

# Seasonal Variation of *n*-Alkanes and Polycyclic Aromatic Hydrocarbon Concentrations in PM<sub>10</sub> Samples Collected at Urban Sites of São Paulo State, Brazil

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**Abstract** Two campaigns were conducted in 2003 and 2004 at sites of different characteristics in São Paulo State. Atmospheric samples were collected twice a month during a 1-year campaign (an extensive campaign) from April 2003 to May 2004 at São Paulo City (SPA) site. The results showed that the pollutant concentrations were controlled not only by local source emissions but also through pollutant transport, both of which were dictated by the prevailing meteorological conditions. Chrysene, benzo(e)pyrene, and benzo(b)fluoranthene were the major compounds found, and diagnostic ratios indicated the multiplicity of sources: industrial, vehicular emission, and atmospheric transport. Intensive campaign (from July 15 to 30, 2003) samples showed higher cancer risk than those collected in the extensive campaign. Samples collected at the urban site (SPA) presented comparable

values of PM<sub>10</sub> to the urban site influenced by sugarcane burning (Araraquara, ARQ). On the other hand, PAH average concentrations were higher at SPA than at other sites. In both campaigns, the highest value for dry atmospheric deposition flux was found in autumn and winter. Individually, BPe presented the highest deposition flux followed by BbF in the intensive campaign. It seems that during those periods, the dry deposition was the main airborne PAH removal mechanism. Diagnostic ratios suggested also vehicular emissions at the sites and photochemical reactions influencing in the atmospheric particulate matter composition. SPA and PRB samples presented higher cancer risk than ARQ in the intensive campaign.

**Keywords** Air pollutant · Megacity · Organic pollutant · PAH · Seasonal variation

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## 1 Introduction

São Paulo is the largest city in Latin America and has presented large problems concerning air pollution (Vivanco and Andrade 2006). Local sources are being pointed for the responsibility of formaldehyde, acetaldehyde, and polycyclic aromatic hydrocarbon (PAH) emissions in the wintertime; remote sources have also contributed to deterioration of the air quality, such as mainly biomass burning occurring in São Paulo State (Montero et al. 2001; Bourotte

et al. 2007; Vasconcellos et al. 2003). In fact, measurements on PAH have been made mainly in the wintertime when the meteorological conditions propitiate stagnation of the pollutants, but recent studies show that even in cleaner season, air quality of the city is of concern (Vasconcellos et al. 2010).

PAH represents a group of pollutants that are produced either by the incomplete combustion of fossil fuels or organic matter and are considered ubiquitous contaminants in the environment (Simoneit 2002; Zhang and Tao 2004). They are found in an urban atmosphere impacted by vehicles, domestic heating, tobacco smoke, and industrial emissions. Natural sources include forest fires, volcanic activities, and biosynthesis by bacteria and plants (Magalhães et al. 2007). Several PAHs are regarded as priority pollutants by the US Environmental Agency and the European Community. PAHs can be precursors of nitro-PAH and oxy-PAH, which are found as carcinogenic and/or mutagenic compounds in the atmosphere (Ciccioli et al. 1996; Vasconcellos et al. 2007a). Under ambient temperature, the non-volatile PAH can be condensed or adsorbed onto solid particles. These aerosols could remain in the atmosphere for several days, being used as tracer of anthropogenic activities. Literature describes several compounds that can be used as molecular markers to assess the transport and the major emissions (Oros and Simoneit 1999; Alves 2008).

*n*-Alkane determination is interesting for studies directed to the origin and fate of atmospheric aerosols. They are ubiquitous in urban, continental, or marine samples. They can be derived from both biogenic and anthropogenic sources which can be differentiated based on their *n*-alkane distribution. Their relatively low reactivity and volatility make them interesting tracers for both atmospheric transport and particle origin (Omar et al. 2007).

The increasing number of vehicles observed in South America has impacted the air conditions and worsened both living organism and human health. Several studies have linked the concentrations of inorganic pollutants and meteorological conditions in South America (Bogo et al. 2003; Sanchez-Ccoylo et al. 2006). However, data about the variation of organic compounds with the meteorology are scarce in Brazil.

This work aimed to study both meteorological and seasonal influences on the levels of *n*-alkanes and

polycyclic aromatic hydrocarbons in the São Paulo atmosphere in the extensive and intensive campaigns conducted in 2003 and 2004.

## 2 Experimental

### 2.1 Sampling, Sample Preparation, and Analysis

In this study, three sampling sites in São Paulo State were chosen, namely São Paulo City (SPA), Araraquara (ARQ), and Piracicaba (PRB), where samples were collected in two different situations: in an extensive and intensive campaign. The São Paulo site (SPA) is at approximately 800 m above sea level (23°33'34" S and 46°44'01" W). The sampling site is located in a green area, within approximately 2 km from a major highway carrying relatively heavy traffic consisting of a mixed contribution of gasohol-, diesel-, and ethanol-fueled vehicles. The Hi-Vol PM<sub>10</sub> sampler was placed in an open area on the rooftop of the Department of Atmospheric Sciences Building, located on the campus of the University of São Paulo, ~20 m above ground level. At the ARQ site (300 km far from São Paulo), filter collection was conducted inside the university campus (21°47'40" S and 48°10'32" W). It consisted of an urban site surrounded by sugarcane plantations. Sampling was carried out 4 m above the ground level, situated 50 m away from a rural road. The third site is Piracicaba (PRB), situated at 180 km from the capital (22°42'20" S and 47°38'27" W); it is characterized by intense sugarcane burning during the dry season, like the ARQ site. Samples were collected in the university campus, on the ground level.

