and organic compounds of most PM_{10} samples collected at three sites (Buenos Aires (BAI), Bogotá (BOG) and São Paulo (SPA)) is below the air quality standard of the respective countries. At the sites n-alkanes and carbon preference index distribution indicated the influence of petroleum residues derived from vehicular emissions. Most PAH detected are attributed to light-duty gasoline vehicles and to stationary sources. At all sites benzo[a]pyrene equivalent values mean a significant cancer risk. Sulfate, nitrate, ammonium, calcium and sodium are the most abundant water-soluble ions at the three sites. Ammonium sulfate is likely the form presented for these species formed by photochemical reactions of precursors emitted mainly by vehicles. At BAI and SPA, formate/acetate ratios indicated the contribution of photochemical reactions; on the contrary, at BOG site, acetate is predominant, indicating strong contribution of vehicular emissions. São Paulo samples showed the highest concentrations of elements among all the sites. None of the toxic or potentially toxic elements exceed the guideline values of the World Health Organization. At BAI site earth crust seems to be the major source of Fe and Mn; at SPA, anthropogenic source is responsible for Pb and Zn presences. Traffic related element is well correlated at the three sites.

1. Introduction

The issue of urban air quality is receiving increasing attention as a growing share of the world's population is now living in urban centers and demanding a cleaner urban environment. The exposure to certain atmospheric compounds is responsible for potential harmful effects on human health and the environment. Although organic compounds have a high contribution (10–70%) in the atmospheric aerosol mass, their determination still needs more investigation since they take part in a complex mixture of different classes of compounds.

The atmosphere over South American cities is influenced by a variety of emissions sources. Some cities like São Paulo (Brazil) and Bogotá (Colombia) are strongly influenced by local emissions while others like Santiago (Chile), weather and topographic conditions are also important (Zárate et al., 2007). Buenos Aires atmosphere differs from the others because there is no accumulation of gas pollutants. Due to the proximity of the La Plata River, the action of winds and the flat topography, the atmosphere is cleaned during the night.

In addition to the organic compounds, metals and metalloids constitute hazardous elements for human health and the environment; their release from airborne particulate matter can eventually affect human health since they can be adsorbed into lung tissues during breathing.

This paper discusses the results obtained in the framework of an international project (South American Emissions megacities, and climate project (SAEMC, http://saemc.cmm.uchile.cl/)) focused on the study of different aspects of emissions and climate in South American Megacities.

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2. Sampling sites

Atmospheric particulate matter was collected at three cities, São Paulo (SPA), Bogotá (BOG) and Buenos Aires (BAI) (Fig. 1): The SPA site is located at the top of a building in the University of São Paulo, in a green area, within ~2 km of a major highway carrying heavy traffic consisting of gasohol, diesel and ethanol fueled vehicles. The sampling was carried out during dry season in 2008 (August 7th to 29th, $n = 11$). During the sampling period at SPA (2008), 2455 fires were observed in the São Paulo State. The capital city of Colombia, Bogotá, is the largest city with approximately 8 million inhabitants and about 1.2 million vehicles. PM_{10} samples were collected at BOG site between November 24th and December 9th, 2008 ($n = 15$). In Buenos Aires the samples were collected on the roof of a building at Comisión Nacional de Energía Atómica at an elevation of 12 m, over 15 m distance from a highway, between August 13th and September 15th, 2008 ($n = 14$). The city is located at approximately 300 km from the open sea and mainly influenced by emissions from residential sources and urban vehicular traffic. During the sampling time burning plumes were observed coming from the North of the country.

3. Meteorological conditions

São Paulo State presents an upland tropical climate with a dry season during wintertime. Monthly winter temperatures are around 16 °C (from June to August). The local circulation is given mainly associated with the Atlantic Ocean breeze. There are often polar mass arrivals associated with cold front systems that can intensify the circulation coming from southeast. No rain episodes were observed during the sampling days. The temperatures ranged between 21 and 24 °C, and the wind speed between 0.8 and 2.6 m s^{-1}. The climate in Bogotá is characterized by a bimodal precipitation regime with stronger rains in March and April as well as in October and November. Annual average wind speed is about 1 km h^{-1}. During the sampling campaign, temperatures varied from 12 °C to 16 °C (average 12.9 °C). Most of these days were dry and the wind speed varied between 2.0 and 13.0 km h^{-1} (DAMA, 2006). Climate in Buenos Aires presents the four seasons well defined. Mean maximum temperatures are recorded in January ~30 °C, whereas the minimum is ~7 °C in July. The minimum precipitations are recorded between June and September. During the sampling period the mean variables recorded were: temperature, 13.3 °C; relative humidity, 75%; and wind intensity 3.1 m s^{-1}.

