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Determination of anthropogenic and biogenic compounds on atmospheric aerosol collected in urban, biomass burning and forest areas in São Paulo, Brazil

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ABSTRACT

This study was conducted at three sites of different characteristics in São Paulo State: São Paulo (SPA), Piracicaba (PRB) and Mata Atlântica Forest (MAT). PM_{10}, n-alkanes, pristane and phytane, PAHs, water-soluble ions and biomass burning tracers like levoglucosan and retene, were determined in quartz fiber filters. Samplings occurred on May 8th to August 8th, 2007 at the MAT site; on August 15th to 29th in 2007 and November 10th to 29th in 2008 at the PRB site and, March 13th to April 4th in 2007 and August 7th to 29th in 2008 at the SPA site.

Aliphatic compounds emitted biogenically were less abundant at the urban sites than at the forest site, and its distribution showed the influence of tropical vascular plants. Air mass transport from biomass burning regions is likely to impact the sites with specific molecular markers.

The concentrations of all species were variable and dependent of seasonal changes. In the most dry and polluted seasons, n-alkane and cation total concentrations were similar between the megacity and the biomass burning site. PAHs and inorganic ion abundances were higher at São Paulo than Piracicaba, yet, the site influenced by biomass burning seems to be the most impacted by the organic anion abundance in the atmosphere. Pristane and phytane confirm the contamination by petroleum residues at urban sites; at the MAT site, biological activity and long range transport of pollutants might influence the levels of pristane.

1. Introduction

It is well established that organic and inorganic compounds are emitted to the atmosphere by natural and anthropogenic sources. In the tropics biomass burning introduces to the atmosphere compounds that can be harmful to people's health due to their carcinogenic and/or mutagenic properties (Ciccioli et al., 1996; Umbuzeiro et al., 2008). In Brazil, not only forest fires have contributed to changes in the atmosphere composition but emissions from sugarcane burning and those related to the use of different fuels have been responsible for air degradation (Allen et al., 2004; Vasconcellos et al., 2007).

The determination of compounds which can be used as molecular markers is important to assess the atmospheric transport and the major emission sources. Compounds derived from natural emission and from pyrolysis of vegetation can be used as specific indicators of their emission sources. Levoglucosan and retene have been utilized as tracers for conifer smoke in urban aerosols and phenanthrene, fluoranthene and pyrene have been found abundant in biomass burning smoke (Simoneit, 2002; Magalhães et al., 2007).

Several studies have been done in São Paulo, Brazil, on atmospheric samples to study compounds that can impact human health (Sato et al., 1995; Umbuzeiro et al., 2008). However, the composition of the changing atmosphere due to mixed influences including the introduction of new fuel (biodiesel) is still poorly known.

São Paulo is the largest producer of alcohol and the Brazilian cities are implementing the biodiesel for heavy duty fleet. These different fuels can impact the air composition in a way not yet understood. This study presents the analysis of the aerosol chemical composition in different geographic regions in São Paulo State.

The major objective is to investigate the seasonal change in the particulate matter composition, the origin of organic and inorganic compounds and the long range transport influence.

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2. Experimental

2.1. Characteristics of sampling sites and sampling

Aerosol samples were collected at three sites within São Paulo State, Brazil. The first one is located in the Mata Atlântica forest (MAT, 23°14′50″S and 45°19′22″W). The site is situated 171 km from the capital (São Paulo City), and is a clean area with primary hydrocarbon emissions from vegetation. Due to the low concentrations, samples were collected for 48 h during May 8th to August 8th, 2007. The second site is in Piracicaba (PRB, 22°42′20″S and 47°38′27″W), situated at 180 km from the capital and it is characterized by intense sugarcane burning during the dry season (May to October). Samples were collected in two campaigns in the campus of the University of São Paulo (ESALQ), the first one during the sugarcane burning season, August 15th to 29th in 2007, and the other one in the beginning of the wet season, November 10th to 29th in 2008.

The third site is São Paulo City (SPA, 23°33′34″S and 46°44′01″W) and samples were collected in two campaigns at the top of the building inside the University of São Paulo, in a green area located at 2 km from the road with intense traffic of heavy and light vehicles. The sampling was carried out during wet season in 2007 (March 13th to April 4th) and dry season in 2008 (August 7th to 29th). During the sampling period at SPA (2007), 2990 fires were observed in the São Paulo State, 2455 fires during the PRB (2008) sampling period and 6045 fires during the MAT sampling period.

PM_{10} samples were collected for 24-h periods using a high-volume air sampler in a flow rate at 1.13 m^3 min^{-1}. Quartz fiber filters (20×25 cm^2) were pre-cleaned by heating in an oven at 800 °C for 8 h. After sampling filters were wrapped in an aluminum foil and stored in a freezer at −20 °C, until they were weighted and extracted.

2.2. Analytical procedure

N-alkanes and polycyclic aromatic hydrocarbon (PAH) compounds were extracted from the filters with dichloromethane using a Soxhlet apparatus for 24 h. The different fractions were obtained using a silica gel column (2.5 g) and different solvents of increasing polarity following the procedure proposed by Gogou et al. (1998). The first fraction containing the n-alkanes was eluted from the silica gel column with 15 ml of n-hexane. PAHs were eluted with a mixture of 9.6 ml of hexane and 5.4 ml of toluene and the oxygenated compounds were eluted following the procedure but are not considered in this work.

Quantitative and qualitative analyses for n-alkanes were carried out by using a gas chromatograph with flame ionization detection (GC-FID, 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 as follows: temperatures used on the injector and detector were, respectively, 250 °C and 290 °C; temperature ramp: 40 °C (1 min); 40–150 °C (10 °C/min); 150–290 °C (5 °C/min); and 290 °C (30 min). Nitrogen was the carrier gas. A 1 μL sample was injected using the splitless mode. Limits of detection ranged from 0.12 to 0.39 ng m^{-3} for n-alkanes and from 0.25 to 0.79 ng m^{-3} for PAHs.

For extraction of ionic species, the sample and blank filters (47 mm diameter punches of the quartz fiber filter) were extracted using a shaker for 90 min with 20 ml deionized water (18 MΩ). After passing through microporous membranes (Millipore Millex® GV PVDF 0.22 μm pore size; 33 mm diameter), the ionic concentrations of the aqueous extracts were determined by ion chromatography (Metrohm AG, Herisau, Switzerland) with chemical suppression (50 mM H_2SO_4) and conductivity detector. For anion detection (SO_4^{2-}, Cl^-, NO_2^-, NO_3^-, F^-, PO_4^{3-} including $C_2O_4^{2-}$), samples were injected via a 20 μL loop through a Metrosep A Supp 5 250/4.0 mm analytical column. Mixture of 1.0 mM $NaHCO_3$ and 3.2 mM Na_2CO_3 was used as eluent. The system was regenerated by a solution of 50 mM H_2SO_4 pumped through a suppressor unit simultaneously with deionized water.