Firstly, the extensive campaign was performed only at the SPA site, by collecting 24-h atmospheric particulate matter samples every 15 days, by filtration of the ambient air through a quartz fiber filter (20×25 cm) using a conventional Hi-Vol air sampler (Energética, Brazil) with a PM<sub>10</sub> inlet (Sierra Andersen, Atlanta, GA, USA), during a 1-year term, from April 2003 to May 2004 (*n*=31). Secondly, in the intensive campaign, 24-h PM<sub>10</sub> samples (SPA and ARQ) and TSP samples (PRB) were collected simultaneously in the three sites, during events of air pollution (July 15 to 29, 2003; *n*=15 for each site), often observed at this time of year (Fig. 1). All quartz filters utilized in the samplings were previously heated at 800°C for 8 h in order to remove any

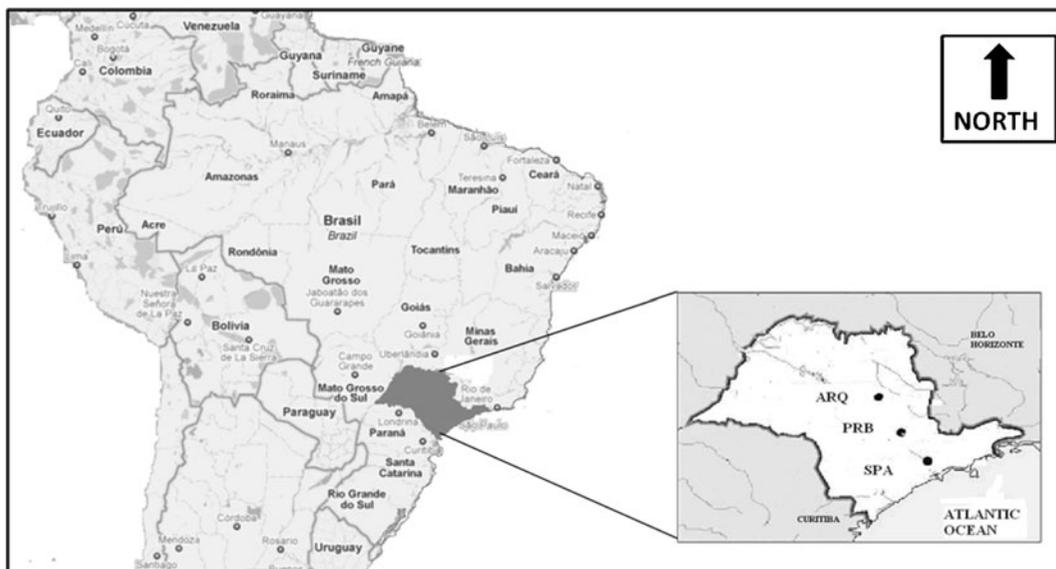
organic contaminants, and after that, each collection sample was kept under refrigeration until sample preparation and analysis.

Organic compounds were extracted by Soxhlet for 24 h (60 cycles), with 200 mL dichloromethane (DCM) as solvent for extraction. Sample extracts were concentrated to 1 mL by a rotary evaporator and N<sub>2</sub> flux. Separation of the PAH and *n*-alkane fraction from other organic compounds was achieved by high performance liquid chromatography using a column packed with silica (Erbasil Carlo Erba; *L*=250 mm, *D*=4 mm, *d*=10 μm). In order to obtain conditions to reproduce, the column was pre-washed with DCM (1.5 mL min<sup>-1</sup> during 20 min) and with *n*-hexane (1.5 mL min<sup>-1</sup> for 10 min) before each analysis. The elution gradient of *n*-hexane and dichloromethane was of 2% (v/v) per minute for separation of the compound of different polarities. Four fractions were collected: *n*-alkanes (from 0% to 30% of DCM), PAH (from 30% to 54% DCM), nitro-PAH (from 55% to 75% DCM), and oxy-PAH (>75% DCM). This work was focused on *n*-alkanes and PAH fractions (Ciccioli et al. 1996).

The *n*-alkanes and PAHs were identified previously using a gas chromatography coupled to a mass spectrometry detector (Shimadzu model GCMS-QP5000) and a NIST library, and gas chromatogra-

phy with flame ionization (Shimadzu model GC-17A) was used for quantification. The detection mode used for identification was the single ion monitoring (Vasconcellos et al. 2003). A 30-m fused-silica capillary column, DB-5 (0.2 mm ID, 0.25 μm film thickness), was used for separation. The temperature program used has been described elsewhere (Vasconcellos et al. 2003). Recoveries of PAHs were calculated using EPA 610 Polynuclear Aromatic Hydrocarbons Mix from SUPELCO and determined by adding a known PAH standard amount in the blank filter. The recovery of these compounds were between 58% for phenanthrene and 92% for benzo(g,h,i)perylene. The limit of detection (LOD) ranged from 0.080 ng μL<sup>-1</sup> (phenanthrene) to 0.859 ng μL<sup>-1</sup> (benzo(b)fluoranthene). PAH concentrations in laboratory and field blanks were consistently below LOD, and data were not subjected to any blank correction. The limit of detection is defined as three times the standard deviation of the linear coefficient (Miller and Miller 1988).