Samples in Buenos Aires and SPA were collected in August 2008 whereas the field campaign in Bogotá took place in Nov/Dec 2008. Different dates were chosen for the campaigns due to different cities' latitude and meteorological conditions. The three cities are mainly impacted by pollution in the wintertime (BOG, Nov–Jan; SPA and BAI, Jun–Sep). PM concentrations have proven to be affected by meteorological parameters such as wind speed, wind direction and ambient temperature. In general, the higher the wind speeds, the lower the ambient PM concentrations. Daily variations in meteorological conditions, which control the formation, transport and removal of airborne sulfate, have a significant influence on short-term variations in sulfate concentrations and contribute to high-frequency variations in sulfate time series. According to Seinfeld and Pandis (1996) depending on the ambient temperature, relative humidity, and the amounts of each species, semi volatile HNO_3 and NH_3 can partition between the gas and particle phases in order to establish a thermodynamic equilibrium. This in turn will affect formation of secondary particles.

4. Analytical procedure

PM_{10} samples were collected at all sites using a high-volume air sampler and quartz fiber filters. Before sampling, filters were pre-cleaned by heating in oven for 8 h (at 800 °C). Soxhlet apparatus

Fig. 1. Sampling sites in South America.

filled with methylene chloride was used for extraction of *n*-alkanes and PAH. The samples were extracted for 24 h and concentrated on a rotary evaporator. Then, a fractionation was used to obtain the individual compounds classes. The procedure is described elsewhere (Vasconcellos et al., 2010). Quantitative and qualitative analyses were carried out by gas chromatography with flame ionization detection (Varian 3800). A fused-silica capillary column, DB-5 (30 m × 0.25 mm I.D., 0.25 μm film thickness) was used for separation. The chromatographic conditions were: temperatures used on the injector and detector were 250 °C and 290 °C, respectively; temperature ramp: 40 °C (1 min); 40–150 °C (10 °C min^{-1}); 150–290 °C (5 °C min^{-1}); 290 °C (30 min). Nitrogen was the carrier gas. A 1 μL sample was injected in split less mode. Thirteen compounds of the 16 major PAH listed by the USEPA as priority pollutants were analyzed. The PAH according to their elution order were: Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Benzo[*a*]anthracene (BaA), Chrysene (Chr), Benzo[*b*]fluoranthene (BbF), Benzo[*k*]fluoranthene (BkF), Benzo[*e*]pyrene (BeP), Benzo[*a*]pyrene (BaP), Indeno[*cd*]pyrene (InP), Dibenzo[*ah*]anthracene (DBA) and Benzo[*ghi*]perylene (BPe). Concentrations of low molecular weight PAH compounds were not considered in this work due to the low reproducibility of their results (recovery ≤ 50%).

For ion determination the filter was extracted with 20 ml of ultra pure deionized water added to a flask containing the filter. Following shake extraction and membrane filtration of the extracts were analyzed for anion and cation contents. The recovery of the species was from 81% to 100% for carboxylic acids, 71 to 95% for *n*-alkanes, 77 to 104% for PAH, 102% to 116% for anions and 91% to 111% for cations. Detection limits ranged from 9.1 to 48.5 ng m^{-3}, 11.5 to 47.6 ng m^{-3}, 1.2 to 16.1 ng m^{-3}, 0.04 to 0.13 ng m^{-3}, 0.1 to 0.3 ng m^{-3} for the inorganic ions, cations, organic acids, *n*-alkanes and PAH, respectively.

For metals and metalloids determination filters were digested using a mixture of nitric and hydrofluoric acids (8:2) applying a microwave optimized procedure described elsewhere (Marrero et al., 2007). The solution obtained was evaporated up to about 5 ml and made up to 25 ml with deionized water. The resulting solutions were analyzed by ICP OES and the content of Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, S, Sb, Ti and V was determined. Enrichment factor (EF) is a useful index employed to estimate how enriched is an element in the airborne particles related to its concentration in the earth's crust. Titanium was used as the reference element. A value of EF <10 indicates that the composition of the particles is consistent with that expected if they were formed by erosion of the earth's surface, and if EF >10 there is an anthropogenic influence.

$$EF_X = (X/E)_{sample} / (X/E)_{reference\ soil} \qquad (1)$$

Where *X* sample is the concentration of the element under consideration and *E* is the concentration of the chosen reference element. The subscripts sample and reference soil indicates which medium the concentration refers to.

5. Results and discussion

5.1. PM$_{10}$ chemical composition

Mean PM$_{10}$ concentrations at SPA site were 64 μg m^{-3} (Table 1). This value is comparable to those found in winter by the São Paulo Environmental Agency (60 μg m^{-3}, CETESB, 2008) and is lower than daily standard for Brazilian cities (150 μg m^{-3}). The sampling was conducted during the sugarcane burning season that occurs in the vicinities of the city. This pollution is frequently transported to São

Table 1
n-alkanes average concentrations found at the sites.

