

PM_{2.5} and PM₁₀: The influence of sugarcane burning on potential cancer risk

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ABSTRACT

In Brazil, sugarcane fields are often burned to facilitate manual harvesting, and this burning causes environmental pollution from the large amounts of soot released into the atmosphere. This material contains numerous organic compounds such as PAHs. In this study, the concentrations of PAHs in two particulate-matter fractions (PM_{2.5} and PM₁₀) in the city of Araraquara (SE Brazil, with around 200,000 inhabitants and surrounded by sugarcane plantations) were determined during the sugarcane harvest (HV) and non-harvest (NHV) seasons in 2008 and 2009. The sampling strategy included four campaigns, with 60 samples in the NHV season and 220 samples in the HV season. The PM_{2.5} and PM₁₀ fractions were collected using a dichotomous sampler (10 L min⁻¹, 24 h) with Teflon™ filters. The filter sets were extracted (ultrasonic bath with hexane/acetone (1:1 v/v)) and analyzed by HPLC/Fluorescence. The median concentration for total PAHs (PM_{2.5} in 2009) was 0.99 ng m⁻³ (NHV) and 3.3 ng m⁻³ (HV). In the HV season, the total concentration of carcinogenic PAHs (benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(a)pyrene) was 5 times higher than in the NHV season. B(a)P median concentrations were 0.017 ng m⁻³ and 0.12 ng m⁻³ for the NHV and HV seasons, respectively. The potential cancer risk associated with exposure through inhalation of these compounds was estimated based on the benzo[a]pyrene toxic equivalence (BaP_{eq}), where the overall toxicity of a PAH mixture is defined by the concentration of each compound multiplied by its relative toxic equivalence factor (TEF). BaP_{eq} median (2008 and 2009 years) ranged between 0.65 and 1.0 ng m⁻³ and 1.2–1.4 ng m⁻³ for the NHV and HV seasons, respectively. Considering that the maximum permissible BaP_{eq} in ambient air is 1 ng m⁻³, related to the increased carcinogenic risk, our data suggest that the level of human exposure to PAHs in cities surrounded by sugarcane crops where the burning process is used is cause for concern.

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1. Introduction

São Paulo State (SE, Brazil) has the largest area of sugarcane plantations in the country and is responsible for 60% of the national production (UNICA, 2010). The city of Araraquara, located at central area from São Paulo State, has around 200,000 inhabitants and is surrounded by sugarcane plantations (46,994 ha of total cultivated area, in the harvest 2008/2009) (INPE, 2010a).

In the sugarcane harvest season, from May to November, the crops are burned to facilitate the process of manual harvesting. The burning protects the cane cutters from the cutting leaves and snakes, and increases the sugar content by weight due to water evaporation (Zamperlini et al., 2000). This process causes environmental pollution from the large amounts of dust and ash that

are released into the atmosphere. This particulate matter (PM) contains mutagenic/carcinogenic contaminants such as polycyclic aromatic hydrocarbons (PAHs) (Andrade et al., 2010a, submitted for publication; Umbuzeiro et al., 2008; Bosso et al., 2006; Godoi et al., 2004; Azevedo et al., 2002; Santos et al., 2002). These compounds are ubiquitous in the environment, and 16 PAHs are included in the priority list of pollutants of the US Environmental Protection Agency (EPA, 1998). Lung cancer is the principal cause of cancer-related mortality in Western countries, and its pathogenesis involves the accumulation of multiple molecular abnormalities over a long period of time and has been associated to PAHs exposure (Farmer et al., 2003; Lewtas, 2007; Silva et al., 2006). Several other cardiovascular, respiratory and reproductive effects has been reported for PAH human and animal exposure (Brito et al., 2010; Lewtas, 2007; Cançado et al., 2006).

PAHs are compounds derived from incomplete combustion and pyrolysis of fossil fuels and other organic substances, and have many natural and anthropogenic sources. For the most part, however, they are generated from anthropogenic sources such as vehicular emissions (Callén et al., 2008; Tavares et al., 2004; Nielsen et al., 1999),

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biomass burning (Ströher et al., 2007; Magalhães et al., 2007; Simoneit, 2002; Zamperlini et al., 1997), and waste incineration (Chen et al., 2008). PM is one of the main air-pollution problems resulting in hospital visits, as observed by Arbex et al. (2000). The characteristics of the PM_{2.5}/PM₁₀ fraction of particulate matter have received much attention because of their possible health impact (Pengchai et al., 2009; Ravindra et al., 2008). Determination of individual types of particle-bound PAHs is very important because compounds with more rings have the greatest toxicological interest (Viana et al., 2008; Omar et al., 2006; Pozzoli et al., 2004).

The World Health Organization recommends a maximum permissible concentration of 1 ng m⁻³ benzo[a]pyrene (BaP) in the atmosphere, based on the carcinogenic potential of inhaled particulate PAHs (Ravindra et al., 2008). The carcinogenic risk assessment of PAH remains difficult due to the very high number of these contaminants (in the hundreds) present in complex samples such as airborne particulate matter.