The determination of the organic anions was performed injecting the samples via a 20 μL loop using a Metrosep Organic acids 250/7.8 mm analytical column. The system was run in the isocratic mode with a solution of perchloric acid (0.5 mM) as eluent and the chemical suppressor system was regenerated by a solution of 10.0 mM LiCl pumped through the suppressor unit simultaneously with deionized water.

Metrosep C2-150 150/4.0 mm analytical column was used for cation detection (K^+, NH_4^+, Ca^{2+}, Mg^{2+} and Na^+) and the eluent used was a solution 2.7 mM oxalic acid. The system was run in the isocratic mode.

The recoveries of the inorganic anions were from 109% to 118%, from 80% to 101% of the cations and from 87% to 107% of the organic anions. The detection limits (S/N = 4) ranged between 3–45 ng m^{-3} (inorganic anions), 4–24 ng m^{-3} (cations) and 13–35 ng m^{-3} (organic acids). Blank values were subtracted from sample determinations.

For levoglucosan determination, two procedures were followed. A 47 mm diameter filter of each sample was extracted three times for 30 min with a mixture (dichloromethane:methanol, 4:1 v/v) under ultrasonic agitation. The extracts were dried by rotary evaporation until 3 ml; the residue was filtered through a membrane Millex LCR (PTFE 0.45 μm pore size; 13 mm diameter). After dryness, the extract was dissolved (200 μL) with a mixture of dichloromethane:methanol (1:1). An aliquot of the extract was used for these analyses. Levoglucosan in each sample was converted to its trimethylsilyl derivative by reaction with 50 μL N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 10 μL pyridine at 70 °C for 1 h (Simoneit et al., 1999) in sealed vial. After the reaction and cooling, aliquots of 1 μL were analyzed with a Shimadzu GC-17A gas chromatograph coupled to a Shimadzu GCMS-QP5000 mass spectrometer. Separation was performed with DB-5 column (30 m, 0.25 mm i.d., 0.25 μm film thickness) with a temperature program: isothermal at 65 °C for 2 min, 7 °C min^{-1} to 185 °C, isothermal for 5 min at 185 °C, 10 °C min^{-1} to 260 °C, and isothermal for 7 min at 260 °C. The splitless injector was maintained at 260 °C, with helium as carrier gas. The mass spectrometer was operated in the electron impact mode at 70 eV ion source energy, and the data acquisition was performed with the full scan mode in the 30–400 m/z range. Compounds were identified by GC retention index, mass spectra (base peak at m/z 204 and 217 in mass fragmentograms) and comparison with an authentic standard of levoglucosan. The second procedure used for PRB 2008 samples was performed at the Finnish Meteorological Institute, Helsinki, Finland. From quartz filter a 1 cm^2 piece was punched and each one was extracted with a 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. Concentrations of monosaccharide anhydrides (levoglucosan, mannosan and galactosan) were measured using a Dionex ICS-3000 system designed for ion chromatography analysis coupled to a quadrupole mass spectrometer (Dionex MSQ™). The complete procedure is described in Saarnio et al. (in press).

The recoveries of levoglucosan ranged from 88% to 102% (n = 7) and the detection limit was 0.7 ng $μL^{-1}$ for the first procedure. For the second one the recovery and detection limit were from 90% to 98% and 1 μg L^{-1} (Saarnio et al., in press) respectively. Blank values were subtracted from sample determinations.

3. Results and discussion

3.1. Composition of SPA particulate matter

Particulate matter average mass concentrations were 38 μg m^{-3} in the samples collected at SPA in the wet season (2007) and 64 μg m^{-3} in the dry season (2008) campaigns (Table 1). The dry season in São

Table 1
Concentrations and standard deviations of the species studied at the sites investigated.