n-alkanes (ng m^{-3})	BOG (mean ± SD)	BAI (mean ± SD)	SPA[b] (mean ± SD)
C$_{16}$	0.7 ± 0.9	3.1 ± 1.1	0.5 ± 0.1
C$_{17}$	1.3 ± 1.2	5.2 ± 1.7	1.1 ± 0.5
C$_{18}$	2.6 ± 3.8	6.3 ± 2.2	1.5 ± 0.5
C$_{19}$	0.8 ± 1.4	6.5 ± 2.7	1.2 ± 0.7
C$_{20}$	1.4 ± 1.8	6.3 ± 2.6	1.2 ± 0.5
C$_{21}$	2.3 ± 2.4	7.2 ± 3.0	1.4 ± 0.7
C$_{22}$	2.4 ± 2.8	10.0 ± 4.4	2.2 ± 0.9
C$_{23}$	8.9 ± 6.1	11.8 ± 5.9	3.2 ± 1.2
C$_{24}$	2.4 ± 2.4	11.9 ± 5.5	4.5 ± 2.0
C$_{25}$	1.1 ± 1.0	16.8 ± 4.8	5.5 ± 3.1
C$_{26}$	4.1 ± 5.3	19.4 ± 5.9	3.7 ± 2.0
C$_{27}$	2.3 ± 2.6	22.3 ± 5.8	5.8 ± 3.4
C$_{28}$	1.4 ± 1.5	19.0 ± 5.2	5.9 ± 4.0
C$_{29}$	0.8 ± 0.7	22.8 ± 6.5	6.6 ± 4.7
C$_{30}$	1.0 ± 0.7	16.6 ± 5.0	5.5 ± 4.5
C$_{31}$	0.6 ± 0.5	12.6 ± 3.4	5.5 ± 3.7
C$_{32}$	0.4 ± 0.3	9.2 ± 3.1	4.2 ± 3.2
C$_{33}$	0.3 ± 0.2	5.9 ± 2.7	4.2 ± 3.5
C$_{34}$	0.6 ± 0.5	4.6 ± 3.1	1.9 ± 2.7
C$_{35}$	nd	2.9 ± 1.5	2.1 ± 2.8
Total	37.6 ± 38.9	229.1 ± 47.4	67.3 ± 40.2
Pristane (ng m^{-3})	0.6 ± 0.5	5.2 ± 1.8	1.1 ± 0.6
Phytane (ng m^{-3})	1.7 ± 2.6	4.0 ± 1.4	0.9 ± 0.5
CPI	1.2 ± 0.7	1.1 ± 0.1	1.2 ± 0.4
C$_{max}$	C$_{23}$	C$_{29}$	C$_{29}$
U/R	10.2	8.2	11.3
% WNA[a] in PM	0.13	1.13	0.38
PM$_{10}$ (μg m^{-3})	47 ± 12	61 ± 49	64 ± 19

[a] % Plant wax *n*-alkanes (%WNA) = ((WNA/24.3105)/PM) × 100 (Rogge et al., 1993).
[b] *n*-alkanes, PAH and ions concentrations published recently (Vasconcellos et al., 2010).

Paulo city and has a significant influence on its air quality conditions.

In Bogotá, standard value for PM$_{10}$ is 143 μg m^{-3} (24 h) and the average PM$_{10}$ concentration in this sampling period was over 47 μg m^{-3}. The air quality standards of PM$_{10}$, O$_3$ and NO$_2$ are frequently exceeded. In 2001, PM$_{10}$ standard values were exceeded 510 times out 98,612 hourly measurements in 14 monitoring stations reaching the maximum of 225 μg m^{-3} (Zárate et al., 2007).

In Buenos Aires the mean PM$_{10}$ concentration was 61 μg m^{-3}, higher concentration than those were found in 1997 (49–59 μg m^{-3}), between 1998 and 1999 in summer (52 μg m^{-3}) and in winter (44 μg m^{-3}) (Bogo et al., 2003). The standard value for PM$_{10}$ is 150 μg m^{-3} (24 h) and only in two samples was exceed.

Data of *n*-alkanes, PAH and ions obtained at SPA site was published recently (Vasconcellos et al., 2010) and are compared with those obtained at BAI and BOG sites.

