POLYCYCLIC AROMATIC HYDROCARBONS, DIOXINS AND FURANS LEVELS IN THE ATMOSPHERE OF CENTRAL AREA OF SÃO PAULO CITY

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), commonly known as dioxins and furans and Polycyclic Aromatic Hydrocarbons (PAHs) and their derivatives are chemical groups with compounds with proven carcinogenicity[1, 2], although the carcinogenic potency varies greatly[3]. In this work the levels of these pollutants (PAHs and PCDD/Fs) in the atmosphere of the central area of São Paulo city will be presented. The air quality in the area is mainly affected by vehicle emissions, according to inventory of sources from the Environmental Company of the State of Sao Paulo (CETESB)[4].

Materials and methods

Sample collecting and analysis of PAHs were performed in accordance with US EPA Method TO-13A[5] with Polyurethane Foam (PUF) Sampler PS1, from Andersen Instruments Inc. (Smyrna, GA, USA). PS1 Sampler was assembled with the combination of 10.16 cm diameter quartz micro fiber filters, Whatman Inc. (Clifton, NJ, USA), and a 6 cm diameter and 7.62 cm length PUF, Tisch Environmental, Inc. (Cleves, OH, USA). The extraction and chemical analysis of 16 target PAHs, was undertaken by gas chromatograph/mass spectrometer (GC/MS). PAHs samples were collected for 24 h in eight days during colder months (June, July and August, 2014), when pollutant dispersion conditions are more critical due to more frequent low wind speeds, decreased rainfall levels, thermal inversions of low altitude and consequently increased air pollution levels. Data on PM_{10}, NO_2 and O_3 concentrations and meteorological parameters were obtained from the State Air Quality Monitoring Station Network, which is operated by the CETESB-Environmental Agency of the State of São Paulo.

Results and discussion

The measured data were statistically analyzed and along with the data of CO, MP_{10}, NO_2, O_3, temperature and carcinogenic group presented in Table 1. The revealed showed the presence of almost all of the 16 PAHs listed as priority pollutants by United States Environmental Protection Agency (USEPA) according on their availability and adverse effects on human health[6]. The sum of the concentrations of 16 HPAs (sum of concentrations of all PAHs both in gas phase and in particles) ranged from 7.61 $ng.m^{-3}$ to 38.07 $ng.m^{-3}$. The overall mean was 19.97 $ng.m^{-3}$ standard deviation of 10.91 $ng.m^{-3}$. PAHs with low molecular weight, making up about 55% of the total PAHs content (2-rings 4%; 3-rings 51%) and PAHs with high molecular weight, making up about 45% of the total PAHs content (4-rings 30%; 5-rings 9%; 6-rings 6%). With increases of molecular weight, the carcinogenicity of PAHs also increases, and acute toxicity decreases[7]. The higher concentrations were observed for Phenanthrene (Phe) (3-rings) that accounted for 39.5 % of ΣPAHs. Other abundant PAHs were Fluoranthene (Flt) (14 % of ΣPAHs), the most abundant 4-rings PAHs in air, following Pyrene (Pyr) (12 % of ΣPAHs). Naphthalene (Nap), a compound with 2-rings, accounted for 4 % of ΣPAHs.

Health risk of mixtures of PAHs compounds can be performed with the use of Toxic Equivalence Factors (TEFs) proposed by Nisbet and LaGoy (1992)[8], being BaP a reference compound. Total equivalent concentration of PAHs was determined for the 2014 PAH data resulted in 1.06 $ng\text{-}TEQ.m^{-3}$. And BaP contributed to approximately 2/3 of the carcinogenic activity for the site (75%). The second highest BaP equivalent compound was IcdP, occupying 7% of total carcinogenic activity for the site. Sum of BaP, IcdP, BbF, BkF and BghiP carcinogenic activities accounted for 93% of the total BaPeq carcinogenic activity, which is similar to results from Osaka, Japan[9]

De Assunção et al. (2007)[10] performed sampling campaigns for PAHs and PCDD/Fs at the same site in May, June, July and August 2006. The total carcinogenic activity of PAHs was 4.9 $ng\text{-}TQ.m^{-3}$. It is important to

emphasize that in this collection campaign Dibenz[ah]anthracene (DahA) concentrations ranged from 0.45 to 2.62 ng/m^3 (mean 1.35 ng/m^3) contributing to approximately 1/4 of the activity for the site (27%). The second highest BaP equivalent compound was Bap, occupying 26.5% of total carcinogenic activity for the site and the carcinogenic PAHs (BaP, IcdP, BbF, BkF and BghiP) accounted for 66.5% of the total BaPeq concentrations.

