A PILOT STUDY ON THE PAH PROFILE IN AIR PARTICULATE MATTER FROM DIFFERENT SAMPLING POINTS IN FEIRA DE SANTANA (BAHIA, BRAZIL)

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Introduction

Feira de Santana is the biggest city of the country part of the Bahia State (Brazil). One of the important peculiarities of the city is the intense automotive vehicle traffic, which is a consequence of the fact that the city is crossed by two important federal highways (BR116 and BR101).

Polycyclic Aromatic Hydrocarbons (PAHs) are substances known by their carcinogenic properties. These compounds are originated by incomplete burning of organic matter. As expected considering the origin of this chemical class, the presence of PAHs in the environment constitutes a common finding. However, the association of these compounds to atmospheric particulate material sampled in urban areas has been highlighted. It has been more than thirty years since soot particle was first correlated to occupational exposure to Polycyclic Aromatic Hydrocarbons (PAHs)[1]. This correlation was verified in European chimney cleaning workers, who presented tumor growth in skin and scrotum[1]. According to the Ambient Air Pollution by PAH Position Paper[2] lung cancer is the main risk associated to PAH inhaling. The carcinogenicity of a PAHs can be estimated through its benzo[a]pyrene equivalent concentration (B[a]PEq). The toxic equivalent factor (TEF) of each PAH is used for calculating the B(a)PEq concentration of the compound. The TEF corresponds to the carcinogenic potency of the certain PAH relatively to benzo[a]pyrene, which is used as a reference. As the benzo[a]pyrene concentration values, the B(a)PEq represents the exposure level of individuals. Therefore, the B(a)PEq can be also used for calculating the theoretical risk of lung cancer development through PAH mixture inhaling. The B(a)PEq is commonly assessed through the multiplication of the concentrations of the different carcinogenic PAHs by their TEFs[3].

The aim of the present study was to evaluate the contamination of the total particulate matter (TPM), providing data for a realistic assessment of the exposure to PAHs.

Materials and methods

The sample collection of total atmospheric particulate matter was carried out in quartz fiber filter (Pallflex™ 22.8X17.7cm) using a high volume sampler (ENERGETICA), in three different days in may 2003 (dry period) at Feira de Santana city, Bahia state, Brazil. The three sampling points were (1) the Campus of the Feira de Santana State University (control area), (2) Campo Limpo (roadway), and (3) Getúlio Vargas Avenue (downtown area).

PAHs were extracted according to Pereira et al[4]. The filter was extracted three times with 4mL of an acetonitrile / methylene chloride mixture (3/1; v/v) in ultrasound bath for 10 minutes. The extracts were combined and the volume was reduced to 2mL and filtered through Millex filter (0.22μ pore size, Millipore).

PAHs in the filtered extracts were separated by HPLC with fluorescence detection. The separation of the studied PAHs (naphtalene, phenanthrene, fluoranthene, anthracene, pyrene, benzo[a] anthracene, benzo[b]fluoranthene, benzo[k] fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, indene[1,2.3-cd]pyrene, and benzo[g,h,i]perylene) was performed in a C18 reversed phase column (25cm X4,6mm i.d) with 5μm particles and 120Å of pore size. The isocratic mobile phase was composed by acetonitrile/water (80/20; v/v). The volume injection was 1.5μL at a flow rate of 1,5mL/min.

Benzo(a)pyrene equivalent (B[a]Peq) calculation was performed adopting individual factors for different PAHs[3].

Limits of detection (LD) were calculated for a signal-to-noise ratio equal to 10 and varied from 0.228 to 0.056 ng/mL. The coefficient of determination (r^2) obtained from the calibration curves ranged from 0.9971 (for anthracene) to (1.0 for fluorene and benzo(k)fluorantene). Analyses were performed using the mean value obtained from three extractions of the Standard Reference Material (SRM) 1649 Urban Dust, Organics (NIST, Washington, DC), with recovery values varying from 45.3% for fluorene to 120.5% for benzo(k)fluorantene[4].

Results and discussion

All the targeted PAHs were detected in at least one of the samples. The air samples from Getúlio Vargas Avenue and from UEFS Campus showed to be contaminated with all the studied PAHs. In the former sample, the concentrations of the individual PAHs (in ng/m^3) varied from 0.21, for dibenz[a,h]-anthracene, to 2.24, for pyrene. In the latter sample, the levels (in ng/m^3) varied from 0.01, for fluoranthene, to 1.00, for benzo[b]fluoranthene. However, in the air sample from Rotatória do Campo Limpo, naphthalene and fluoranthene were not detected. In this sample, concentrations of the detected PAHs (in ng/m^3) varied from 0.30, for dibenz[a,h]-anthracene, to 1.48, for pyrene.