At São Paulo the average concentration of total *n*-alkanes varied from 32.5 to 164.2 ng m^{-3} (average 67.3 ng m^{-3}). The CPI values measured indicate a major contribution from petroleum residues derived from vehicular emissions. It can be observed from Fig. 2 a strong odd carbon number predominance, with C$_{max}$ at C$_{29}$, which is characteristic of wax from plants. In Buenos Aires the concentration of total *n*-alkanes ranged from 141 to 298 ng m^{-3} (average 229.1 ng m^{-3}). The distribution of the homologous showed an odd carbon predominance, with C$_{max}$ at C$_{29}$, associated with biogenic source. The CPI values close to 1 indicated petrogenic input. At the Bogotá site the average concentration of total *n*-alkanes ranged from 6.4 to 112.3 ng m^{-3} (37.6 ng m^{-3}). Like the other two sites, the CPI near unity exhibits the importance of petroleum and diesel residues and gasoline emissions. The C$_{max}$ at BOG was C$_{23}$ and C$_{26}$ respectively, indicated once more the presence of *n*-alkanes emitted by fossil fuel burning. The unresolved complex mixture (UCM) of branched and cyclic hydrocarbons is
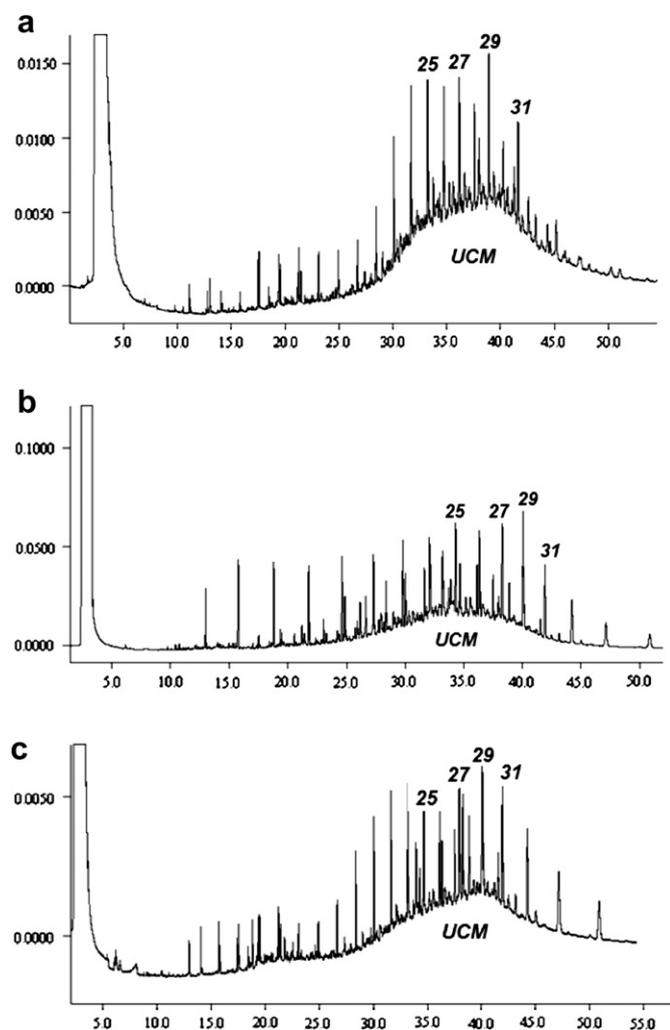
Fig. 2. Chromatograms for *n*-alkanes samples in each site studied: a) SPA; b) BAI; c) BOG.

derived from fossil fuel utilization (i.e., the major components of diesel and auto engine exhaust, the lubricant oil) (Simoneit et al., 2007). In all samples from SPA, BAI and BOG, the UCM (Fig. 2) indicates a contamination by petroleum residues.

The ratio of the unresolved to resolved hydrocarbon compounds (U/R) is a diagnostic parameter that can be used to evaluate the extent of petroleum contributions to atmospheric aerosols (Bi et al., 2008). The U/R values (Table 1) were comparable to that found in urban Brazilian areas (0.9–25) (Azevedo et al., 1999) and are attributed to vehicular emissions (>4.0; Kavouras et al., 2001). Comparing the sites, SPA presented higher value (11.3) than the other sites (BOG 10.2 and BAI 8.2) despite the frequent changes in the fuel mix by alternative fuels. Unresolved mixtures contain branched and cyclic hydrocarbons derived mainly from fossil fuel combustion; no study yet showed the composition of the unresolved compounds emitted by mixtures of fossil and alternative fuels.

The contribution of *n*-alkanes derived from plants wax in PM_{10} was calculated (Rogge et al., 1993a). At SPA samples 0.38% of PM_{10} mass are biogenic *n*-alkanes and at BOG and BAI these fractions are 0.13% and 1.13% respectively. SPA site is a highly urbanized area with heavy vehicles traffic, and it contains a small forest. BAI site seems to be the site most influenced by biogenic *n*-alkanes. The isoprenoids hydrocarbons pristane and phytane were identified in

the fraction from *n*-alkanes. They are present in diesel fuel, lubricating oil, and in both auto and diesel engine exhaust. The levels were very variable from site to site. The presence of pristane and phytane together with the UCM confirm the contamination by petroleum residues. Pristane/phytane ratio much higher than 1 is an indicative of biogenic origin of pristane. BAI and SPA site presented values close to 1 and BOG presented a value even lower (0.4).

At São Paulo the PAH total concentration was 25.9 ng m^{-3} (Table 2), much lower results were obtained the winter of 2000 (av. 3.1 ng m^{-3}, Vasconcellos et al., 2003) and comparable levels were found in 2003 (27.4 ng m^{-3}, Vasconcellos et al., in press).