Considering that benzo[a]pyrene (BaP) is the most studied PAH with regard to the risk of cancer, a TEF (Toxic Equivalent Factor) was proposed to measure the relative toxicity of a specific PAH in relation to BaP (Nisbet and LaGoy, 1992). Specifically, the concentration of each PAH classified as carcinogenic is multiplied by the TEF and then summed to provide an estimate of the benzo[a]pyrene equivalent concentration (BaPeq) in ambient air. In a mixture of PAHs, the total TEF can be related to the potential increase in cancer risk (Jung et al., 2010; Pengchai et al., 2009; Zhang et al., 2009; Barbosa et al., 2006).

The main objective of this study was to assess the potential cancer risk associated with human exposure to PAH in outdoor air in a city surrounded by sugarcane plantations (Araraquara, SE Brazil) in two seasons: non-harvest (NHV) (December–March) and harvest (HV) (April–November) seasons. This study may also provide useful information about the potential health risks from sugarcane burning, and to support environmental policies related to atmospheric limits of PAHs and sugarcane harvesting, including the burning process.

2. Material, methods, and sampling

2.1. Chemicals and apparatus

The solvents used, acetone, *n*-hexane, and acetonitrile, all HPLC grade, were purchased from JT Baker (Xalostoc, Mexico). Ultra-pure water was obtained from a Milli-Q system (Waters, Midford, MA, USA). All solvents were analyzed for possible contamination by the use of procedural blanks. PAH standards (purity grade >99%) were acquired from Aldrich (Milwaukee, WI, USA), including naphthalene (Naph), acenaphthene (Aceph), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene(B(a)A), chrysene (Chry), benzo[b]fluoranthene (B(b)F), benzo[k]fluoranthene (B(k)F), benzo[a]pyrene (B(a)P), benzo[e]pyrene (B(e)P), dibenz[ah]anthracene (D(a,h)A), and benzo[ghi]perylene (B(ghi)P). Indene[1,2,3-cd]pyrene (Ind) was purchased from Dr. Ehrenstorfer (Augsburg, Germany). For the sampling, the polytetrafluoroethylene (PTFE) filters (37 mm × 2 μm porosity) were purchased from Pall Corporation (New York, NY, USA). A dichotomous sampler (10 L min⁻¹, PM_{2.5} and PM₁₀), “Harvard” type, constructed at Harvard University (Boston, MA, USA).

2.2. Instrumental analyses

The analyses were performed using a Varian HPLC/Fluorescence Model LC920 (Varian, Walnut Creek, CA, USA) equipped with a Supelcosil™ LC-PAH column (25 cm × 4.6 mm, 5 μm) (Supelco, Bellefonte, PA, USA). A gradient of acetonitrile/water (*T* = 25 °C) was used beginning with 60% acetonitrile (5 min), followed by a linear

gradient (20 min), until reaches 100% acetonitrile, remaining for 15 min in isocratic elution with acetonitrile. The flow rate was 1.5 mL min⁻¹. The sample volume injected was 20 μL. For the PAHs fluorescence detection a wavelength program was used: 0–9.7 min: excitation wavelength (λ_{ex}) 220 nm and emission wavelength (λ_{em}) 322 nm [for Naph, Aceph, and Flu detection]; 9.8–29.3 min: 240 nm (λ_{ex}) and 398 nm (λ_{em}) [for Phe, Ant, Flt, Pyr, B(a)A, Chry, B(b)F, B(k)F, B(a)P, B(e)P, D(a,h)A and B(ghi)P detection]; 29.4–35.0 min: 300 nm (λ_{ex}) and 498 nm (λ_{em}) for Ind detection.

2.3. Site characterization and sampling

Particulate matter <2.5 μm (PM_{2.5}) and <10 μm (PM₁₀) were sampled in Araraquara (21° 47′31″S and 48° 10′52″W) at Southeast Brazil (Fig. 1). A dichotomous sampler operating with an average flow rate of 10 L min⁻¹ was placed at a height of 2 m at a sampling site located at the Institute of Chemistry of São Paulo State University (UNESP), in a suburban area of Araraquara. The closest sugarcane fields are approximately 5 km distant.

The PM_{2.5} fractions were collected for 20 days in February 2008, 170 days in April–November 2008, 20 days in January–February 2009, and 30 days in May–July 2009. The PM₁₀ fractions were collected for 20 days in February–March 2009 and for 20 days in July–August 2009. Each filter was exposed for 24 h, and then wrapped in aluminum foil, labeled, and stored at –17 °C.

2.4. PAH extraction

The PAHs were extracted from the sampled PM_{2.5} and PM₁₀ filters using *n*-hexane:acetone (1:1) solvent, according to the procedure evaluated previously by Cristale (2008). Briefly, the method consists of extracting ten PTFE filters with three washes of 30 ml hexane:acetone (1:1), in an ultrasonic bath (Thornton, Vinhedo, SP, Brazil) for 10 min at 40 Hz. The extract was concentrated in a rotary evaporator (40 °C) until its volume was reduced to about 10 ml, and then to dryness with nitrogen flow. The dry residue was dissolved in 0.50 ml acetonitrile, followed by HPLC-FL analysis.

PAH recoveries from particulate matter were evaluated by analysis of standard reference material (SRM 1649a), and recoveries were between 74 and 95% (RSD < 20%). Naph, Aceph, and Flu showed low recoveries due to high vapor pressures, therefore these PAHs were not evaluated in this study.