Regarding the sum of PAHs (ΣPAH), the values found (in ng/m^3) were 3.94 at UEFS Campus, 7.76 at Campo Limpo, as well as 10.7 at Getúlio Vargas Avenue. The explanation for the highest concentration might be given by the fact that the sampling point at Getúlio Vargas Avenue presents intense automotive traffic, comprising small, medium and large sized vehicles.

The values (in ng/m^3) of the sum of carcinogenic PAHs were 3.53, 2.25 and 3.59, at Getúlio Vargas Avenue, UEFS Campus and Campo Limpo, respectively. The concentrations of the individual carcinogenic PAHs (in ng/m^3) oscillated between values lower than the limit of quantification (LOQ) for dibenz[a,h]-anthracene at UEFS Campus, and 0.94 for benzo[b]fluoranthene at Getúlio Vargas Avenue. The percent contributions of carcinogenic PAHs to the sum of PAHs (ΣPAH) were 33.0% at Getúlio Vargas Avenue, 57.1% at UEFS Campus and 46.2% at Campo Limpo.

In the present study, the B[a]PEq values (calculation based on EPA[3]) were 0.31, 0.79 and 0.32 ng B[a]PEq /m^3, at UEFS Campus, Campo Limpo and Getúlio Vargas Avenue, respectively.

Still regarding carcinogenicity, the number of rings of the different PAH structures is strongly correlated with the carcinogenic potential of the molecules. In fact, the carcinogen PAHs are only found among the molecules that present from four to six rings[5]. Through histograms on the summed concentrations (in ng/m^3) of PAHs grouped by the number of rings in the molecule (Figure 1), it is possible to observe that Getúlio Vargas Avenue presents the highest level for the sum of four, five and six-ringed PAHs.

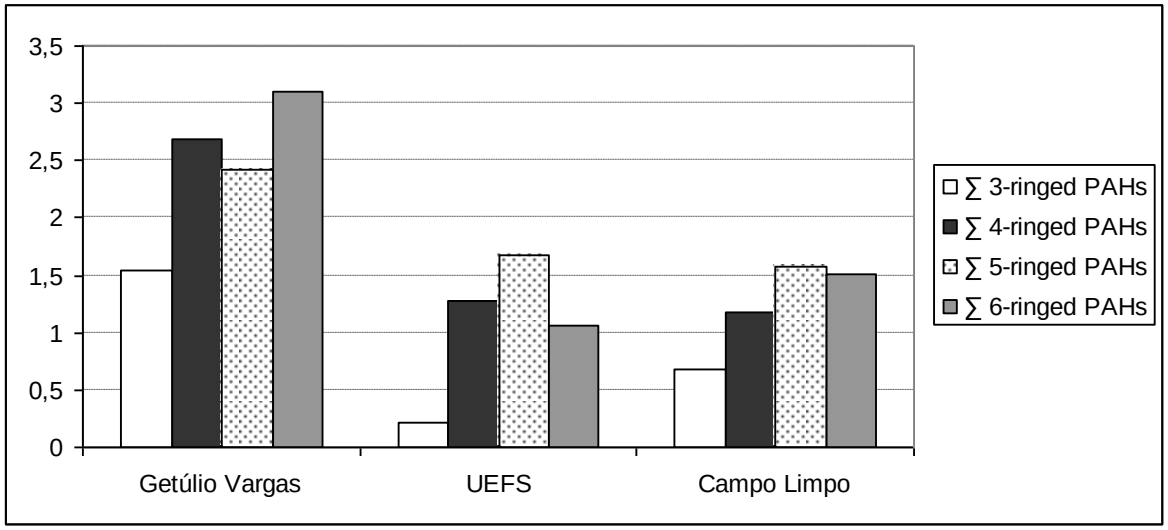

Figure 1. Histograms on the summed concentrations (in ng/m^3) of PAHs grouped by the number of rings in the molecule for the three sampling points, i.e., for UEFS Campus, Campo Limpo and Getúlio Vargas Avenue.