Concentrations of lower molecular weight PAH compounds were not considered in this work (from naphthalene to fluorene), since their recoveries were very low (<50%). These losses can occur due to the high temperature and the blowoff of the compounds



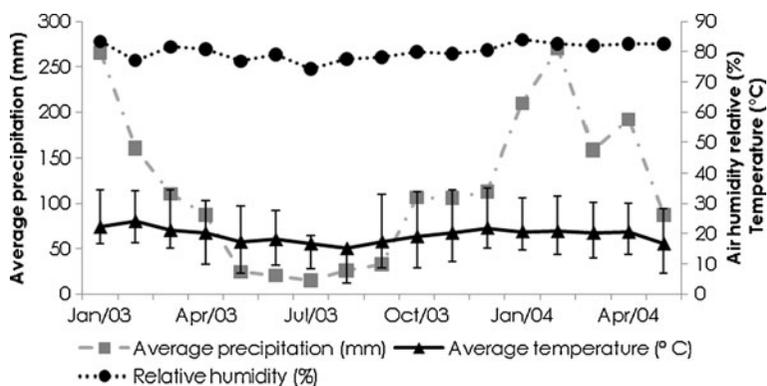
**Fig. 1** Map of the sites investigated within São Paulo State

in the sampling procedure (Vermylen et al. 2005). The standard PAH mixture containing phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF), benzo[a]pyrene (BaP), and indeno[1,2,3-c,d]pyrene (InP), dibenz[a,h]anthracene (DBA) and benzo[g,h,i]perylene (BPe) was used for comparing retention time of the peaks and for quantification as external standard. Benzo(e)pyrene standard solution was prepared with individual product purchased from Sigma Chemical Co.

## 2.2 Meteorological Conditions

São Paulo presents an upland tropical climate with a dry season during wintertime and a wet season during summertime. Fig. 2 presents the meteorological conditions during the extensive campaign. May 2003 was marked by reduction of the rain events in a large part of the country. In June, there was also a reduction of rain and low relative humidity of air, which contributed mainly to the increase of the burning events in Central Brazil and the Southeastern Region. In September 2003, there was a decrease of rain in the southeast area of Brazil, where the accumulated totals were inferior to 25 mm. In December, strong winds prevailed ( $8 \text{ km h}^{-1}$ ), and on March of 2004, it rained in the southeast area of Brazil (average in São Paulo, 159 mm), with the presence of intense winds (from 10 to  $14 \text{ km h}^{-1}$ ). Four masses of cold air, coming in April 2004, contributed to the decreasing of the temperature ( $14^\circ\text{C}$ ). In May 2004, no intense rain was observed.

**Fig. 2** Meteorological conditions during the extensive campaign



## 3 Results

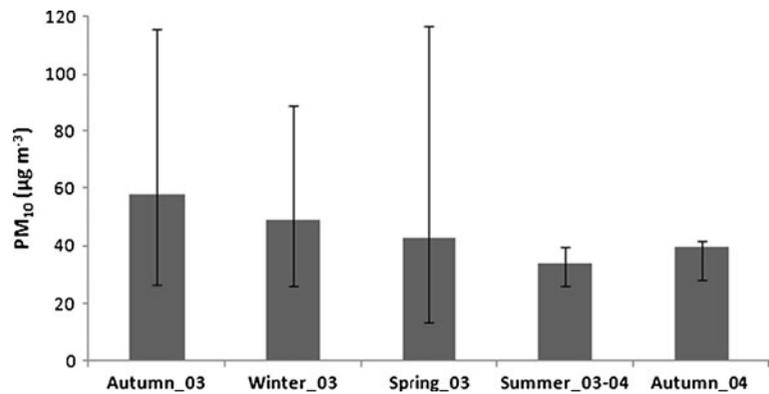
### 3.1 Extensive Campaign

Typical meteorological conditions (lower boundary layer and temperatures) of cold and dry months favored the pollutant accumulation. Low wind velocity ( $4.0$  to  $7.5 \text{ km h}^{-1}$ ), low precipitation ( $\sim 2 \text{ mm}$ ), and temperature between  $14^\circ\text{C}$  and  $24^\circ\text{C}$  between April and September (2003) resulted in the higher particulate matter concentration ( $27\text{--}116 \mu\text{g m}^{-3}$ ). In the average, the autumn season (2003) presented the highest  $\text{PM}_{10}$  concentrations (average,  $\sim 58 \mu\text{g m}^{-3}$ ) and large concentration range in the individual samples. On the other hand, rain events (from November to May and from January to April 2004) removed the particles from the atmosphere and are presented decreasing in levels during spring and summer seasons (Fig. 3).  $\text{PM}_{10}$  average concentration all throughout the year was over  $46 \mu\text{g m}^{-3}$ , below the one recommended by the Brazilian legislation (annual average,  $50 \mu\text{g m}^{-3}$ ).

Total *n*-alkanes, individual PAH, and particulate matter average concentrations of the samples collected in the different seasons are shown in Table 1. For *n*-alkanes, also in autumn, the total concentration was higher ( $35.7 \mu\text{g m}^{-3}$ ) and decreasing with the following seasons: winter,  $21.2 \mu\text{g m}^{-3}$ ; spring,  $16.5 \mu\text{g m}^{-3}$ ; and summer,  $12.4 \mu\text{g m}^{-3}$  and increasing in the next autumn,  $21.6 \mu\text{g m}^{-3}$ . These values are lower than those found recently in the same site in dry ( $67.3 \mu\text{g m}^{-3}$ ) and wet ( $36.4 \mu\text{g m}^{-3}$ ) seasons (Vasconcellos et al. 2010).

The distribution of *n*-alkanes showed an odd to even carbon number predominance (CPI range from 1.2 to 2.0). The CPI is a diagnostic parameter, and

**Fig. 3** PM<sub>10</sub> concentrations in different seasons 2003/2004



high CPI indicates the major incorporation of biological constituents into the aerosol sample. The anthropogenic contaminants reduce the CPI to values close to 1 (Oros and Simoneit 2001; Omar et al. 2007).