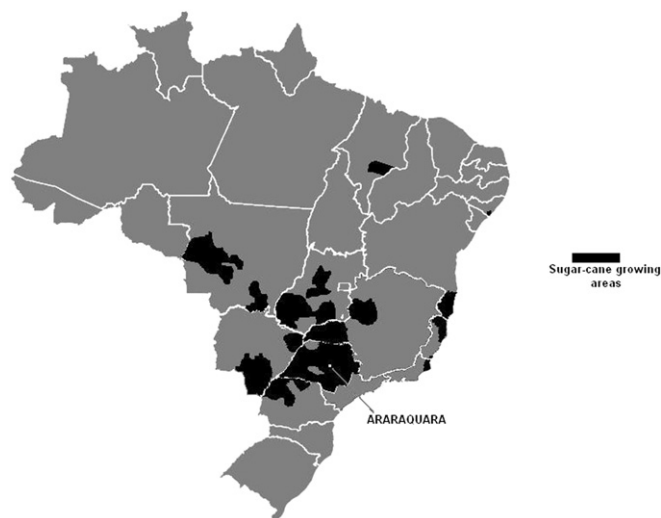


Fig. 1. Map of Brazil showing the location of Araraquara city and the sugarcane growing areas (adapted from http://www.ibge.gov.br/mapas_ibge/tem_agricultura.php).

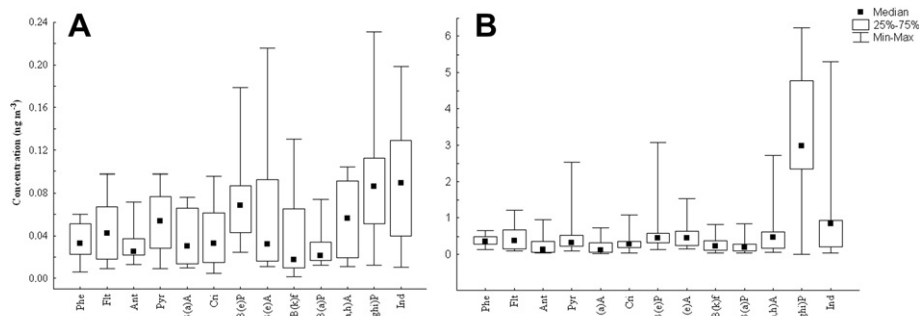


Fig. 2. Multiple Box Whiskers of concentrations of the each PAH in particulate matter of a) NHV season, b) HV season.

2.5. Principal component analysis (PCA) and hierarchical cluster analysis (HCA)

Ward's hierarchical cluster analysis (HCA), which identifies homogeneous groups of samples, was employed according to the average linkage between groups method on the Euclidean distances matrix. PCA was used to reduce the set of original variables (measured PAHs content in the particulate matter samples) and to extract a small number of latent factors (principal components, PCs) for analyzing relationships among the observed variables. Individual PAHs concentrations were used as HCA and PCA parameters (both seasons) allowing the summarized data to be further analyzed and plotted. The number of factors extracted from the variables was analyzed according to Kaiser's rule (Stevens, 2002). This criterion retains only factors with eigenvalues > 1. Statistica 7.0 (StatSoft, 2009) was used for these analyses.

3. Results and discussion

According to HCA data treatment, the concentrations of PAHs differed in the two seasons (HV and NHV) to 61% of samples. Fig. 2 shows PAHs data (median, 25–75% percentiles and the minimum and the maximum concentration) in NHV and HV seasons.

The cluster analysis (Fig. 3) indicated the presence of three data groups. Groups 1 and 2 correspond mainly to HV and NHV samples, respectively; while the third group includes samples collected in rainy days in both seasons. The lower concentrations of PAHs were

found for group 3 samples. Fig. 4 shows two different behaviors: positive correlation between PAH concentrations and burning focus number occurring in the São Paulo state (INPE, 2010b), and negative correlation between PAH concentrations and accumulated rainfall in Araraquara city (São Paulo, 2010a). Wang et al. (2010) reported that PAHs in rain water from Mount Taishan, in China, have significant correlations with rainfall intensity corroborating with our data.

Because the influence of the rainfall events, the data from group 3 from HCA were excluded of the PCA analysis, that was performed only with data from groups 1 and 2, indicating that 80.1% of the total variance of data is explained by three major components. The PC1 and PC2 represent 68.6% of total variance, while PC3 explains 11.5% of observed variance. Table 1 shows the loadings of the most important factors for each principal component.

PC1 explained 53.6% of data variance. The substances that had high loading (>0.7) were: Phe, Flt, and Pyr. According to Simoneit (2002), these substances are associated with burning grass, then PC1 was mainly associated with the burning of sugarcane. In PC2, BaA, BkF and BbF showed high loadings. These PAHs are considered markers of vehicle emissions (Daisey et al., 1979; Harkov and Greenberg, 1985; De Luca et al., 2004), thus PC2 was mainly associated with the gasoline, and diesel combustion emissions. The PC3 explained 11.5% of total variance. Due to the low loading we could not associate this component with a specific source. As a part of statistical analysis was used a biplot graph (Fig. 5) to present the position of HV/NHV samples and PAH components together.