	MAT	SPA 2007	SPA 2008	PRB 2007	PRB 2008
n-alkanes (ng m^{-3})					
C_{16}	0.5 ± 0.3	0.5 ± 0.23	0.5 ± 0.1	2.5 ± 2.8	1.9 ± 0.6
C_{17}	1.0 ± 0.7	0.3 ± 0.2	1.1 ± 0.5	0.6 ± 0.5	1.0 ± 0.7
C_{18}	2.0 ± 1.3	0.5 ± 0.3	1.2 ± 0.5	2.8 ± 4.3	1.4 ± 1.0
C_{19}	1.1 ± 1.0	0.6 ± 0.4	1.2 ± 0.5	1.4 ± 0.6	1.0 ± 0.8
C_{20}	2.2 ± 2.0	0.8 ± 0.7	1.2 ± 0.7	4.1 ± 6.2	0.6 ± 0.5
C_{21}	1.3 ± 1.0	0.8 ± 0.6	1.4 ± 0.6	1.8 ± 0.9	0.5 ± 0.3
C_{22}	1.4 ± 2.0	1.0 ± 0.7	2.2 ± 0.8	2.7 ± 2.6	0.7 ± 0.3
C_{23}	2.2 ± 1.6	1.1 ± 0.6	3.2 ± 1.2	2.3 ± 0.4	1.3 ± 0.3
C_{24}	12.9 ± 23.0	1.9 ± 1.1	4.5 ± 1.8	3.1 ± 1.3	1.9 ± 0.3
C_{25}	18.9 ± 26.1	2.7 ± 0.5	5.5 ± 3.0	3.6 ± 0.6	2.5 ± 0.5
C_{26}	12.6 ± 17.4	3.0 ± 0.7	3.7 ± 1.9	3.4 ± 1.6	1.8 ± 0.5
C_{27}	34.4 ± 32.5	3.6 ± 1.0	5.8 ± 3.3	5.8 ± 1.4	2.9 ± 0.8
C_{28}	22.9 ± 21.7	3.5 ± 1.1	5.9 ± 3.8	4.0 ± 2.0	1.8 ± 0.5
C_{29}	38.1 ± 25.2	3.3 ± 1.0	6.6 ± 4.5	7.1 ± 1.7	3.5 ± 1.0
C_{30}	25.4 ± 16.8	2.9 ± 1.6	5.5 ± 4.2	3.1 ± 1.5	1.0 ± 0.3
C_{31}	30.8 ± 21.9	3.5 ± 1.4	5.5 ± 3.5	7.0 ± 1.8	3.3 ± 1.1
C_{32}	20.6 ± 14.6	2.8 ± 0.9	4.2 ± 3.1	3.4 ± 0.9	1.5 ± 0.5
C_{33}	24.5 ± 19.3	2.4 ± 0.9	4.2 ± 3.3	5.5 ± 1.4	2.7 ± 0.8
C_{34}	16.0 ± 12.4	2.0 ± 1.5	1.9 ± 2.5	1.9 ± 0.8	1.8 ± 1.0
C_{35}	19.7 ± 10.2	1.3 ± 0.5	2.1 ± 2.7	1.9 ± 0.5	2.2 ± 0.7
Total	288.5	36.4	67.3	67.8	35.1
Pristane (ng m^{-3})	2.0 ± 1.1	0.4 ± 0.2	1.1 ± 0.5	0.8 ± 0.5	1.3 ± 0.9
Phytane (ng m^{-3})	1.6 ± 0.9	0.4 ± 0.2	0.9 ± 0.5	0.9 ± 0.6	0.9 ± 0.7
PAH (ng m^{-3})					
Phe	0.1 ± 0.1	0.3 ± 0.1	2.0 ± 0.8	0.5 ± 0.1	0.1 ± 0.1
Ant	0.4 ± 0.3	0.5 ± 0.2	2.6 ± 1.5	0.8 ± 0.2	0.3 ± 0.1
Flu	1.6 ± 1.9	0.6 ± 0.1	2.2 ± 2.6	1.3 ± 0.9	0.4 ± 0.2
Pyr	0.1 ± 0.1	0.4 ± 0.2	1.7 ± 0.6	0.9 ± 0.1	0.3 ± 0.4
BaA	0.1 ± 0.1	0.6 ± 0.1	1.4 ± 1.3	0.6 ± 0.1	0.2 ± 0.1
Chr	0.1 ± 0.2	0.8 ± 0.5	1.6 ± 1.0	0.8 ± 0.4	0.3 ± 0.1
BbF	0.1 ± 0.1	1.8 ± 0.5	2.4 ± 1.5	1.5 ± 0.4	0.2 ± 0.1
BkF	0.1 ± 0.1	1.0 ± 0.1	2.9 ± 3.7	0.7 ± 0.1	0.2 ± 0.2
BeP	3.4 ± 2.1	0.7 ± 0.3	2.5 ± 2.5	1.6 ± 0.7	0.7 ± 0.6
BaP	0.1 ± 0.1	0.7 ± 0.3	2.2 ± 2.1	1.2 ± 0.6	0.2 ± 0.2
InP	<DL	0.4 ± 0.3	1.4 ± 1.1	1.1 ± 0.6	0.2 ± 0.1
DBA	0.1 ± 0.1	1.5 ± 0.8	1.5 ± 1.1	1.7 ± 0.1	0.2 ± 0,1
BPe	3.1 ± 1.7	1.1 ± 0.6	1.6 ± 1.1	1.8 ± 1.1	0.2 ± 0.1
Retene	0.1 ± 0.1	<DL	1.0 ± 0.6	0.9 ± 0.1	0.3 ± 0.3
Total	9.3	10.6	25.9	15.2	3.4
BaPE*	0.1	1.9	3.7	2.1	0.4
Levoglucosan (ng m^{-3})	11 ± 9	39 ± 30	201 ± 146	129 ± 90	102 ± 57
Inorganic anions (ng m^{-3})					
F^-	<DL	<DL	9 ± 6	21 ± 8	<DL
Cl^-	47 ± 55	331 ± 235	942 ± 509	321 ± 80	156 ± 175
NO_2^-	0.3 ± 0.2	1 ± 1	11 ± 3	4 ± 1	<DL
Br^-	0.8 ± 0.3	4 ± 1	12 ± 5	2 ± 1	6 ± 4
NO_3^-	213.5 ± 178.0	3353 ± 2119	3681 ± 1887	3426 ± 1808	759 ± 293
PO_4^{3-}	10.8 ± 3.3	64 ± 58	51 ± 14	125 ± 26	56 ± 20
SO_4^{2-}	1435.9 ± 659.2	5117 ± 2746	4375 ± 2106	3551 ± 2182	2357 ± 1206
Total	1708.1	8871	9083	7450	3334
Organic anions (ng m^{-3})					
CH_3COO^-	6 ± 3	15 ± 10	40 ± 11	26 ± 13	9 ± 7
$HCOO^-$	16 ± 7	30 ± 13	77 ± 39	77 ± 33	17 ± 16
$C_2O_4^{2-}$	114 ± 67	285 ± 102	250 ± 94	443 ± 300	149 ± 57
Fumarate	11 ± 7	96 ± 23	30 ± 3	269 ± 102	9 ± 4
Succinate	39 ± 18	103 ± 102	40 ± 11	161 ± 145	18 ± 9
Glutarate	<DL	24 ± 2	31 ± 3	26 ± 2	<DL
Total	186	553	471	1002	202
Cations (ng m^{-3})					
Na^+	384 ± 502	476 ± 200	368 ± 130	244 ± 66	185 ± 144
NH_4^+	1169 ± 1579	1915 ± 1477	1792 ± 1243	1308 ± 955	1345 ± 902
K^+	517 ± 427	357 ± 81	579 ± 241	838 ± 252	372 ± 84
Mg^{2+}	82 ± 88	115 ± 43	121 ± 45	281 ± 82	93 ± 38
Ca^{2+}	327 ± 333	643 ± 180	810 ± 404	866 ± 207	311 ± 96
Total	2479	3506	3670	3537	2306
PM_{10} (µg m^{-3})	9 ± 3	38 ± 13	64 ± 19	55 ± 26	47 ± 30

* $BaPE = BaA \times 0.06 + B(b+k)F \times 0.07 + BaP + DBA \times 0.6 + InP \times 0.08$ (Yassaa et al., 2001).

Paulo City is accompanied with lower temperature that decreases the mixing heights and, very often inversion layers lead to lower dilution of the pollutants (Sanchez-Ccoyllo et al., 2008).

For total n-alkanes average concentrations were 36.4 ng m^{-3} and 67.3 ng m^{-3} respectively in wet and dry seasons at SPA. The distribution of the homologues series of n-alkanes ranged from C_{16} to C_{35}, presenting contribution of anthropogenic and biogenic emissions. A small forest inside the university campus might have influenced the emissions of the homologues higher than C_{22}. These natural compounds account in average for 90% (in 2007 and 2008) of n-alkanes found in the samples. This value was obtained calculating the ratio of biogenic n-alkane concentrations greater than C_{22} to the total n-alkanes in the same range. Although compounds lesser than C_{20} can be associated with the presence of biological materials, Pio et al. (2001) report that they are possible imprint of some anthropogenic sources. In fact, extensive vehicular emissions of heavy and light cars have been observed coming from the highway at a distance of 2 km from the sampling site.