The *n*-alkane distribution presented the input of natural sources. Homologue series of *n*-alkanes from C<sub>16</sub> to C<sub>35</sub> indicated anthropogenic and natural emission sources. The split of the carbon range into low (C<sub>16</sub> to C<sub>25</sub>) and high (C<sub>26</sub> to C<sub>35</sub>) ends gave CPI values from 1.3 to 1.4 (C<sub>16</sub> to C<sub>25</sub>) and from 1.3 to 1.7 (C<sub>26</sub> to C<sub>35</sub>) all throughout the year. These CPI values demonstrate the relative input of contemporary biogenic versus anthropogenic materials. The low end is representative of contaminant species, and the high end demonstrates a major input of higher plant wax (Simoneit 1989). Autumn 2003 and spring 2003 samples presented the highest CPI at the high end (1.7).

C<sub>max</sub> for samples collected in autumn, winter, and spring (2003) was C<sub>29</sub>, and for the samples collected in the summer and autumn (2004), it was C<sub>31</sub>. The determination of C<sub>max</sub> gives an indication of relative source input. A C<sub>max</sub> ≥ C<sub>27</sub> reflects the incorporation of higher plant wax, whereas C<sub>max</sub> at lower carbon numbers indicates a major input of fossil fuel combustion compounds.

The presence of petroleum residues is observed by biomarkers as pristane and phytane. Their concentrations varied from 0.1 to 0.4 ng m<sup>-3</sup> during the year, and they confirm the fossil fuel residue contamination. The ratio between them was from 0.5 and 1. Pristane can be found in biological material with pristane/phytane ratio >> 1 (Alves 2008).

Total PAH concentrations decreased from autumn 2003 to autumn 2004 (Table 1). Autumn 2003 presented the highest (7.8 ng m<sup>-3</sup>), and autumn

2004, the lowest concentration (1.6 ng m<sup>-3</sup>). Autumn 2003 was characterized with low precipitation (0.2 mm accumulated rain) and temperatures (average, 18°C) in São Paulo city.

Among the 16 PAHs considered in this work, the most abundant ones in all seasons were Chr, BeP, and BbF. Chr and BeP were predominant PAHs in other studies (Castellano et al. 2003; Fang et al. 2004; Kalaitzoglou et al. 2004), and in previous studies at the SPA site, BbF and Chr were the most abundant PAHs found (Cecinato et al. 1997; Vasconcellos et al. 2010).

Chrysene is considered a marker compound of industrial oil burning emission and is abundant in vehicular and incinerator emissions (Yang et al. 1998; Fang et al. 2004). Chr presence associated with BbF suggests diesel burning emissions (Vasconcellos et al. 2003). Literature reports BeP as indicative of stationary source emissions (industries) and emitted with Ant, Fla, and Pyr can be indicative of diesel burning (Ciccioli et al. 1996; Yang et al. 1998).

Previous studies have shown that PAH concentrations have large variations in the composition and different emission sources, and some ratios between compounds can be helpful to suggest different kinds of emissions (Sicre et al. 1987; Li and Kamens 1993; Vasconcellos et al. 2003). Diagnostic ratios calculated for all samples indicated a multiplicity of sources. Phe/(Phe+Ant) ratios ranged from 0.68 to 0.85 in the spring samples. It suggested gasoline-fueled vehicle emissions (Sicre et al. 1987) while BeP/(BeP+BaP) ratios indicated vehicular, motor oil, and coal burning emissions in all samples studied (Miguel et al. 1998) (Table 2).

BaP and BeP are supposed to be emitted in the same concentration; however, BeP is currently chosen to be the reference compound for being more stable in

**Table 1** *n*-alkanes and PAH concentrations identified in the samples collected in São Paulo city in the different seasons