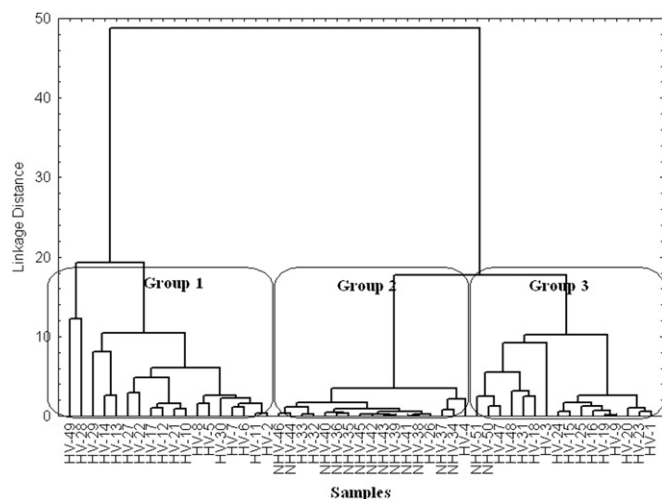


Fig. 3. Cluster analysis dendrogram for PAHs at NHV and HV seasons. The numbers indicate sample code.

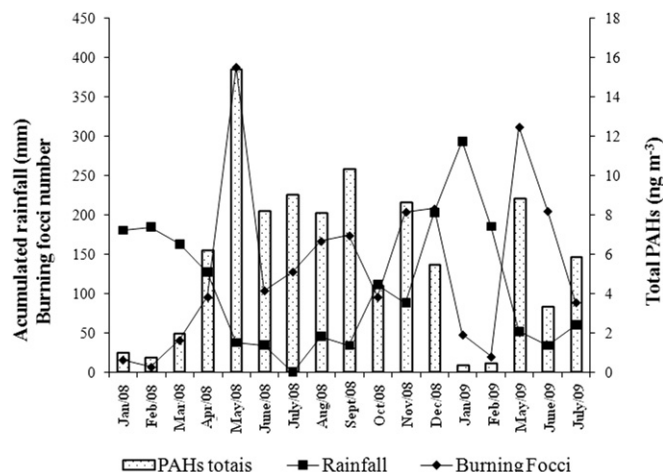


Fig. 4. Accumulated rainfall, burning focus number and total PAHs.

Table 1
Loadings of the factors extracted from principal components.

	PC 1	PC 2	PC 3
Phen	0.91	−0.24	−0.03
Ant	0.16	0.06	0.15
Flt	0.85	0.15	0.07
Pyr	0.76	0.59	−0.17
B(a)A	0.41	0.77	−0.06
Chry	0.17	−0.34	0.12
B(b)F	0.44	− 0.81	−0.65
B(k)F	0.37	− 0.73	−0.04
B(a)P	0.43	−0.61	0.24
B(e)P	0.57	−0.54	0.34
D(a,h)A	0.29	−0.09	0.55
B(ghi)P	0.53	−0.47	−0.62
Ind	0.18	−0.58	−0.07

Values above 0.7 (in modulus) are in bold.

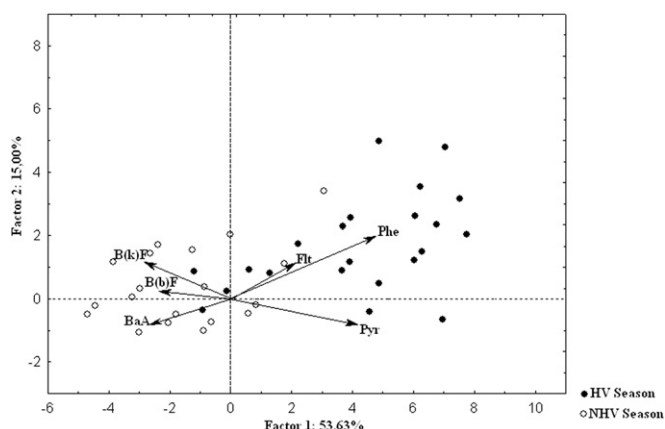


Fig. 5. Biplot graph for sugarcane seasons and the PAH components.

3.1. Distributions of PAHs in atmospheric particles

Total PAHs levels in HV season were 6.3, 3.3, and 8.9 ng m^{−3} for PM_{2.5} (2008), PM_{2.5} (2009), PM₁₀ (2009), respectively. These values are comparable to PAHs concentrations in PM₁₀ at same sampling point obtained by Andrade et al. (2010a) in 2002–2003 (12 ng m^{−3}), whereas lower than concentrations reported in São

Paulo city (65.1 ng m^{−3}) (De Martinis et al., 2002) and in Hong Kong (38 ng m^{−3}) (Guo et al., 2003), but higher than in Rio de Janeiro (2.2 ng m^{−3}) (Quiterio et al., 2007).

The genotoxic behavior of PAHs is associated with the number of their aromatic rings (WHO, 2005). In PM_{2.5}/PM₁₀, the distribution of the aromatic rings showed the same profile for both seasons (HV and NHV). PAHs containing 4, 5, and 6 aromatic rings accounted for 31, 17, and 46%, respectively, of the data presented in this work. These compounds are of great interest because they are considered genotoxic (WHO, 2005).

The median concentration of PAHs in PM_{2.5} in the HV season decreased 30% from 2008 to 2009. This decreasing can be explained by the decreasing of the burning focus in São Paulo State, that were 1629 in 2008 and 1314 in 2009 (INPE, 2010b), during the same months as our sampling campaigns were done, i.e., a year-to-year reduction of 20%.