The branched alkane pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6-10,14-tetramethylhexadecane) confirm the petroleum residue contamination. The ratio between them was 1. This value is comparable with others described for typical urban samples. Andreou and Rapsomanikis (2009) reported these ratios over 1.9 for $PM_{10-2.5}$ and 1.1 for $PM_{2.5}$ in Athens, Greece. Their presence is consistent with fossil fuel sources. Phytane is rarely found in biological material and most biological hydrocarbon has a pristane/phytane ratio $\gg 1$ (Alves, 2008).

Cmax at C_{27} in 2007 and C_{29} in 2008 (Table 1) fits with the interpretation that in the tropics vegetation waxes are composed of higher epicuticular wax components which are biosynthesized due to the higher temperatures. Carbon Preference Index (CPI) values were expressed as a sum of the odd carbon number homologues, divided by a sum of even carbon homologues over the same range (Alves, 2008; Bi et al., 2008). CPI values were close to the unity in São Paulo samples and are in agreement with the contribution of fossil fuel burning.

The ratio of unresolved to resolved hydrocarbons (U/R) can be used to assess the petroleum contributions to atmospheric aerosols. At SPA site U/R values averaged 9 (from 7 to 11, in 2007) and 11 (from 6 to 20, in 2008). These values are higher than those found in other Brazilian cities. Azevedo et al. (1999) found 1.9 to 4.6 in samples collected in polluted areas of Rio de Janeiro, lower values in urban forested areas (1.9–2.1) and higher values (4.4–4.6) in tunnel and downtown samples. Abas and Simoneit (1996) reported values from 1.9 to 35.6 for samples collected in residential areas impacted by industries.

Back trajectories showed air masses coming predominantly (73% of the sampling period) from the sugarcane burning region in the sampling period. The highest PM_{10} (97 μg m^{-3}) and n-alkane (164 μg m^{-3}) concentrations were found in August 20th and August 18th respectively. Air mass trajectories coming from the sea and from biomass burning areas are shown in the Fig. 1. Before reaching the site, air masses coming from the sea pass over the biggest industrial park of the state.

PAHs associated to airborne particles were determined. Long sampling time was required to obtain sufficient mass. Volatilization and/or chemical and photochemical transformations lead to underestimated PAH concentrations. Since the sampling equipment used in this study was not appropriate to collect the most volatile PAHs, (naphtalene, acenaphtylene, acenaphtene and fluorene) and the recuperation efficiency are low (≤50%), they were not taken into consideration.

The PAHs considered were: phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), retene (Ret), benzo[a] anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF) benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (InP), dibenzo[ah]anthracene (DBA) and benzo[ghi]perylene (BPe). Total PAH concentrations at SPA averaged 10.6 ng m^{-3} in 2007 and 25.9 ng m^{-3} in 2008. These levels are higher than those found in the same site on total suspended particles, over 3.10 ng m^{-3} in 2000 (Vasconcellos et al., 2003).

The higher concentration values for 2008 may be related to higher vehicular emission observed in wintertime and to the transport of sugarcane smoke taking place in many cities of the state. The city of São Paulo has experienced the increase of number of vehicles, from 6.5 million (in 2003) to over 7 million automotive vehicles in 2009 (CETESB, 2008).

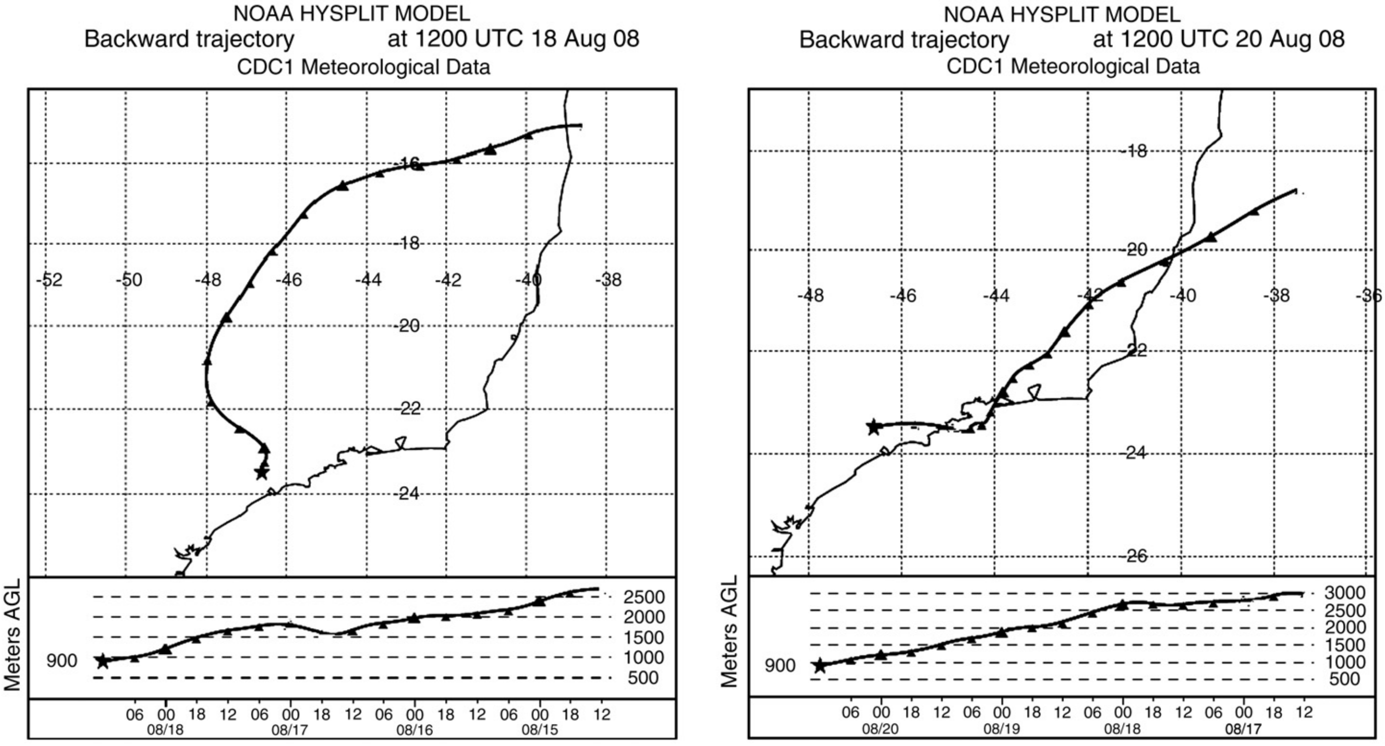

Fig. 1. Back trajectories calculated for SPA site on August 18th and 20th, 2008.