The question replacing the use of gasoline by alcohol has generated many important discussions concerning air quality. Abrantes et al. (2009) reported that PAH emissions from the ethanol vehicle were on average 92% lower than PAH emission from the gasohol vehicle. The estimative are that 50% of the vehicular fleet is using hydrated ethanol. On the other side, an increasing number of vehicles are observed in the metropolitan area of São Paulo, with 7.2 million vehicles. In Buenos Aires PAH total average concentration was 16 ng m^{-3}, and at Bogotá 15 ng m^{-3}. BAI and BOG sites presented good conditions for pollutant dispersion, wind speed over 3.7 and 4.8 m s^{-1} respectively. The most abundant PAH at the different sites are: BkF > Ant > BeP at SPA, DBA > BbF > BkF = BPe at BAI and BPe > Pyr > BkF at BOG. Marr et al. (1999) found that light-duty gasoline vehicles were the dominant sources of higher molecular weight PAH. BOG samples presented the highest BPe average concentration (4.3 ng m^{-3}). This PAH was specifically used as vehicular emission tracer in previous studies (Cincinelli et al., 2003). DBA, more abundant PAH at BAI than at other sites is pointed out as ten times more carcinogenic than BaP (Okona-Mensah et al., 2005), and its emission is attributed to stationary sources. BaP, mutagenic compound found in all samples presented the highest average concentration at SPA (1.4 ng m^{-3}). In 2000, much lower concentration was found at SPA site (280 pg m^{-3}) in total particulate matter (Vasconcellos et al., 2003). Benzo[*a*]pyrene-equivalent carcinogenic power (BaPE) is an index that has been used instead of using only benzo[*a*]pyrene since the latter is easily decomposed in reactive air (Yassaa et al., 2001). It indicates the health risk for humans related to ambient PAH exposition and is calculated by multiplying the concentrations of each carcinogenic congener. The ranges for each site are presented in Table 1. BaPE presented the values at SPA 1.1–12.1 and BAI 2.5–3.0 and at Bogotá site 0.8–4.4. At all sites the average value for BaPE were above 1.0 ng m^{-3}, which means a significant cancer risk.

Table 2
PAH average concentrations found at the sites.

PAH	BOG (mean ± SD)	BAI (mean ± SD)	SPA (mean ± SD)
Phe	1.6 ± 1.7	1.0 ± 0.6	2.0 ± 0.8
Ant	1.2 ± 1.0	1.2 ± 0.6	2.6 ± 1.5
Fla	0.6 ± 0.1	1.2 ± 0.3	2.2 ± 2.6
Pyr	2.5 ± 2.8	0.8 ± 0.2	1.6 ± 0.7
BaA	1.0 ± 0.5	0.9 ± 0.2	1.4 ± 1.3
Chr	0.4 ± 0.1	0.9 ± 0.3	1.6 ± 1.0
BbF	0.8 ± 0.7	1.6 ± 0.6	2.4 ± 1.6
BkF	1.7 ± 0.9	1.5 ± 0.4	2.9 ± 3.6
BeP	0.8 ± 0.2	1.1 ± 0.3	2.5 ± 2.5
BaP	0.7 ± 0.2	1.0 ± 0.1	2.2 ± 2.1
InP	1.1 ± 0.8	1.2 ± 0.3	1.4 ± 1.1
DBA	0.9 ± 0.1	2.1 ± 0.1	1.1 ± 0.6
BPe	4.3 ± 2.1	1.5 ± 0.5	1.6 ± 0.2
Total	15.0 ± 6.0	16.0 ± 2.0	26.9 ± 16.4
BaPE[a]	0.8–4.4	2.5–3.0	1.2–12.1

[a] BaPE = BaA × 0.06 + B(b + k)F × 0.07 + BaP + DBA × 0.6 + InP × 0.08 (Yassaa et al., 2001).

Table 3
Water-soluble ions average concentrations found at the sites.

Ions	BOG (mean ± SD)	BAI (mean ± SD)	SPA (mean ± SD)
Inorganic anions (ng m^{-3})			
F$^-$	<DL	17 ± 2	10 ± 6
Cl$^-$	89 ± 152	397 ± 198	942 ± 508
NO$_2^-$	2 ± 1	<DL	11 ± 3
Br$^-$	<DL	92 ± 9	12 ± 5
NO$_3^-$	618 ± 31	821 ± 506	3681 ± 1887
PO$_4^{3-}$	<DL	37 ± 29	52 ± 14
SO$_4^{2-}$	1338 ± 844	1308 ± 470	4375 ± 2106
Total	2046	2525	9083
Organic anions (ng m^{-3})			
Acetate	24 ± 26	39 ± 48	40 ± 11
Formate	95 ± 52	71 ± 84	78 ± 39
Oxalate	152 ± 80	68 ± 45	250 ± 94
Fumarate	<DL	<DL	25 ± 7
Succinate	24 ± 10	4 ± 5	53 ± 24
Glutarate	ND	ND	31 ± 3
Total	210	182	250
Cations (ng m^{-3})			
Na$^+$	696 ± 60	542 ± 379	445 ± 215
NH$_4^+$	635 ± 504	559 ± 389	2084 ± 1255
K$^+$	88 ± 29	170 ± 133	634 ± 224
Mg^{2+}	40 ± 17	80 ± 38	130 ± 37
Ca^{2+}	792 ± 369	1090 ± 391	884 ± 374
Total	2250	2442	4176

<DL = below detection limit. ND = not detected.