	Autumn/2003 ( <i>n</i> =6)	Winter/2003 ( <i>n</i> =7)	Spring/2003 ( <i>n</i> =7)	Summer/2003 ( <i>n</i> =6)	Autumn/2004 ( <i>n</i> =5)
<i>n</i> -alkanes (ng m <sup>-3</sup> )					
C <sub>16</sub>	0.1±0.1	0.1±0.1	0.1±0.1	0.2±0.2	0.1±0.1
C <sub>17</sub>	0.2±0.1	0.2±0.1	0.1±0.1	0.2±0.1	0.1±0.0
C <sub>18</sub>	0.5±0.3	0.3±0.2	0.2±0.1	0.5±0.3	0.2±0.1
C <sub>19</sub>	0.4±0.3	0.2±0.1	0.2±0.1	0.4±0.2	0.2±0.1
C <sub>20</sub>	0.4±0.3	0.2±0.1	0.2±0.1	0.5±0.2	0.2±0.1
C <sub>21</sub>	0.5±0.4	0.3±0.2	0.3±0.1	0.4±0.2	0.2±0.1
C <sub>22</sub>	0.8±0.6	0.5±0.3	0.4±0.2	0.3±0.1	0.2±0.1
C <sub>23</sub>	1.5±1.3	0.8±0.5	0.5±0.5	0.5±0.2	0.5±0.1
C <sub>24</sub>	2.4±2.4	1.4±0.8	0.9±1.0	0.6±0.3	0.7±0.3
C <sub>25</sub>	3.5±3.3	1.9±1.3	1.4±1.7	1.1±0.6	1.2±0.4
C <sub>26</sub>	3.2±3.2	1.7±1.3	1.4±1.9	1.0±0.5	1.2±0.5
C <sub>27</sub>	3.8±3.7	2.2±1.7	1.8±2.6	1.4±0.7	1.7±0.7
C <sub>28</sub>	2.6±2.6	1.4±1.0	1.3±1.9	1.0±0.6	1.2±0.5
C <sub>29</sub>	3.7±3.4	2.6±2.9	2.1±3.3	1.3±0.7	2.1±1.1
C <sub>30</sub>	1.6±1.7	0.9±0.7	0.8±1.4	0.6±0.4	0.8±0.4
C <sub>31</sub>	4.1±3.9	2.8±2.9	2.1±4.1	1.1±0.64	2.2±1.4
C <sub>32</sub>	1.2±1.5	0.7±0.7	0.8±1.5	0.4±0.3	0.7±0.5
C <sub>33</sub>	3.0±3.4	1.7±1.7	1.0±2.1	0.5±0.3	1.1±0.8
C <sub>34</sub>	0.7±0.7	0.6±0.6	0.4±0.5	0.1±0.1	0.3±0.2
C <sub>35</sub>	1.0±1.4	0.6±0.7	0.3±0.7	0.1±0.1	0.4±0.3
Total	35.7	21.2	16.5	12.4	21.6
Pristane	0.2±0.1	0.2±0.1	0.1±0.1	0.2±0.1	0.1±0.0
Phytane	0.4±0.2	0.2±0.1	0.2±0.1	0.2±0.1	0.1±0.1
CPI	1.6	1.6	1.5	1.4	1.3
C <sub>max</sub>	C <sub>29</sub>				
PAH (ng m <sup>-3</sup> )					
Phe	0.1±0.2	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1
Ant	0.1±0.1	0.1±0.0	0.3±0.6	0.1±0.1	0.1±0.1
Fla	0.4±0.2	0.2±0.2	0.2±0.2	0.1±0.1	0.1±0.1
Pyr	0.5±0.1	0.3±0.2	0.2±0.2	0.1±0.1	0.1±0.1
BaA	0.8±0.1	0.6±0.4	0.2±0.3	0.1±0.1	0.2±0.1
Chr	1.2±1.0	0.7±0.3	0.5±0.6	0.2±0.1	0.3±0.1
BbF	0.8±0.6	0.7±0.6	0.5±0.5	0.3±0.2	0.1±0.1
BkF	0.8±0.4	0.2±0.1	0.2±0.4	0.2±0.1	0.1±0.1
BeP	1.0±0.6	0.6±0.3	0.5±0.6	0.2±0.1	0.1±0.1
BaP	0.7±0.5	0.4±0.2	0.3±0.3	0.1±0.1	0.1±0.1
InP	0.3±0.1	0.5±0.4	0.1±0.1	0.1±0.1	0.1±0.1
DBA	0.1±0.1	0.2±0.1	0.1±0.1	0.1±0.1	0.1±0.1
BPe	0.8±0.8	0.5±0.2	0.4±0.4	0.1±0.1	0.2±0.1
Total (ng m <sup>-3</sup> )	7.8	5.1	3.6	1.8	1.6
BaPE <sup>a</sup>	0.5–2.0	0.6–0.9	0.1–1.1	0.1–0.3	0.1–0.3
PM <sub>10</sub> (μg m <sup>-3</sup> )	58±38	49±21	43±35	34±5	40±16

*Phe* phenanthrene, *Ant* anthracene, *Fla* fluoranthene, *Pyr* pyrene, *BaA* benzo(a)anthracene, *Chr* chrysene, *BbF* benzo(b)fluoranthene, *BkF* benzo(k)fluoranthene, *BeP* benzo(e)pyrene, *BaP* benzo(a)pyrene, *InP* indeno(c,d)pyrene, *DBA* dibenzo(a)anthracene, *BPe* benzo(g,h,i)perylene

<sup>a</sup> BaPE=BaA×0.06+B(b+k)F×0.07+BaP+DBA×0.6+InP×0.08 (Yassaa et al. 2001)

**Table 2** Diagnostic ratios found in the literature and in this work

	PAH sources				Season/year				
	Vehicular emissions	Gasoline motor exhaust	Motor oil burning	Coal burning	Autumn/2003	Winter/2003	Spring/2003	Summer/2003	Autumn/2004
Phe/(Phe+Ant)	–	0.65–0.89 <sup>a</sup>	~0.78 <sup>a</sup>	–	0.39–0.90	0.55–0.77	0.68–0.85	0.09–0.82	0.27–0.91
Fla/(Fla+Pyr)	0.41–0.49 <sup>bc</sup>	0.35–0.51 <sup>a</sup>	0.26–0.44 <sup>a</sup>	0.56–0.60 <sup>a</sup>	0.40–0.85	0.65–0.87	0.13–0.95	0.40–0.79	0.64–0.97
BaA(BaA+Chr)	0.38–0.60 <sup>bc</sup>	–	~0.5 <sup>a</sup>	0.39–0.47 <sup>a</sup>	0.20–0.52	0.26–0.41	0.29–0.42	0.33–0.43	0.28–0.49
BeP/(BaP+BeP)	0.47–0.76 <sup>c</sup>	0.48–0.58 <sup>a</sup>	0.54–0.74 <sup>a</sup>	0.37–0.49 <sup>a</sup>	0.48–0.72	0.55–0.70	0.49–0.72	0.59–0.70	0.51–0.67
InP/BPe	0.51–0.57 <sup>d</sup>	–	–	–	0.33–0.42	0.41–0.43	0.28–0.51	0.32–0.80	0.29–0.41
BaP/BeP <sup>e</sup>	–	–	–	–	0.4–1.0	0.4–0.8	0.4–1.0	0.4–0.7	0.5–1.0

<sup>a</sup> Sicre et al. 1987<sup>b</sup> Li and Kamens 1993<sup>c</sup> Miguel et al. 1998<sup>d</sup> Vasconcellos et al. 2003<sup>e</sup> BaP/BeP, index for calculating the aging of the particles (Panther et al. 1999; Bi et al. 2003).

the atmosphere (Panther et al. 1999; Bi et al. 2003). BaP/BeP ratios can be an important index for calculating the aging of the particles (Vasconcellos et al. 2010). BaP/BeP ratios <1 in 97% of the samples suggested that the particulate matter was submitted to photochemical reactions during the transport. These reactions depend on solar radiation intensity, and it is expected to happen in warmer months in the tropics.