In 2007 highest concentrations were found for BbF (1.8 ng m^{-3}) and DBA (1.5 ng m^{-3}), and in 2008 for BkF (2.9 ng m^{-3}) and Ant (2.6 ng m^{-3}). In previous work (Vasconcellos et al., 2003) InP, BPe, Chr and BbF were the most abundant PAHs in total suspended particle samples.

Previous studies have pointed out that DBA is ten times more carcinogenic than BaP (Okona-Mensah et al., 2005). DBA is associated to stationary sources, suggesting that SPA samples (2007) were influenced by industrial emissions (Fang et al., 2004). In some studies BPe is cited as the tracer of vehicular emissions (Harrison et al., 1996). Lower PAH concentrations in 2007 can indicate lower direct emissions and the degradation of some compounds as result of the photochemical activities prevailing during the summer time. The relative contribution between reactive species may indicate the age of the aerosol. In 2007 BaP and BeP concentrations were quite similar, indicating that local sources are important to be considered (BaP/BeP ~ 1). In 2008, BaP concentrations were low compared to the more stable BeP and the compounds undergo photolytic degradation (BaP/BeP ~ 0.87). Technical literature published previously (Masclet et al., 1995; Ciccioli et al., 1996) reports that a decrease in BaP/BeP and BaA/Chr ratios should occur when particles are exposed to sunlight and to chemical agents for periods longer than three days. Further calculations and comparison with published data from other cities are difficult to evaluate due to distinct emission sources and combustion of different fuels observed in Brazilian cities. In order to explain qualitatively the relative importance of vehicular emissions in São Paulo, the PAH ratios were calculated in Brazilian tunnels (Vasconcellos et al., 2003). Based on the comparing of those values with those found in this work, heavy and light cars are responsible for the emissions of these high molecular compounds.

The impact from combustion sources can be better evaluated by looking at selected PAHs considered as molecular markers. Retene ($C_{18}H_{18}$) was found in all samples collected at SPA in 2008 (average 0.9 ng m^{-3}) and were not found in 2007 samples. In Santiago, Chile, retene presence was attributed to wood burning for domestic heating (Didyk et al., 2000), and its concentration (7 ng m^{-3}) was much higher than that found in São Paulo samples (from 0.4 to 2.5 ng m^{-3}).

Another compound recognized as a tracer for biomass burning is levoglucosan (1,6-anhydro-ß-D-glucopyranose) including its isomers galactosan and mannosan (Simoneit et al., 1999; Schkolnik and Rudich, 2006). Some levoglucosan is consumed in various reactions during combustion but some remains in the resulting smoke aerosol (Wang et al., 2007). In the atmosphere, levoglucosan was detected in oceanic aerosol samples, confirming the long range transport of biomass burning plumes.

Levoglucosan concentrations ranged from 13 to 112 ng m^{-3} in samples collected in the summer (average 38 ng m^{-3}) and from 16 to 410 ng m^{-3} in samples collected in the winter (average 201 ng m^{-3}). The highest concentration was found on August 19th, 2008 (410 ng m^{-3}). In the previous 7 days, air masses were found to come from north of São Paulo State where sugarcane burning was intense.

Total ion concentration at the SPA site in 2007 was 12930 ng m^{-3} and 13231 ng m^{-3} in 2008 samples (Table 1). The sum of SO_4^{2-}, NO_3^- and NH_4^+ accounted for over 80% of total soluble ionic species measured in 2007 and 74% in 2008. Main differences in the total average concentrations were found in the concentrations of chloride and potassium. Their concentrations were much higher in 2008 than in 2007, as expected on the basis of seasonal differences.

Sulfates are formed in the gas to particle conversion process that can occur on the surface of particles. SO_4^{2-} and NO_3^- are secondary pollutants due to vehicles, industries and biomass burning emissions. The ratio SO_4^{2-}/NO_3^- varied from 0.4 to 3.1 in 2007 (average 2.1, wet period) and from 0.7 to 2.2 in 2008 (average 1.2, dry period), in more polluted samples. At the SPA site the ratios were higher for higher humidity (2007). The heterogeneous conversion rates from SO_2 and NOx to SO_4^{-2} and NO_3^- can be sensitive to humidity and can increase in pollution episodes when the humidity is high (Kai et al., 2007).

SO_4^{2-} and NH_4^+ concentrations were higher in 2007 than 2008 samples, NO_3^- presented similar average concentrations. In general, these species and PM_{10} concentrations are well correlated (Fig. 2).

Chloride presence is often attributed to sea breeze contribution, but at this site it has been associated to local waste burning emissions, still observed in Brazilian cities (Vasconcellos et al., 2007). Cl^-/Na^+ ratios in 2007 averaged 0.7 and in 2008 averaged 2.8. Literature points to reactions that can remove chloride from the

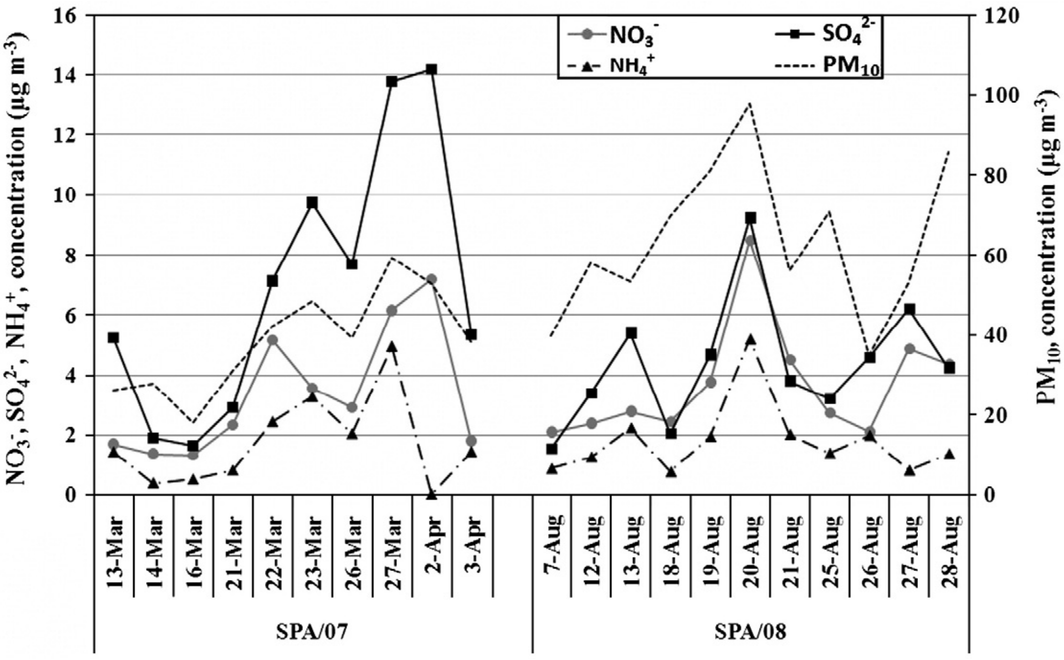

Fig. 2. Concentrations of major species and PM10 found at SPA site.

atmosphere. If HCl becomes supersaturated in the gas phase, it dissolves into water-containing particles and dissociates. This dissociation is pH dependent. When nitric acid or sulfuric acid enters a particle and dissociates, they force Cl^- to associate with H^+ and evaporate as gaseous HCl (Jacobson, 2002).