If only BaP were taken into account, the carcinogenic power from PAH would be underestimated. PAH have significant variation in their composition due to the diversity in combustion sources, thereby emission sources are identified from diagnostic ratios. These ratios were calculated and compared with those cited by the literature. Most of the fresh exhausts have similar contents of benzo[e]pyrene and benzo[a]pyrene. BeP/(BaP + BeP) ratio indicates the influence of atmospheric reactivity on particulate organic matter composition, since BeP is much more inert and BaP is easily decomposed by light and oxidants. The values measured in this study at all sites were near 0.5, indicating the local or fresh emission of particulate matter. BaA/Chr ratios obtained at SPA (0.80) and BAI (1.10) sites fall in the range found for gasoline combustion (0.28–1.2) and coal combustion only at BAI site (1.10) (Rogge et al., 1993b; Stroher et al., 2007; Li and Kamens, 1993). BaA/(BaA + Chr) ratios at BAI site (0.50) fall inside the range found for wood combustion (0.48–0.54, Rogge et al., 1993b; Stroher et al., 2007; Li and Kamens, 1993). High ratio was found for SPA samples (2.63). PAH emitted from wood combustion at SPA were observed in previous studies (Vasconcellos et al., 2003, 2010), and may have been long-range transported from the surrounding rural areas. BbF + BkF/BPe ratios from 2.00 (BOG) to 3.11 (SPA) seem to be a signature of domestic soot for all samples studied (1.5–14.0, Smith and Harrison, 1996).

Of all water-soluble ions SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ were the most abundant at SPA; for BAI site SO$_4^{2-}$, Ca^{2+} and NO$_3^-$, for BOG SO$_4^{2-}$, Ca^{2+} and Na$^+$ (Table 3).

The amount of SO$_4^{2-}$ and NH$_4^+$ presented large variations at the sites. Correlation between them is moderate ($R > 0.6$). Ammonium sulfate is likely the form presented for these species formed by photochemical reactions of precursors emitted by vehicular emissions. BAI site presented relatively higher concentrations of other species (F$^-$, Cl$^-$, Br$^-$, PO$_4^{3-}$, Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}) (Fig. 3).

SPA site presented the highest average formate/acetate ratio (1.9). This can be associated with the increasing formation of these species due to frequent events of air pollution originating pollutants by photochemical reactions often observed during the dry winter with intense solar radiation. At BOG this ratio (0.4) showed that direct emissions were more important than photochemical reactions in the formation of acetate and formate. SPA presents higher Cl$^-$/Na$^+$ ratios (1.4–7.1) than BAI (0.1–1.5) and BOG (0.1–0.3) sites. Ratios close to 1.8 point to sea salt contribution (Maehaut et al., 2008). On the other hand chloride can be depleted in presence of acidic species like NO$_3^-$ and SO$_4^{2-}$ resulting in low ratios as those observed in most samples from BAI ($n = 13$) and BOG ($n = 15$).

Levoglucosan and K$^+$ correlation were 0.6 for SPA and 0.8 for BAI sites. At these sites air mass transport of these species are expected due to the biomass burning in the vicinities of São Paulo often observed during the winter, and the biomass burning observed during the sampling days arriving at BAI site.
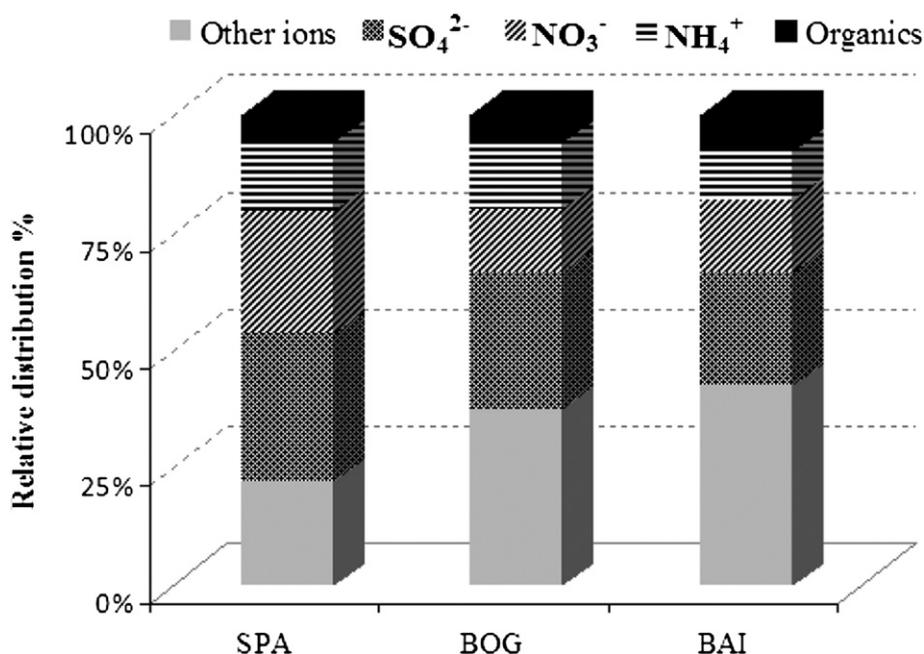

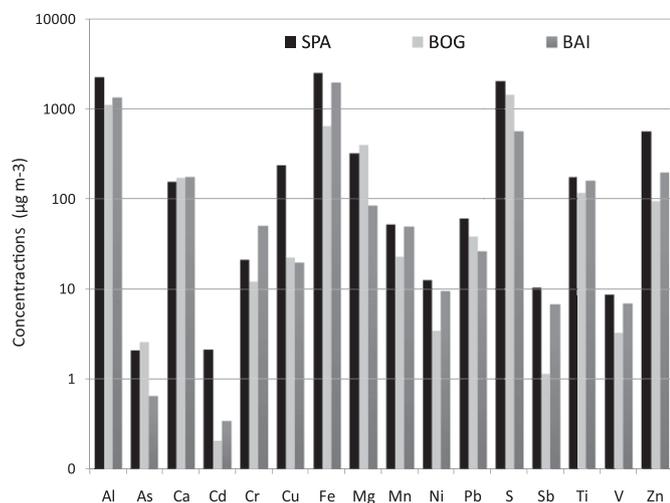**Fig. 3.** The proportion of different species among the sites.