In the study of Azevedo et al.[6], performed in Campos dos Goytacazes city, Rio de Janeiro state (Brazil), the carcinogenic PAHs benz[a]-anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene were quantified. The concentrations of different carcinogenic PAHs generated the values 23.96 and 24.50 ng B[a]PEq /m^3, at two points sampled during the sugar cane burning period. As PAHs may also be generated by this process, the authors suggested the high values to be a consequence of the sugar cane burning.
Other investigations from distinct parts of the world found higher values than those observed in Feira de Santana city. Wada et al[7] verified, in Nagasaki, Japan, similar values (1.29 ng B[a]PEq /m^3) than those found by Menichini et al.[8], in Rome (2.48 ng B[a]PEq /m^3). Nielsen et al[9] verified similar values, in Copenhagen (6.27 ng B[a]PEq /m^3), than those found by Ruchirawat et al[10], in Bangkok (6.83 ng B[a]PEq /m^3). The B(a)PEq values, calculated from distinct carcinogenic PAH mixtures at different sampling points in Feira de Santana city, as well as some B(a)PEq values found in literature, are presented in the Table 1.

Table 1 – B(a)PEq (ng/m^3) calculated from the individual PAH concentrations in the sampling points and literature values.

Country	B(a)Peq	Sampling site
Greece[11]	0.06	Control point
Greece[11]	0.29	Urban
Vietnam	0.33	Rural
UEFS[PS]	0.50	Control point
Spain[12]	0.83	Urban
Greece[11]	0.83	Urban
Greece[11]	1.01	Urban and industrial
Campo Limpo[PS]	1.07	Urban
Getúlio Vargas[PS]	1.09	Urban
Brazil[4]	4.37	Bus terminal
Vietnam[13]	10.4	Urban
Vietnam[13]	11.0	Urban
Vietnam[13]	15.9	Urban
Vietnam[13]	16.3	Urban
Brazil[4]	16.8	Tunnel
Taiwan[14]	230	Urban

References in superscript on the first column. PS stands for present study.

From the individual risk point of view, the highest contamination (considering ΣPAH, benzo[a]pyrene level, as well as the percent contribution of benzo[a]pyrene to the sum of carcinogenic PAHs) observed at Getúlio Vargas Avenue would have a higher impact over human health. Occupational groups, such as, policemen, vehicle traffic agents and, in a more indirect way, workers of the intense commerce of the region, are more exposed to the PAH-contaminated air particulate matter (APM) due to the prolonged presence at the polluted site. However, at UEFS Campus, the groups exposed to the PAH mixture through APM are those connected to open-air activities, *i.e.*, the workers in charge of Campus conservation. Apparently, the sampling point at Campo Limpo suffers the lowest impact regarding human exposure to PAH-contaminated APM. This assumption is based mainly on the absence of occupationally exposed groups in this site.

References:
1. IARC (1985); World Health Organization; 247p.
2. European Communities (2001); Position Paper; 70p.
3. EPA (2001); U.S. Environmental Protection Agency; 13p.
4. Pereira PAP, De Andrade JB, Miguel, AH. (2002); *J Environ Monit.* 4(4): 558-61.
5. IARC (1983); World Health Organization; 222p.
6. Azevedo DA, dos Santos CYM, Aquino Neto FR. (2002). *Atmosph Environ*. 36(14): 2383-95.
7. Wada M, Kido H, Kishikawa N, Tou T, Tanaka M, Tsubokura J, Shironita M, Matsui M, Kuroda N, Nakashima K. (2001); *Environ Pollut.* 115(1): 139-47.
8. Menichini E, Monfredini F, Merli F, (1999). *Atmosph Environ*. 33(23): 3739-50.
9. Nielsen T, Jørgensen HE, Larsen JC, Poulsen M. (1996). *Sci Total Environ*. 189–190(0): 41-9.
10. Ruchirawat M, Mahidol C, Tangjarukij C, Pui-ock S, Jensen O, Kampeerawipakorn O, Tuntaviroon J, Aramphongphan A, Autrup H. (2002). *Sci Total Environ*. 287(1-2): 121-32.
11. Mantis J, Chaloulakou A, Samara C. (2005). *Chemosphere*. 59(5): 593-604.
12. Gutiérrez-Dabán A, Fernández-Espinosa AJ, Ternero-Rodríguez M, Fernández-Álvarez F. (2005). *Anal Bioanal Chem*. 381(3): 721-36.
13. Anh MT, Triet LM, Sauvain JJ, Tarradellas J. (1999). *Bull Environ Contam Toxicol*. 63(6): 728-35.
14. Chang KF, Fang GC, Chen JC, Wu YS. (2006). *Environ Pollut*. 142(3): 388-96.