The use of diagnostic ratios to identify PAH sources can give some indication about the impact of different sources of particulate matter (Pio et al., 2001). For example, the Ind/(Ind + B(ghi)P) ratio in PM_{2.5} (NHV) in 2008 was 0.21 ± 0.04, indicating that there are contribution of vehicular emissions to these contaminants into airborne particulate matter. (Ravindra et al., 2008). However, for PM_{2.5} (NHV) in 2009, the same ratio was 0.52 ± 0.08 indicating coal emissions (Ravindra et al., 2008), but this type of fuel is not used in any activity near Araraquara city. The use of diagnostic ratios to identify PAH sources can give contradictory results, e.g., Li and Kames (1993) attribute a Flt/[Flt + Pyr] ratio of 0.56 ± 0.05 the source comes from wood carbonization while Rogge et al. (1993) and Mandalakis et al. (2002) found the same ratio (>0.5) indicates combustion of diesel. Therefore, in this article we prefer do not to use the diagnostic ratio to discuss the PAH sources.

Median values of individual PAHs concentrations in PM_{2.5} and PM₁₀ in NHV and HV season are presented in Table 2. In order to compare the seasons, the values between the detection (LOD) and quantification (LOQ) limits were assigned with ½ LOQ as the PAH concentration.

3.2. Cancer risk assessment

Some compounds found in the samples are considered carcinogenic and/or mutagenic, including B(a)A, B(b)F, B(k)F, B(a)P, Pyr, D(a,h)A, and Flt (WHO, 2005). Because of the carcinogenic/

Table 2
Concentrations (median) of PAHs and their BaP_{eq} concentrations, using Nisbet and LaGoy's (1992) TEFs.

PAH	TEF	Median concentration (ng m ^{−3})					
		2008/PM _{2.5}		2009			
				PM _{2.5}		PM ₁₀	
		NHV (n = 20)	HV (n = 170)	NHV (n = 20)	HV (n = 30)	NHV (n = 20)	HV (n = 20)
Phe	0.001	0.036	0.39	0.046	0.12	0.19	0.47
Ant	0.010	0.040	0.070	0.093	0.090	0.041	0.050
Flt	0.001	0.049	0.18	0.054	0.89	0.60	1.7
Pyr	0.001	0.046	0.38	0.11	0.19	0.18	0.43
B(a)A	0.100	0.032	0.12	0.023	0.093	0.039	0.15
Cri	0.010	0.049	0.29	0.090	0.34	0.15	0.44
B(e)P	—	0.11	0.27	0.045	0.23	0.14	0.51
B(e)A	0.100	0.070	0.41	0.098	0.41	0.18	0.52
B(k)F	0.100	0.025	0.36	0.023	0.18	0.070	0.24
B(a)P	1.00	0.019	0.19	0.017	0.12	0.041	0.14
D(a,h)A	5.00	0.14	0.16	0.12	0.21	0.16	0.15
B(ghi)P	0.01	0.46	0.56	0.13	0.14	0.53	1.65
Ind	0.10	0.10	2.9	0.14	0.32	1.3	2.4
Total PAHs		1.2	6.3	0.99	3.3	3.6	8.9
Total BaP _{eq}		0.75	1.4	0.65	1.3	1.0	1.2

PAHs – Polycyclic aromatic hydrocarbons; TEF – Toxic equivalency factor; BaP_{eq} – Benzo[a]pyrene toxic equivalence.

mutagenic potential of PAHs, regulatory standards have been proposed. Slooff et al. (1989) proposed a maximum permissible level of 1 ng m^{-3} benzo[a]pyrene (BaP) in the atmosphere. In some European countries, the maximum allowed is $0.7\text{--}1.3 \text{ ng m}^{-3}$ of BaP in outdoor air (Omar et al., 2006). In this study, for samples collected in 2008, BaP in $\text{PM}_{2.5}$ ranged from 0.38 to 1.2 ng m^{-3} (NHV season) and $0.62\text{--}6.4 \text{ ng m}^{-3}$ (HV season); whereas in 2009, BaP ranged from 0.51 to 0.73 ng m^{-3} (NHV season) and $0.20\text{--}2.2 \text{ ng m}^{-3}$ (HV season). For PM_{10} (2009) the range was $0.47\text{--}1.51 \text{ ng m}^{-3}$ (NHV season) and $0.428\text{--}2.050 \text{ ng m}^{-3}$ (HV).

Considering a limit of 1 ng m^{-3} BaP, as recommended by WHO (Zhang et al., 2009), this threshold was exceeded in 10 of 40 sampling days (25%) during the NHV season, while 30 of 40 sampling days for the HV season (75%) for $\text{PM}_{2.5}$ in 2008/2009. Therefore the BaP increased ten times from the NHV to the HV seasons, for $\text{PM}_{2.5}$ and PM_{10} for both years. Additionally, the BaP levels in the HV season (median of 1.4 ng m^{-3}) were similar to that measured in the city of São Paulo (BaP 1.6 ng m^{-3} , Bouriotti et al., 2005) and higher than in the city of Rio de Janeiro (BaP 0.922 ng m^{-3} , Quiterio et al., 2007). Considering that the main PAH source in urban areas is fossil fuels (gasoline and diesel) in automotive vehicles, and that the number of vehicles in Araraquara (115,120) is around ten times lower than in São Paulo (6,126,477) and Rio de Janeiro (1,939,520) (São Paulo, 2010b), the role of sugarcane burning is still more important.