Carcinogenic PAHs (BbF, BkF, BaP, InP, and BaA) are responsible for 35% of the PAH mass found in Autumn 2004 and over 45% found in the other seasons. These values are comparable to those found by Da Rocha et al. (2009) at coast sites (40%). Since BaP is easily decomposed in a reactive atmosphere, another index has been used to indicate the health risk for humans related to PAH exposition (Yassaa et al. 2001). If only BaP were taken into account, the carcinogenic power from PAH would be underestimated. Benzo[*a*]pyrene-equivalent carcinogenic power (BaPE) is an index that has been used instead of using only benzo(a)pyrene. The ranges for each season are shown in Table 1. Only few samples collected in autumn 2003 and spring presented BaPE higher than 1, what may be presenting a significant cancer risk. Higher temperatures in summer (average, 24°C) may have favored higher PAH volatilization. Besides, higher wind speed (average, 7 km h<sup>-1</sup>) may have favored pollutant dispersion. In the urban atmosphere of Guangzhou, China, the BaPE ranged from 0.95 to 21.69 (Bi et al. 2002), and samples collected in São

Paulo State in sites where strong air pollution events occurred presented those values between 0.4 and 3.7 (Vasconcellos et al. 2010).

To better understand the PAH removal mechanisms, dry deposition fluxes were calculated for the different seasons (Table 3). Dry atmospheric deposition fluxes ( $F_d$ ) were calculated by multiplying the geometric mean of each PAH concentration ( $C_i$ ) in the particulate matter to PAH dry settling velocity ( $V_d$ ) ( $F_d = C_i \times V_d$ ). Although there are some uncertainties related to the term  $V_d$  (since this may vary considerably due either to particle size and climatological or physical conditions of the atmosphere), the particulate matter dry deposition flux calculations bring broad but helpful insights in order to better understand PAH removal mechanisms (Sheu et al. 1996; Nielsen 1984). Therefore, in this study, PAH particle dry deposition was calculated by using  $V_d$  stated on the latter cited study as observed in Table 3.

The highest value for dry atmospheric deposition flux was found in autumn and winter 2003 seasons (2.803  $\mu\text{g m}^{-3} \text{ day}^{-1}$ ). In the other seasons, the fluxes are lower and comparable (0.713  $\mu\text{g m}^{-3} \text{ day}^{-1}$ , 0.697  $\mu\text{g m}^{-3} \text{ day}^{-1}$ , and 0.589  $\mu\text{g m}^{-3} \text{ day}^{-1}$ ). Individually, BPe presented the highest deposition flux followed by BbF. Due to particular meteorological conditions found in the autumn and winter seasons resulting in more stagnant conditions of the atmosphere (which have favored the accumulation of pollution) and few rain events (that have disfavored

**Table 3** Dry deposition fluxes calculated for the different seasons (2003)

	Phe	Ant	Flu	Pyr	BaA	Chr	BbF	BkF	BeP	BaP	InP	DbA	BPe	TOTAL
Autumn 2003														
Geom. mean (ng m <sup>-3</sup> ) <sup>a</sup>	0.07	0.027	0.294	0.436	0.608	1.094	0.607	0.666	0.861	0.590	0.260	0.145	0.720	6.379
Dry depos. flux (μg m <sup>-2</sup> day <sup>-1</sup> ) <sup>b</sup>	0.01	0.009	0.104	0.075	0.184	0.511	0.288	0.357	0.000	0.362	0.200	0.095	0.604	2.803
Winter 2003														
Geom. mean (ng m <sup>-3</sup> )	0.06	0.030	0.184	0.248	0.353	0.652	0.780	0.152	0.479	0.285	0.157	0.093	0.374	3.842
Dry depos.	0.01	0.009	0.104	0.075	0.184	0.511	0.288	0.357	0.000	0.362	0.200	0.095	0.604	2.803
Spring 2003														
Geom. mean (ng m <sup>-3</sup> )	0.043	0.065	0.074	0.110	0.121	0.227	0.340	0.091	0.179	0.111	0.072	0.049	0.153	1.635
Dry depos. flux (μg m <sup>-2</sup> day <sup>-1</sup> )	0.009	0.023	0.026	0.019	0.037	0.106	0.162	0.049	0.000	0.068	0.055	0.032	0.128	0.713
Summer 2004														
Geom. mean (ng m <sup>-3</sup> )	0.017	0.034	0.073	0.114	0.102	0.169	0.251	0.124	0.135	0.076	0.045	0.043	0.081	1.578
Dry depos. flux (μg m <sup>-2</sup> day <sup>-1</sup> )	0.003	0.012	0.026	0.019	0.031	0.079	0.119	0.066	0.000	0.047	0.035	0.028	0.070	0.536
Autumn 2004														
Geom. mean (ng m <sup>-3</sup> )	0.051	0.020	0.067	0.158	0.142	0.240	0.112	0.098	0.172	0.108	0.053	0.039	0.152	1.412
Dry depos. flux (μg m <sup>-2</sup> day <sup>-1</sup> )	0.010	0.007	0.024	0.027	0.043	0.112	0.053	0.052	0.000	0.066	0.040	0.026	0.127	0.589

the wet deposition of them), it seems that during those periods, the dry deposition was the main airborne PAH removal mechanism.