Calcium and magnesium are associated to coarse particles. The correlations between these two species were high ($R = 0.8$ in 2007 and in 2008). Soil has been considered the main source other than foundry activities and biomass burning. The metropolitan area has been subjected to a large property expansion in the last decades. Soil resuspension of this kind of activity may impact the city atmosphere for the whole year.

Potassium concentration was also higher in 2008 (579 ng m^{-3}) than in 2007 (357 ng m^{-3}). Nitrite and bromide have been found in low concentrations (from 1 to 20 ng m^{-3}).

Dicarboxylic acids are often present in atmospheric aerosols. Their vapour pressure is lower by a factor of between 10^2 and 10^4 than that of corresponding monocarboxylic acids (Chebbi and Carlier, 1996). Among these organic anions found in these samples, oxalate was the most abundant organic anion followed by succinate, fumarate and glutarate. Oxalate ion mean values are 285 ng m^{-3} in 2007 and 250 ng m^{-3} in 2008. Differently to most of the other species, the concentrations of these organic anions were higher in 2007 campaign than in 2008.

Sulfate and oxalate showed a good correlation in 2007 ($R = 0.6$) and low in 2008 ($R = 0.2$). Previous studies have suggested that in-cloud and heterogeneous formations can yield a good correlation between these species (Yao et al., 2002, 2003). Wang et al. (2007) have reported a good correlation of formate with Cl^-, SO_4^{-2} and K^+ indicating coal/biomass/waste burning or from secondary formation of previous gases. In this work a good correlation was found between formate and sulfate ($R = 0.6$) in 2007 and lower correlation in 2008 ($R = 0.4$). In 2007 secondary formation from traffic activities might have been the major origin for these two species and in 2008 long range transport might have enhanced the composition of the aerosols with these species.

Measurements of carboxylic acids in previous studies (Montero et al., 2001) showed formate-to-acetate ratio as an indicator of direct emission (low ratio, <1) and in situ formation by photochemical processes (high ratio, >1). Also direct emission from vehicular exhaust leads to increased acetic acid whereas direct emission from vegetation may provide higher levels of formate than acetate (Kawamura et al., 1987; Talbot et al., 1988; Vasconcellos et al., 2005).

Fig. 3 presents the formate/acetate ratios at the studied sites. These ratios ranged from 1 to 3 (average 2.6) in 2007 and from 1 to 5 (average 1.8) in 2008 at the SPA site. Both acids have been attributed to direct emissions and from photochemical reactions (Souza et al., 1999; Viana et al., 2008).

Also biogenic emissions and biomass combustion processes and gas-particle conversion have been proposed to explain the formate and acetate presence in the aerosols (Yamasoe et al., 2000). Direct emissions of carboxylic acids from biomass burning were observed by Talbot et al. (1988), and the formate/acetate ratio found ranged from 2 to 10.

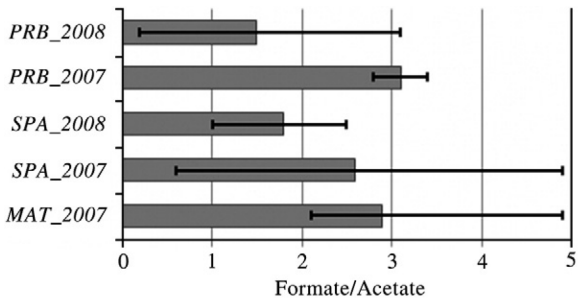

Fig. 3. Formic/acetic acids ratios calculated for the sites studied.

The average concentrations found in this work for formate and acetate were 30 ng m^{-3} and 15 ng m^{-3} (2007) and 77 ng m^{-3} and 40 ng m^{-3} (2008), respectively. These values are much lower than those found in the same site previously (Souza et al., 1999). Those results showed low difference between formate (0.48 µg m^{-3}) and acetic acid (0.43 µg m^{-3}) concentrations in airborne aerosols, but slightly higher concentrations of formate in gaseous samples. Photochemical production and direct emissions appeared to be the sources of these acids.

Formate and acetate measurement were associated with sorption and desorption artifacts, and were strongly dependent on the aerosol acidity and the relative humidity of the ambient (Wang et al., 2007).

3.2. Composition of PRB particulate matter

This urban site in Piracicaba is strongly impacted by agricultural activities. Sugarcane burning takes place from May to October modifying the atmospheric chemistry and impacting the population health.

Samples of PM_{10} particulate matter were collected at the PRB site both in dry and wet periods. Average concentrations were 55 µg m^{-3} and 47 µg m^{-3} for dry and wet seasons respectively.

The concentrations of n-alkanes in the urban atmosphere at PRB are comparable with those of the SPA site in the dry and wet seasons. The total average concentration (from C_{16} to C_{35}) of n-alkanes in sugarcane burning samples was almost twice than that measured in the period with no burning events. Samples collected during biomass burning presented n-alkane concentrations over 66.8 ng m^{-3} (67.3 ng m^{-3} at the SPA site, more polluted season) and 35.1 ng m^{-3} in the period with no burning (av. 37.9 ng m^{-3} for the SPA site, less polluted season).

At the PRB site, pristane concentrations were lower in the samples collected during the dry season (0.8 ng m^{-3}) than in the wet season (1.3 ng m^{-3}) and phytane presented the same average concentration (0.9 ng m^{-3}) in both seasons. The pristane/phytane ratios averaged 0.9 and 1.4 (2007 and 2008). Low ratios indicate hydrocarbon signature derived from petrochemical uses, while ratios $\gg 1.0$ indicate predominance of biogenic inputs (Alves, 2008; Andreou and Rapsomanikis, 2009).