4. Conclusion

This study indicated that there is a significant increase in the concentration of PAHs from the sugarcane non-harvest to the harvest seasons, which can be represent a public health risk for the entire population of the city and the surrounding area. Considering that the maximum permissible BaP_{eq} in ambient air is 1 ng m^{-3} , related to the increased cancer risk, our data suggest a worrying PAH human-exposure scenario in cities that are surrounded by sugarcane fields where the burning process is used. The BaP_{eq} in the sugarcane harvest season in Araraquara was higher than the levels measured in large Brazilian cities. The data indicated a decrease in the concentration of PAHs between the 2008 and 2009 harvest seasons, probably due to the decreased field burning. It is necessary to drastically reduce or altogether halt the burning of sugarcane, adopting mechanical-harvesting processes and implementing public policies to redirect cane cutters to other work.

References

- Andrade, S.J., Cristale, J., Silva, F.S., Zocolo, G.J., Marchi, M.R.R., 2010a. Contribution of sugar-cane harvesting season to atmospheric contamination by polycyclic aromatic hydrocarbons (PAHs) in Araraquara city, Southeast Brazil. *Atmospheric Environment* 44, 2913–2919.
- Andrade, S.J., Varella, S.D., Zocolo, G.J., Marchi, M.R.R., Varanda, E.A., Mutagenic activity of airborne particulate matter (PM₁₀) in a sugar-cane farming area (Araraquara City, Southeast Brazil). *Environmental Research* (submitted for publication).
- Arbex, M.A., Bohm, G.M., Saldiva, P.H.N., Conceição, G.M.S., 2000. Assessment of the effects of sugar-cane plantation burning on daily counts of inhalation therapy. *Journal of Air Waste Management Association* 50, 1745–1749.
- Azevedo, D.A., Santos, C.Y.M., Aquino Neto, F.R., 2002. Identification and seasonal variation of atmospheric organic pollutants in Campos dos Goytacazes, Brazil. *Atmospheric Environment* 36, 2383–2395.
- Barbosa, J.M.S., Re-Poppi, N., Santiago-Silva, M., 2006. Polycyclic aromatic hydrocarbons from wood pyrolysis in charcoal production furnaces. *Environmental Research* 101, 304–311.
- Bosso, R.M.V., Amorim, L.M.F., Andrade, S.J., Rossini, A., Marchi, M.R.R., de Leon, A.P., Carareto, C.M.A., Conforti-Froes, N.D.T., 2006. Effects of genetic polymorphisms CYP1A1, GSTM1, GSTT1 and GSTP1 on urinary 1-hydroxypyrene levels in sugarcane workers. *Science of the Total Environment* 370, 382–390.
- Bouriotti, M.C., Forti, M.C., Taniguchi, S., Bícero, M.C., Lotufo, P.A., 2005. A wintertime study of PAHs in fine and coarse aerosols in São Paulo city, Brazil. *Atmospheric Environment* 39, 3799–3811.
- Brito, J.M., Belotti, L., Toledo, A.C., Antonangelo, L., Silva, F.S., Alvim, D.S., Andre, P.A., Saldiva, P.H.N., Rivero, D.H.R.F., 2010. Acute cardiovascular and inflammatory toxicity induced by inhalation of diesel and biodiesel exhaust particles. *Toxicological Sciences* 116, 67–78.
- Callén, M.S., Cruz, M.T., López, J.M., Murillo, R., Navarro, M.V., Mastral, M., 2008. Long-range atmospheric transport and local pollution sources on PAH concentrations in a South European urban area. Fulfilling of the European Directive. *Water, Air & Soil Pollution* 190, 271–285.
- Cançado, J.E.D., Saldiva, P.H.N., Pereira, L.A.A., Lara, L.B.L.S., Artaxo, P., Martinelli, L.A., Arbex, M.A., Zanobetti, A., Braga, A.L.F., 2006. The impact of sugar-cane burning emissions on the respiratory system of children and the elderly. *Environmental Health Perspectives* 114, 725–729.
- Chen, J.C., Huang, J.S., Chen, C.M., Guo, J.S., 2008. Emission characteristics of PAHs, benzene and phenol group hydrocarbons in O2/RFG waste incineration processes. *Fuel* 87, 2787–2797.
- Cristale, J., 2008. Influência da queima de cana-de-açúcar na presença de HPAs em ambiente residencial. 103 pp. Dissertação (Mestrado em Química) – Instituto de Química. Universidade Estadual Paulista, Araraquara, São Paulo, Brazil.
- Daisey, J.M., Leyko, M.A., Kneip, T.J., 1979. Source identification and allocation of polynuclear aromatic hydrocarbon compounds in the New York City aerosol: methods and applications. In: Jones, P.W., Leber, P. (Eds.), *Polynuclear Aromatic Hydrocarbons*. Ann Arbor Science, Ann Arbor, pp. 201–215.