### 3.2 Intensive Winter Campaign

In the dry season, an intensive campaign (July 16 to 29,  $n=15$  samples at each site) took place at the three chosen sites in order to study the most polluted period of the year at different sites of São Paulo State, during the sugarcane harvest time conducted within the São Paulo State. These sites present different characteristics. Piracicaba and Araraquara sites are urban areas strongly impacted by agricultural activities including sugarcane burning. In this period, back trajectory analysis revealed that air masses are transported into São Paulo State from the northeast of Brazil. Within the state of São Paulo, air masses passed over industrial areas and sugarcane burning before arriving at the SPA site. During those months, many biomass burnings in the central part of São Paulo State have occurred, resulting from both accidental fires and human activities (Vasconcellos et al. 2007b).

The PM<sub>10</sub> average concentration found at ARQ was over 75 μg m<sup>-3</sup>, slightly higher than that of the SPA site (68 μg m<sup>-3</sup>). At the PRB site, the TSP

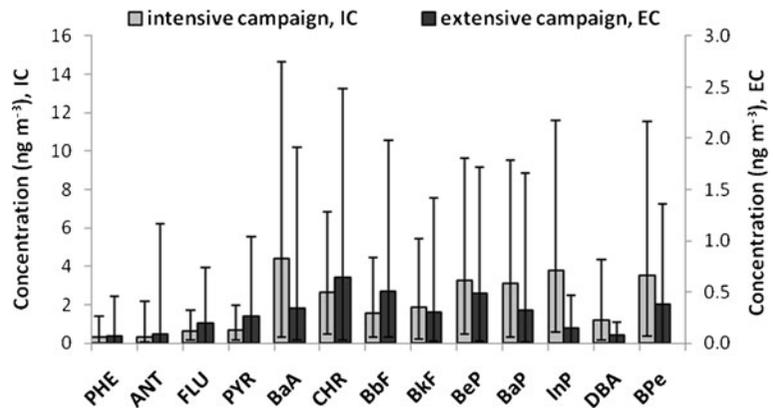
concentration was over 108 μg m<sup>-3</sup>, lower than those found at Rio de Janeiro State sites with similar influences (Campo dos Goytacazes City, 195–397 μg m<sup>-3</sup>; Azevedo et al. 2002).

In total, petrogenic and biogenic CPIs were higher at ARQ (2.9, 2.7, and 2.7) and PRB (2.4, 1.7, and 2.4) than at SPA (1.5, 1.4, and 1.5). At PRB, CPI values were 2.4, 1.7, and 2.4. These values showed higher biogenic contribution from biomass burning sites during the sugarcane harvest.

PAH average concentrations were higher at SPA (27.4 ng m<sup>-3</sup>) than the other sites, PRB (13.9 ng m<sup>-3</sup>) and ARQ (10.9 ng m<sup>-3</sup>). BaP concentrations found in the intensive campaign (3.1 for SPA, 1.5 for PRB, and 0.9 for ARQ) were higher than those in the extensive campaign (from 0.1 to 0.7). For DBA, higher levels were found in the intensive experiment for SPA (1.2) and for ARQ (0.3) than the 2003/2004 campaign (from 0.1 to 0.2). The DBA presence is attributed to industrial emissions and is considered ten times more carcinogenic than BaP (Okona-Mensah et al. 2005). PAH concentrations in the samples collected during both campaigns are shown in Fig. 4.

Diagnostic ratios were also calculated to suggest emission sources. Vehicular emissions are strongly suggested for the three sites for Fla/(Fla+Pyr) and

**Fig. 4** Comparison of the PAH concentrations between intensive and extensive campaigns at the SPA site



BeP/(BaP+BeP) ratios. BaP/BeP values over 0.7 for ARQ and 0.8 for SPA and PRB samples suggest photochemical reactions during the particulate matter transport.

Simoneit (2002) reports Phe, Flu, Pyr, and smaller amounts of Ant in Gramineae burning emissions. The relative concentrations of these PAHs were higher at ARQ (3.2%, 8.2%, and 9.3%) than at SPA (1.2%, 2.3%, and 2.5%). Principal component analysis of PAH showed that fluoranthene and pyrene are responsible for the formation of a group composed of ARQ samples and most of the Piracicaba samples, both biomass burning sites (Magalhães 2005).

Samples collected during the harvest period in the Campo dos Goytacazes, in Rio de Janeiro State, also presented a marked increase in PAH concentrations, and the main contribution was attributed to the pyrogenic sources (Maioli et al. 2009). In a previous work made in Rio de Janeiro City, at different urban sites, the main source of PAH is vehicle emissions, and the decrease in the degree of pollution followed the traffic density (Azevedo et al. 1999).

Another study made in Campo Grande City (Ré-Poppi and Santiago-Silva 2005), inside the university campus surrounded with Cerrado vegetation and receiving biomass combustion smoke in the period of low precipitation, presented a PM concentration much lower (average,  $32.85 \mu\text{g m}^{-3}$ ) than those found at ARQ, PRB, and SPA sites. BaP, a PAH indicator of carcinogenic risk, was found in concentrations ( $0.26 \text{ ng m}^{-3}$ ) also much lower than those found in this work (3.1 for SPA, 1.5 for PRB, and 0.9 for ARQ).

At the ARQ site, samples collected also in harvest season (September, 2003) presented  $\text{PM}_{10}$  concentrations between  $41$  and  $86 \mu\text{g m}^{-3}$  (average,

$67 \mu\text{g m}^{-3}$ ) and total PAH concentration around  $11.6 \text{ ng m}^{-3}$  (Andrade et al. 2010). These concentrations are comparable with those found at ARQ in this work, in July 2003 ( $75 \mu\text{g m}^{-3}$  for  $\text{PM}_{10}$  and  $10.9 \mu\text{g m}^{-3}$  for the total PAH concentration).