Fig. 4. The average total concentrations (ng m^{-3}) of metals and metalloids.

SO_4^{2-}/NO_3^- close to 2.0 were found for BAI (0.4–5.9, av. 2.1) and BOG samples (0.9–5.9, av. 2.0). At SPA site this ratio was lower (0.7–2.2, av. 1.2). At BOG site higher ratios were found in few samples may be due to the NO_3^- volatilization that occur under higher temperatures (Rastogi and Sarin, 2009).

NH_4^+ reacts with SO_4^{2-}, NO_3^- and Cl^- forming salts. Good correlation ($R > 0.7$) of oxalate with NO_3^-, SO_4^{2-} and NH_4^+ only in SPA samples can indicate secondary formation and vehicular contribution.

SPA also presented higher organic anions content (250 ng m^{-3}) than BAI site (182 ng m^{-3}) and BOG (210 ng m^{-3}). The atmospheric sources of carboxylic acids are numerous and a large number of production pathways are presented in the literature (Chebbi and Carlier, 1996). In this work, formate average concentration is higher than acetate at three sites (Table 1). Secondary photochemical production of formate and acetate rather than primary emissions from vehicles is more important at these sites. Formate and acetate are weakly correlated at BAI and BOG sites suggesting that the emissions sources and formation processes of these acids are different, differently of SPA when high correlation ($R = 0.9$) was found. At SPA and BOG sites, oxalate was the most abundant organic anion, 250 ng m^{-3} for SPA, 152 ng m^{-3} for BOG and

68 ng m^{-3} for BAI (Table 1). SPA presented the highest value but still lower than that reported previously (0.480 μg m^{-3}) conducted at the same site in the wintertime, when high pollution events were observed (Souza et al., 1999) and sugarcane burning affected the local air quality. Many reactions forming oxalate at urban site are reported and direct emissions from vehicles, biogenic activity and biomass burning have also been proposed (Kawamura and Kaplan, 1987). The main air pollution source in the São Paulo metropolitan area has been attributed to vehicular emission. The addition of ethanol to motor vehicle fuels reduces carbon monoxide (CO) but increases aldehyde emissions (especially acetaldehyde), inducing a unique photochemical smog problem in urban areas. Previous studies at SPA site showed that approximately 98% of the total acetic and formic acids were in the gas-phase and the gas–aerosol equilibrium was influenced by high relative humidity (Souza et al., 1999). Gaseous formic to acetic acid ratio fell in the 0.94–1.85 range in this study and ratio higher than that (average 4.3) was found at same site in the winter 1999 (Montero et al., 2001). Photochemical production appeared to be the major source of these species in the gaseous phase. Other carboxylic acids were also detected. Succinate ion was found at three sites and glutarate only at the SPA and fumarate at SPA and BAI at low concentrations. Dicarboxylic acids have received attention because of their role in the global climate. Their hygroscopic property can affect the cloud formation and global radiation reaching the ground (Kerminen, 1997).

Toxic elements Cd, Mn, Pb and V have been determined in all samples and their concentrations resulted to be 2.1, 52.2, 61.6 and 8.9 in SPA; 0.2, 23.1, 38.4 and 3.3 in BOG and 0.3, 49.1, 26.2 and 7.0 ng m^{-3} in BAI, respectively. It's important to emphasize that these elements reach no guideline values of the World Health Organization (WHO, 2000). Fig. 4 shows the concentration of Al, As, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, S, Sb, Ti and V measured for the three cities.

Aluminum, Fe, Mg, S, Ti and Zn were the elements found at higher concentration in the three cities, average concentrations exceed the 500 ng m^{-3}. São Paulo showed the higher concentrations for major and several trace elements among the cities. Average concentrations within the range 20–400 ng m^{-3} were measured for Mg (except for Buenos Aires) > Cu (only for São Paulo) > Ti > Ca. Calcium and Ti also exhibited a comparable concentration among the cities. None of the toxic or potentially toxic elements exceed the guideline values of the World Health Organization (2000). In Buenos Aires city Fe and Mn are
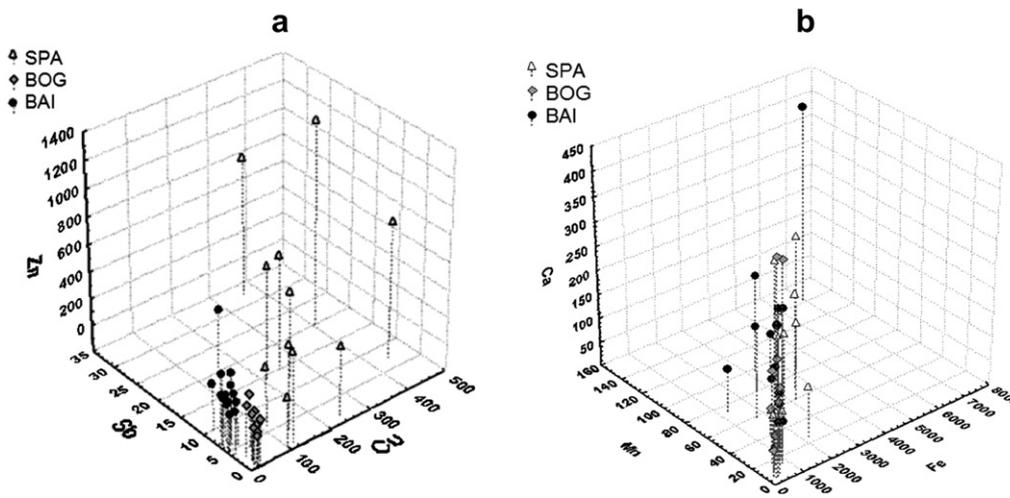