Homologues with odd carbon number predominated, and Cmax at C_{29} showed the influence of the vegetation emission. The CPI determined the degree of biogenic versus petrogenic input. The CPI value of these samples over 1.1 and 1.2 (2007 and 2008) indicated a major contribution from petroleum residues, derived from vehicular emissions in this site with agricultural and biomass burning influences.

Large hump in the n-alkane chromatogram consisting of branched and cyclic compounds deriving mainly from fossil fuel use was observed. Biogenic hydrocarbons derived from higher plants exhibit no unresolved complex mixture (UCM) and the ratio of UCM to plant wax n-alkanes (NA) can be used to assess the level of contamination by petroleum products. UCM/NA values found at the PRB site were over 2 and 3 (both seasons), much lower than those found in Santiago, Chile (from 57 to 80, Didyk et al., 2000) or those in urban and rural sites in Malaysia (from ~54 to 1299, Omar et al., 2007).

An UCM/NA value $\gg 1$ indicates strong contributions from petroleum combustion sources. In addition, this ratio may be used as an indicator for identifying atmospheric transport trajectories from regional biomass burning and fossil fuel combustion emissions containing air parcels (Alves, 2008).

The most abundant PAHs determined at this site were BPe and DBA in 2007 during the burning season and BeP and Flu in the beginning of the wet season (2008). Previous work done at same site at PRB (July, 2003) presented also BPe (13%) and BeP (12%) among the most abundant PAHs (Magalhães et al., 2007).

At the PRB site air masses in August 2007 came from the sea, Northern and Southeastern São Paulo State, regions impacted by vehicular, agricultural emissions and long range transport.

The most polluted day (August 22nd, 2007) SO_4^{2-} and PM_{10} concentrations were 7284 ng m^{-3} and 89 µg m^{-3} respectively. Air masses from Southeastern São Paulo State may bring species from Brazilian agricultural areas. Retene was observed only in 2007 (0.9 ng m^{-3}) and levoglucosan concentrations were 129 ng m^{-3} in 2007 and 102 ng m^{-3} in 2008.

Levoglucosan and potassium were well correlated (R = 0.7) only at PRB, during the burning period. Additionally, acetate, formate, oxalate, nitrite, nitrate, sulfate, ammonium, magnesium and calcium presented good correlation with levoglucosan at this site (R>0.7).

The total average concentrations of water-soluble ions found in the PRB 2007 samples were over two times higher (11978 ng m^{-3}) than in the 2008 samples (5839 ng m^{-3}). SO_4^{2-} (3551 and 2357 ng m^{-3}), NO_3^- (3426 and 759 ng m^{-3}) and NH_4^+ (1308 ng m^{-3} and 1345 ng m^{-3}) were the most abundant species.

Lower levels of nitrate in the 2008 than in 2007 samples could be due to the lower thermal stability of NH_4NO_3 during the warm months. Besides, nitrate collection on quartz fiber filters is subjected to negative artifacts. Literature reports (Viana et al., 2007; Yin and Harrison, 2008) another negative artifact associated to the collection and determination of ammonium. It is the volatilization of NH_4Cl from the filter formed by the reaction of NH_4NO_3 and NaCl.

Fig. 4 shows the chemical species contribution in PM_{10} at this site. In the previous work by Vasconcellos et al. (2007), the soluble ion concentration was over 20 µg m^{-3} in total suspended particulate samples collected at the same site, and the most abundant species were SO_4^{2-}, NO_3^- and Ca^+, with NO_3^-.

The presence of sulfate and nitrate is usually attributed to anthropogenic activities such as vehicle emissions and industries. Industries may be influencing this site as shown in previous work on rainwater composition (Lara et al., 2001). In the wet season these species were found at the PRB site in lower concentrations, being NO_3^- concentrations (759 ng m^{-3}) 4.5 times lower than in the dry season (3426 ng m^{-3}) likely due to sugarcane burning.

The concentrations of formate, acetate and oxalate ions averaged 77 ng m^{-3}, 26 ng m^{-3} and 443 ng m^{-3} in 2007, respectively and on much lower levels in 2008 (18 ng m^{-3}, 9 ng m^{-3} and 149 ng m^{-3}).

Oxalate, the most abundant organic species contributed to 45% and 75% of the studied organic anions in 2007 and 2008 respectively. Kawamura and Kaplan (1987) have suggested that primary vehicular emission is responsible for the dicarboxylic acids in an urban atmosphere. Previous work carried out by Souza et al. (1999) in a tunnel in São Paulo with gasoline and alcohol fueled vehicular traffic showed oxalate concentration below the detection limit. Niemi et al. (2009) have attributed to biomass burning the highest oxalate concentrations found in Southern Finland. Dicarbonyls, such as glyoxal and methylglyoxal, reaction products of photo oxidation of aromatic hydrocarbons, are supposed to be precursors of gaseous oxalate, pyruvate and glyoxalate species.

At the PRB site, oxalate and sulfate were highly correlated (R = 0.9) in 2007 and had no correlation in 2008. High correlations were also found between oxalate and acetate (R = 0.9) in 2007 and no correlation in 2008. Sugarcane burning seemed to be the strongest factor for these high correlations; in the wet season different emission sources should have affected these concentrations. Glutarate and succinate were found also in PRB samples. In laboratory studies these two organic anions have been generated in the reaction between ozone and cyclohexene (Legrand, 2007). In addition, they may derive from wood burning or from motor exhausts (Kawamura and Kaplan, 1987).

The concentration of NH_4^+ was similar in both campaigns (1308 and 1345 ng m^{-3}). Ammonia is found in wastes from animals and humans and also emitted during combustion processes, fertilizer production and sugarcane burning (Blume, 1992). Other ammonia sources include industrial and vehicular emissions, as well as long range transport. Differently, K^+ concentrations were over 2 times higher during sugarcane harvesting period (838 ng m^{-3}) than in the wet season (372 ng m^{-3}). This species is widely found in biomass burning plumes and can be transported to far from emission sources. Magnesium and calcium were found also in higher abundance in 2007 campaign than in 2008 and have been attributed to soil resuspension.

3.3. Composition of the MAT particulate matter

The highest PM_{10} concentration was found on August 8th, (~18.2 µg m^{-3}) and air mass trajectories over biomass burning region passed over this site. In fact, 441 fires were observed that day in the São Paulo State (INPE, 2009).

N-alkanes and PM_{10} total average concentrations were 291 ng m^{-3} and 9 µg m^{-3} respectively at the forest site of MAT. These values are lower than those found for the urban areas studied (Table 1). The major resolved components were the n-alkanes ranging from C_{16} to C_{35}, pristine and phytane. The total CPI values average was 1.4 and biogenic CPI was 1.5, lightly higher than those found for SPA (1.2–1.4) and for PRB (1.1–1.2). The unresolved to resolved component ratios averaged 0.5 (0.1–1.1) and Cmax at C_{29} pointing to a clean area, input from biogenic emission and minor anthropogenic contribution.