BaPEs were also calculated for this campaign. The samples presented variable values ranging from 0.6 to 13.3 for SPA and from 0.3 to 4.6 for ARQ. For PRB samples, BaPE varied from 0.5 to 4.8. SPA (73%) and PRB (71%) samples presented higher cancer risk than ARQ (47%) in the winter campaign.

Dry deposition flux was also calculated for the samples collected in the intensive campaign. In the extensive campaign, BPe (autumn, winter, and spring 2003 and autumn 2004) and BbF (summer 2003) presented the highest values; in this short campaign, BPe ( $3.382 \mu\text{g m}^{-3} \text{ day}^{-1}$ ) and BaP ( $2.201 \mu\text{g m}^{-3} \text{ day}^{-1}$ ) presented the highest values.

### 3.3 Samples Collected in Polluted and Unpolluted Events at SPA and Arq Sites

At the ARQ and SPA sites, some samples were collected also on March, 2003, when clean air conditions and no biomass burnings were observed within the State of São Paulo. For SPA, *n*-alkanes from  $\text{C}_{15}$  to  $\text{C}_{30}$  are more abundant in the unpolluted campaign than in the polluted one; conversely, the higher molecular weight compounds, from  $\text{C}_{31}$  to  $\text{C}_{35}$ , are more abundant during the polluted event. For ARQ samples, the predominance of  $\text{C}_{15}$  to  $\text{C}_{21}$  is observed in the samples collected in the unpolluted season and from  $\text{C}_{22}$  to  $\text{C}_{35}$  in the samples collected in the polluted season.  $\text{C}_{\text{max}}=\text{C}_{27}$  also indicated the strong influence of biogenic sources. Fig. 5 shows

*n*-alkane concentrations of the samples collected during polluted (intensive campaign) and unpolluted (March) episodes.

At the SPA site, Phe, Ant, and DBA are more abundant in the dry season than in the wet season; Flu, Pyr, and BbF are more abundant in the wet season. This March (2003) showed atypical meteorological conditions with low precipitation (over 100 mm) and temperature around 22°C.

In the previous study (Vasconcellos et al. 2007b), linear correlation coefficients between some pollutant concentrations were calculated with the aim of investigating similarities in the aerosols' composition. Correlation for SPA and ARQ samples between N-PAH with PAH was around 0.6, and for PRB, a weak correlation was found. At SPA and ARQ, the sources of N-PAH were the same as for some other pollutants.

Fig. 4 shows PAH concentrations of the samples collected during polluted (intensive campaign) and unpolluted (March) episodes. BaPE values for polluted samples ranged from 1 to 13 for SPA samples and from 0.3 to 4.6 for ARQ samples. For clean episodes (March), BaPE values were over 0.3 for both sites. Samples collected under air pollution episodes presented cancer risk.

#### 4 Conclusions

This work reports the composition of the chemical classes polycyclic aromatic hydrocarbons and *n*-alkanes in the particulate matter collected during four seasons in the city of São Paulo. In the short intensive

campaigns, samples were also collected at the two sites influenced by sugarcane burning.

The highest PM<sub>10</sub> concentration was found in autumn 2003 samples. Carbon number predominance indicated the incorporation of biological constituents in the samples collected throughout the year. Autumn and spring (2003) presented the highest CPI. The C<sub>max</sub> reflected the incorporation of higher plant wax. Besides the natural compounds, petroleum residues were observed by the biomarkers' presence.

At SPA, chrysene associated with BbF between the most abundant PAH suggested diesel burning emissions and with BeP, stationary sources emissions.

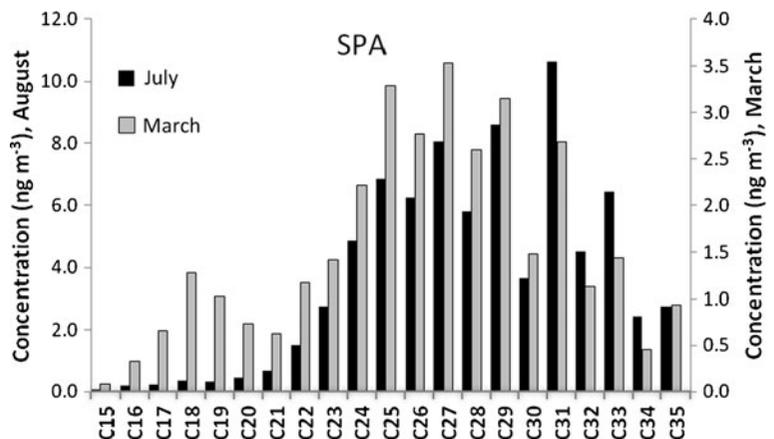
Diagnostic ratios indicated multiplicity of sources: gasoline-fueled vehicles, motor oil, and coal burning emissions. In addition, BaP/BeP ratios suggested that photochemical reactions occurred during the process, influencing the composition of the atmosphere.

Atmospheric deposition flux values calculated in the autumn and winter (2003) showed the highest values for BPe followed by BbF.

Intensive campaign samples showed higher cancer risk than those collected in the extensive campaign. During the intensive campaign, samples collected at the urban site (SPA) presented comparable values of PM<sub>10</sub> to the urban site influenced by sugarcane burning (ARQ). On the other hand, PAH average concentrations were higher at SPA than at other sites.

Diagnostic ratios also suggested vehicular emissions at the three sites. Photochemical reactions influenced in the atmospheric particulate matter composition. SPA and PRB samples presented higher cancer risk than ARQ in the intensive campaign.

**Fig. 5** *n*-Alkane concentrations found in the samples collected during polluted (July 2003) and unpolluted (March 2003) events



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