The sum of BaP equivalents carcinogenic activity of seven PAHs (BaA, Chr, BbF, BkF, BaP, DahA, IcdP) were calculated and compared with the result of studies around the World using also that used the same Nisbet and LaGoy (1992)[8] TEFs (Table 2). Total BaP equivalent carcinogenic activity of Sao Paulo (1.04 ng.m^{-3}) was similar to the one reported for Nagasaki – Japan[11] (1.3 ng.m^{-3} for 1 year), where heavy traffic is frequent, and t was lower than results for central areas of Athens – Greece[12] (2.0 ng.m^{-3}), Bangkok – Thailand[13] (2.1 ng.m^{-3}), and Rome – Italy[14] (2.5 ng.m^{-3}). On the other hand results for Sao Paulo in 2006[10] (4.9 ng.m^{-3}) was the highest one among results listed on Table 2.

Dioxins and furans levels were measured by De Assunção et al. in Sao Paulo, in 2000/2001[15], and in 2006[10], in three sampling sites, including the one used in this study for PAH measurements. For the three sites combined, the average PCDD/Fs concentration in 2006[10] was 104.9 fg TEQ.m^{-3} and was lower than the average for the 2000/2001 study (160 fg TEQ.m^{-3})[15], a decrease of 34.4%. The authors concluded that the decrease could be attributed partially to the decrease in PM_{10} levels in the city of Sao Paulo in the same period, which was about 24%, due to enforcement and also to replacement of old vehicles, not equipped with catalyst converter, by vehicles with improved technology and or equipped with emission control devices, specially the Otto vehicles (light-duty vehicles).

The decrease observed in PAH concentrations in 2014 compared to the 2006 study can be attributed partially to the decrease in ambient concentrations of classic pollutants related to vehicular emission (CO, PM_{10} and NO_2). The linear relationship between concentrations of PAHs compounds and CO, PM_{10}, NO_2, and O_3 was evaluated through the correlation matrices with critical Pearson correlation coefficients with significance level of 0.05, were used in order to identify possible emission sources of PAHs. A strong correlation was obtained between Anthracene (Ant), Benzo[a]anthracene (BaA) and Chrysene(Chry) and PM_{10} (r=0.71; r=0.81 and r=0.82, respectively), and NO_2 (r=0.73; r=0.83 and r=0.82, respectively). Benzo[a]anthracene (BaA) also showed strong correlation with CO (r=0.80). The diversity in PAH sources could also be characterized from diagnostic ratios[7].The ratio BaA/Chry (0.95) found in this study is according to those obtained by Vasconcelos et al (2003)[16], which suggests contributions by vehicular emissions. Abrantes et al. (2009)[17] quantified the PAHs emission from light-duty vehicles (gasohol[1] and flexible-fuel[2]-powered vehicles) and found that emissions of light molecular weight PAHs were predominant. Moreover, the use of fuel additive, on gasohol-powered light vehicle, causes a significant increase in the emission of naphthalene and phenanthrene. Gasohol and hydrated ethyl alcohol are a regular fuel in Brazil.