Pristane and phytane are frequently attributed to two main emission sources: marine biogenic and terrestrial anthropogenic (Bi et al., 2008). Pristane/phytane ratio was 1.3, higher than those found in the urban areas studied. This forest site is 5 km away from the sea and can be influenced by marine contributions. The n-alkanes higher than C_{25} present strong odd homolog predominance attributable to tropical plant wax contribution.

PAH compounds often attributed to emissions of higher temperature combustive processes have been found in forests in emissions of microorganism activities and biomass burning (Ciccioli et al., 1996). The total PAH and PM_{10} concentrations during sampling period are shown in Fig. 5. In the present study, the total PAH average concentrations at MAT were over 8.9 µg m^{-3} and consisted primarily of benzo(e)pyrene, benzo(ghi)perylene and fluoranthene (Table 1). The low BaP/BeP ratio in few samples (over 0.01 ng m^{-3}) and the presence of petrogenic compounds can be attributed to long

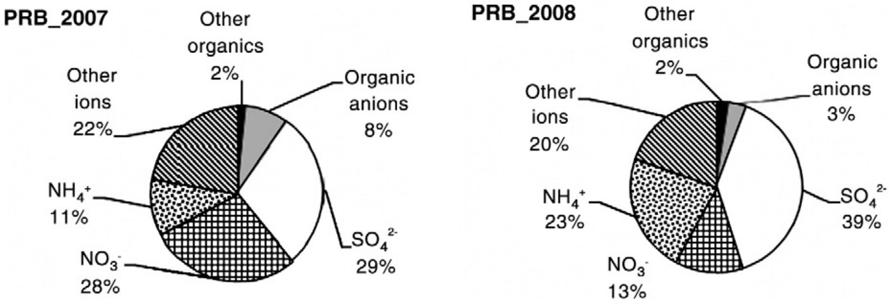

Fig. 4. The proportion of different inorganic and organic compounds at PRB site.

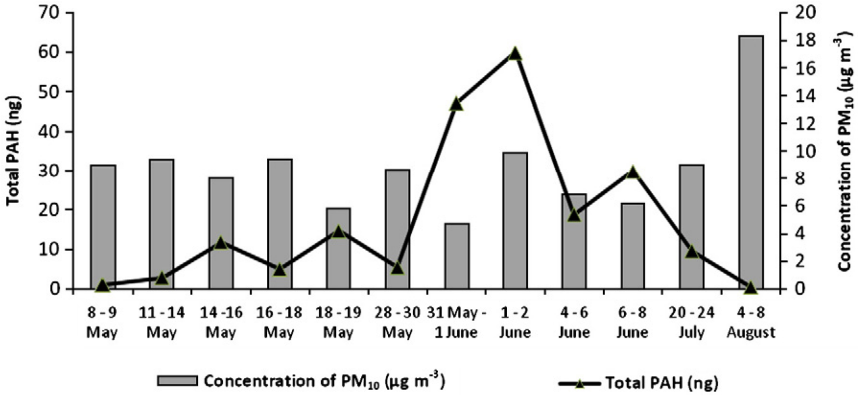

Fig. 5. Concentrations of total PAH and PM10 at MAT site.

range transport. Retene was found in 54% of the samples in lower concentrations (0.08 ng m^{-3}) than those found in the urban areas studied.

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 average values for each site are presented in Table 1 — BaPE at SPA 2007 and 2008 (average 1.9 and 3.7), at PRB 2007 and 2008 (2.1 and 0.4) and at MAT (0.1). Sites in which the average value for BaPE was above 1.0 ng m^{-3}, might indicate cancer risk (Cecinato et al., 1998; Marino et al., 2000). If only BaP was taken into account, the carcinogenic power from PAH would be underestimated.

In the urban atmosphere of Guangzhou, China (Bi et al., 2002) the BaPE values ranged from 0.95 to 21.69.

Levoglucosan (average 11 ng m^{-3}) was found in almost all samples. Previous work has reported that levoglucosan shows no decay over 10 days in acidic conditions due to its stability in the atmosphere (Schkolnik and Rudick, 2006).

On June 2nd the highest concentration of levoglucosan (32 ng m^{-3}) and the lowest BaP/BeP ratio (0.02) were found. Air masses from biomass burning regions might have been responsible for these results.

Sulfate (1410 ng m^{-3}), nitrate (202 ng m^{-3}) and ammonium (1169 ng m^{-3}) were the dominant ionic species of all water-soluble ions.

The SO_4^{2-}/NO_3^- ratio varied from over 3 to 25 at the forest site. Oxalate was also the most abundant organic anion (average 114 ng m^{-3}) at the MAT site and contributed 61% to these studied species. Its presence is attributed to biogenic activity (Kawamura and Kaplan, 1987), but anthropogenic contribution is also considered. Low correlation between oxalate and sulfate ($R = 0.1$) and between oxalate and succinate ($R < 0.1$) suggested biological formation of oxalate (Dutton and Evans, 1996). Conversely, high correlation between ammonium and sulfate (~0.8) may indicate long range transport.

Formate/acetate ratios averaged close to 3 (Fig. 3) suggesting *in situ* emissions. On the other hand, photochemical processes may have been responsible for *in situ* formation.

4. Conclusions

The concentrations of PM_{10}, n-alkanes, PAHs, water-soluble ions and biomass burning tracers between the sites were variable and dependent of seasonal changes, which influenced the local emissions and long range transport. In the most dry and polluted seasons, n-alkanes and cation concentrations were similar between the megacity and the biomass burning sites. PAH and inorganic ion abundances were higher at SPA than PRB, yet, the biomass burning site seems to be the most impacted by the organic anion abundance in the atmosphere.

Pristane and phytane presences coupled with unresolved envelopes confirm the contamination by petroleum residues at urban sites; at the MAT site biological activity might influence the emissions of pristane and long range transport of pollutants is also considered.

Air mass transport from biomass burning regions is likely to impact the sites with specific molecular markers. The anhydrosaccharide levoglucosan presence indicated an input from biomass burning in all samples collected during the dry season, mainly at the SPA site.

In this investigation high formate/acetate ratios indicated that these compounds are originated mainly from photochemical processes at urban sites and contribution of vegetation emission of formate at the forest site.

Oxalate was the most abundant water-soluble ion studied at all sites and its presence is attributed to anthropogenic activities at urban sites, yet the low correlation between oxalate and sulfate and, oxalate and succinate suggests strong biological formation of oxalate at the forest site.

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