Fig. 5. Correlations a) among three typical traffic related elements and b) among typical geological elements.

correlated with a ($R = 0.6$) being consistent with the results reported by Fujiwara et al., (2006). The EF's for Fe and Mn in Buenos Aires resulted to be 1.23 and 1.86 respectively indicating the Earth crust as the main source. In Bogotá the elements that presented significant correlations were: Fe–S ($R = 0.9$), Fe–V ($R = 0.8$), Fe–Mn ($R = 0.8$) and Fe–Ti ($R = 0.8$). In São Paulo, Pb and Zn correlated ($R = 0.9$). This relation confirms the traffic as a major source. In effect, Pb is a traffic tracer being a natural component in automotive fuels. On the other side, Zn is present in tires (as Zinc oxide and Cu/Zn sulphide layers) and in brake pads. Copper, Sb, and Zn are tracers of this source and were determined for studying their presence in the atmosphere of these cities. Levels of Sao Paulo traffic related elements are nearly separated in three clusters, being in the order: Bogotá < Buenos Aires < São Paulo as can be seen in Fig. 5. Significant correlations (at $p < 0.05$) were found for Cu: Sb in the three cities, Sb:Zn for São Paulo and Bogotá, and Cu:Zn only for São Paulo. Fig. 5a shows the correlation among three typical traffic related elements (Cu, Sb and Zn). In addition, it can be seen that the results of each individual city presents a lower variability. As expected, the earth related elements (Ca, Fe and Mn) are widespread and present more variability in comparison with the anthropogenic elements (Fig. 5b).

Since 2001, a series of studies have been carried out and aimed to assess the content of target elements in PM$_{10}$ collected at the metropolitan area of Buenos Aires by employing the same sampler device and analytical techniques used in this work (Smichowski et al., 2004; Bocca et al., 2006; Dos Santos et al., 2009). In general terms, the concentration of Al (936 ng m^{-3} in 2001 *vs* 1336 ng m^{-3} in 2009), Cu (22 ng m^{-3} in 2001 *vs* 20 ng m^{-3} in 2009), Pb (25 ng m^{-3} in 2001 *vs* 26 ng m^{-3} in 2009) and Sb (5 ng m^{-3} in 2001 *vs* 7 ng m^{-3} in 2009) are comparable between both monitoring campaigns. On the contrary, significant differences were observed for Ca (1243 ng m^{-3} in 2001 *vs* 176 ng m^{-3} in 2009) and S (3204 ng m^{-3} in 2001 *vs* 563 ng m^{-3} in 2009). Only Ca and S were the elements present at higher concentrations in 2001.

6. Conclusions

The concentration of most PM$_{10}$ samples collected at three sites is below the air quality standard of the countries. At the sites *n*-alkanes distribution indicated the influence of petroleum residues derived from vehicular emissions. The carbon preference index indicated the contribution of the fossil fuel burning. At BAI and SPA saturated hydrocarbon fractions contained predominantly *n*-alkanes with a strong odd carbon number predominance, derived from terrestrial plants. Unresolved to resolved hydrocarbon compounds ratios were similar to those found in urban areas and for vehicular emissions. At all sites benzo[a]pyrene equivalent values mean a significant cancer risk and most PAH were attributed to light-duty gasoline vehicles and to stationary sources. PAH diagnostic ratios indicated local or fresh emission of particulate matter.

Sulfate, nitrate, ammonium, calcium and sodium are the most abundant water-soluble ion at the sites. Ammonium sulfate is likely the predominant species formed by photochemical reactions of precursors emitted mainly by vehicles. Formate and acetate at BAI sites suggested that their emissions sources and formation processes may be different. At BAI and SPA, formate/acetate ratios >1 indicated a strong contribution of photochemical reactions. On the contrary, at BOG site, acetate is predominant likely due to vehicular emission.

São Paulo samples showed the highest concentrations of elements among the sites. None of the toxic or potentially toxic elements exceeded the guideline values of the WHO. At BAI site earth crust seems to be the major source of Fe and Mn; at SPA, anthropogenic source is responsible for Pb and Zn presences. Traffic related element are well correlated at the three sites.

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