Another cause could be the use better quality of vehicular fuel since sulfur content in diesel fuel went down sharply since 2006, from 500ppm to 10 ppm[11]. Moreover, diesel-powered vehicles (heavy-duty trucks and buses) entered a new phase, Phase 7, of the National Motor Vehicle Air Pollution Control Program (PROCONVE), with emission limits similar to Euro 5 standards. The tightening in emission limits, improvements in the fuel quality and the introduction of new technologies (parts and engines) associated with the implementation of exclusive busways and the intensive use of flexible-fuel vehicle, which may run with any mix of gasoline and ethanol, including plain ethanol. About 50% of the light duty vehicle fleet in São Paulo are now flexible-fuel vehicle[1]. All these together helped to reduce toxic emissions from vehicle exhaust like PAHs and PCDD/Fs. A more systematic monitoring of these toxic pollutants would be very helpful for trend analysis.

References

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[1] Gasohol vehicles, that can use a blend of 22% anhydrous ethanol and 78% gasoline (Silva et al., 2010)[18].

[2] Flexible-fuel vehicles, that can use either gasohol or hydrated ethyl alcohol, or any mixture of them (Abrantes et al., 2009)[17].

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Table 1. Average mass concentrations and other statistically important parameters of PAHs (ng/m^3) and CO (ppm), MP_{10} (µg/m^3), NO_2 (µg/m^3), O_3 (µg/m^3) and temperature (°C) measured at São Paulo central area.

Variable (PAHs)	Ring number	Carcinogenic group[a]	Valid N	Descriptive Statistics			
				C_{med} mean	Cmin minimum	Cmax maximum	Standard deviations
Naphthalene (Nap)	2	3	7	0,96	0,07	1,77	0,68
Acenaphthylene (Acy)	3	3	5	0,72	0,26	1,05	0,37
Acenaphthene (Acp)	3	3	7	0,18	0,07	0,37	0,10
Fluorene (Flu)	3	3	8	0,99	0,47	1,79	0,44
Phenanthrene (Phe)	3	3	8	8,53	4,14	14,23	4,19
Anthracene (Ant)	3	3	7	0,60	0,24	1,42	0,40
Fluoranthene (Flt)	4	3	8	3,02	1,22	6,65	1,95
Pyrene (Pyr)	4	3	8	2,62	0,82	6,18	1,83
Benzo[a]anthracene (BaA)	4	2B	7	0,42	0,13	1,04	0,30
Chrysene (Chry)	4	2B	8	0,44	0,13	1,19	0,39
Benzo[b]fluoranthene (BbF)	5	2B	6	0,74	0,26	1,63	0,52
Benzo[k]fluoranthene (BkF)	5	2B	5	0,31	0,18	0,42	0,09
Benzo[a]pyrene (BaP)	5	1	6	0,81	0,20	1,74	0,56
Indeno[1,2,3-c,d]pyrene (IcdP)	5	2B	4	0,79	0,37	1,32	0,44
Dibenz[ah]anthracene (DahA)	6	2A	0	ND	ND	ND	ND
Benzo[g,h,i]perylene (BghiP)	6	3	5	0,47	0,14	0,97	0,33
CO (ppm)	-	-	8	0,93	0,30	1,79	0,55
MP_{10} (µg/m^3)	-	-	8	45,41	4,96	86,58	33,85
NO_2 (µg/m^3)	-	-	8	53,63	14,17	99,30	33,52
O_3 (µg/m^3) Pinh	-	-	8	18,47	9,62	27,92	7,44
Temperature (°C) Pinh	-	-	8	18,18	12,67	21,09	3,05

[a] Carcinogenic to humans; 1, carcinogenic to humans; 2A, probably carcinogenic to humans; 2B, possibly carcinogenic to humans; 3, not classifiable as to its carcinogenicity to humans – (WHO, 2010)[2].
ND - Not detected

Table 2. Calculated BaP equivalents (ng/m^3) of seven carcinogenic PAHs measured at the residential site.

Sites	BaPeq (ng/m^3)	Measurement period	Reference
Central São Paulo	1.04	Winter 2014	This study
Central São Paulo	4.9	May – August 2006	De Assunção et al., 2007[10]
Nagasaki	1.3	1997/1998	Wada et al., 2001[11]
Athens	2.0	Winter 1996	Marino et al., 2000[12]
Bangkok	2.1	November 2002–April 2003	Norramit et al., 2005[13]
Rome	2.5	1996/1997	Menichini et al., 1999[14]