- De Luca, G., Furesi, A., Leardi, R., Micera, G., Panzanelli, A., Piu, P.C., Sanna, G., 2004. Polycyclic aromatic hydrocarbons (PAHs) assessment in the sediments of the PortoTorres Harbor (Northern Sardinia, Italy). *Marine Chemistry* 86, 15–32.
- De Martinis, B.S., Okamoto, R.A., Kado, N.Y., Gundel, L.A., Carvalho, L.R.F., 2002. Polycyclic aromatic hydrocarbons in a bioassay-fractionated extract of PM₁₀ collected in São Paulo, Brazil. *Atmospheric Environment* 36, 307–314.
- EPA (U.S. Environmental Protection Agency), 1998. Carcinogen Assessment Group. Evaluation and Estimation of Potential Carcinogenic Risks of Polynuclear Aromatic Hydrocarbons Cincinnati.
- Farmer, P.B., Singha, R., Kaur, B., Sram, R.J., Binkova, B., Kalina, I., Popov, T.A., Garte, S., Taioli, E., Gabelova, A., Cebulka-Wasilewska, A., 2003. Molecular epidemiology studies of carcinogenic environmental pollutants Effects of polycyclic aromatic hydrocarbons (PAHs) in environmental pollution on exogenous and oxidative DNA damage. *Mutation Research* 544, 397–402.
- Godoi, A.F.L., Ravindra, K., Godoi, R.H.M., Andrade, S.J., Santiago-Silva, M., Van Vaec, L., Van Grieken, R.J., 2004. Fast chromatographic determination of polycyclic aromatic hydrocarbons in aerosol samples from sugar-cane burning. *Journal of Chromatography A* 1027, 49–53.
- Guo, H., Lee, S.C., Ho, K.F., Wang, X.M., Zou, S.C., 2003. Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmospheric Environment* 37, 5307–5317.
- Harkov, R., Greenberg, A., 1985. Benzo(a)Pyrene in New-Jersey – results from a 27-site study. *Journal of the Air Pollution Control Association* 35, 238–243.
- INPE Instituto Nacional de Pesquisas Espaciais, 2010a. Determinação da área cultivada com cana-de-açúcar na região centro-sul por meio de imagens de satélite de sensoriamento remoto – safras de 2005/06 a 2008/09. <<http://mtc-m18.sid.inpe.br/rep/8JMKD3MGP8W/3578J4B?mirror=dpi.inpe.br/banon/2000/08.18.12.42.15&metadadarepository=>> (accessed 17.03.10).
- INPE Instituto Nacional de Pesquisas Espaciais, 2010b. Monitoramento de Queimadas. <<http://sigma.cptec.inpe.br/queimadas/queimamensaltotal1.html?id=mm#>> (accessed 23.02.10).
- Jung, K.H., Yan, B., Chillrud, S.N., Perera, F.P., Whyatt, R., Camann, D., Kinney, P.L., Miller, R.L., 2010. Assessment of benzo(a)pyrene-equivalent carcinogenicity and mutagenicity of residential indoor versus outdoor polycyclic aromatic hydrocarbons exposing young children in New York. *International Journal of Environmental Research and Public Health* 7, 1889–1900.
- Lewtas, J., 2007. Air pollution combustion emissions: characterization of causative agents and mechanisms associated with cancer, reproductive, and cardiovascular effects. *Mutation Research* 636, 95–133.
- Li, C.K., Kames, R.M., 1993. The use of polycyclic aromatic hydrocarbons as source signatures in receptor modeling. *Atmospheric Environment* 27A, 523–532.
- Magalhães, D., Bruns, R.E., Vasconcellos, P.C., 2007. Hidrocarbonetos policíclicos aromáticos como traçadores de cana-de-açúcar: uma abordagem estatística. *Química Nova* 30, 577–581.
- Mandalakis, M., Tsapakis, M., Tsoga, A., Stephanou, E.G., 2002. Gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece). *Atmospheric Environment* 36, 4023–4035.
- Nielsen, T., Feilberg, A., Binderup, M.L., 1999. The variation of street air levels of PAH and other mutagenic PAC in relation to regulations of traffic emissions and the impact of atmospheric processes. *Environmental Science and Pollution Research* 6, 133–137.
- Nisbet, I.C.T., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regulatory Toxicology and Pharmacology* 16, 290–300.
- Omar, N.Y.M.J., Mon, T.C., Rahman, N.A., Abas, M.R.B., 2006. Distributions and health risks of polycyclic aromatic hydrocarbons (PAHs) in atmospheric aerosols of Kuala Lumpur, Malaysia. *Science of the Total Environment* 369, 76–81.
- Paulo, São, 2010a. Coordenadoria Estadual de Defesa Civil. Dados Observados – Araraquara. <<http://www.defesacivil.sp.gov.br/novo/paginas.asp?pagina=meteorologia>> (accessed 18.07.10).
- Paulo, São, 2010b. Denatran – Departamento Nacional de Trânsito. Frota 2009. <<http://www.denatran.gov.br/frota.htm>> (accessed 06.04.10).

- Pengchai, P., Chantara, S., Sopajaree, K., Wangkarn, S., Tengcharoenkul, U., Rayanakorn, M., 2009. Seasonal variation, risk assessment and source estimation of PM₁₀ and PM₁₀-bound PAHs in the ambient air of Chiang Mai and Lamphun, Thailand. *Environmental Monitoring Assessment* 154, 197–218.
- Pio, C.A., Alves, C.A., Duarte, A.C., 2001. Identification, abundance and origin of atmospheric organic particulate matter in a Portuguese rural area. *Atmospheric Environment* 35, 1365–1375.
- Pozzoli, L., Gilardoni, S., Perrone, M.G., de Gennaro, G., de Rienzo, M., Vione, D., 2004. Polycyclic aromatic hydrocarbons in the atmosphere: monitoring, sources, sinks and fate. I: monitoring and sources. *Annali di Chimica* 94, 17–32.
- Quiterio, L.S., Arbila, G., Bauerfeldt, G.F., Moreira, J.C., 2007. Polycyclic aromatic hydrocarbons and their molecular diagnostic ratios in airborne particles (PM₁₀) collected in Rio de Janeiro, Brazil. *Water, Air & Soil Pollution* 179, 79–92.
- Ravindra, K., Sokhi, R., Grieken, R.V., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmospheric Environment* 42, 2895–2921.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993. Sources of fine organic aerosol: noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environmental Science and Technology* 27, 636–651.
- Santos, C.Y.M., Azevedo, D.A., Aquino Neto, F.R., 2002. Selected organic compounds from biomass burning found in the atmospheric particulate matter over sugarcane plantation areas. *Atmospheric Environment* 36, 3009–3019.
- Silva, B.A.K., Silva, I.S., Pereira, D.M., Aydos, R.D., Carvalho, P.T.C., 2006. Usefulness of argyrophilic nucleolar organizer regions in detection of lung cells alterations after benzo[a]pyrene instillation. *Acta Cirurgica Brasileira* 21, 36–39.
- Simoneit, B.R.T., 2002. Biomass burning — a review of organic tracers for smoke from incomplete combustion. *Applied Geochemistry* 17, 129–162.
- Slooff, W., Janus, J.A., Matthijsen, A.J.C.M., Montizaan, G.K., Ros, J.P.M., 1989. Integrated Criteria Document PAHs. Report No. 758,474,011. The Netherlands National Institute of Public Health and Environmental Protection, Bilthoven.
- StatSoft, Inc., 2009. Statistica 7.0 Tulsa, OK, USA.
- Stevens, J.P., 2002. In: Riegert, D., et al. (Eds.), *Applied multivariate statistics for the social sciences*, fourth ed. Lawrence Erlbaum Associates, Inc. Publishers, United States of America, p. 396.
- Ströher, G.L., Ré-Poppi, N., Raposo Jr., J.L., Souza, J.B.G., 2007. Determination of polycyclic aromatic hydrocarbons by gas chromatography—ion trap tandem mass spectrometry and source identifications by methods of diagnostic ratio in the ambient air of Campo Grande, Brazil. *Microchemical Journal* 86, 112–118.
- Tavares, M., Pinto, J.P., Souza, A.L., Scarmínio, I.S., Solci, M.C., 2004. Emission of polycyclic aromatic hydrocarbons from diesel engine in a bus station, Londrina, Brazil. *Atmospheric Environment* 38, 5039–5044.
- Umbuzeiro, G.A., Franco, A., Magalhães, D., Viana, F.C., Kummrow, F., Rech, C.M., Carvalho, L.R.F., Vasconcelos, P.C., 2008. A preliminary characterization of the mutagenicity of atmospheric particulate matter collected during sugar-cane harvesting using the Salmonella/microsome microsuspension assay. *Environmental and Molecular Mutagenesis* 49, 249–255.
- UNICA União da Indústria de Cana-de-Açúcar, 2010. Cana-de-açúcar processada pelas usinas brasileiras. <<http://www.unica.com.br/downloads/estatisticas/processcanabrazil.xls>> (accessed 16.03.10).
- Viana, M., López, J.M., Querol, X., Alastuey, A., García-Gacio, D., Blanco-Heras, G., López-Mahía, P., Piñeiro-Iglesias, M., Sanz, M.J., Sanz, F., Chi, X., Maenhaut, W., 2008. Tracers and impact of open burning of rice straw residues on PM in Eastern Spain. *Atmospheric Environment* 42, 1941–1957.
- Wang, Y., Li, P.H., Li, H.L., Liu, X.H., Wang, W.X., 2010. PAHs distribution in precipitation at Mount Taishan China. Identification of sources and meteorological influences. *Atmospheric Research* 95, 1–7.
- WHO. World Health Organization, 2005. Air Quality Guidelines, Global Update. WHO, Copenhagen.
- Zamperlini, G.C.M., Santiago-Silva, M.R.S., Vilegas, W., 1997. Identification of polycyclic aromatic hydrocarbons in sugar-cane soot by gas chromatography mass spectrometry. *Chromatographia* 46, 655–663.
- Zamperlini, G.C.M., Santiago-Silva, M., Vilegas, W., 2000. Solid-phase extraction of sugar-cane soot extract for analysis by gas chromatography with flame ionisation and mass spectrometric detection. *Journal of Chromatography A* 889, 281–286.
- Zhang, Y., Tao, S., Shen, H., Ma, J., 2009. Inhalation exposure to ambient polycyclic aromatic hydrocarbons and lung cancer risk of Chinese population. *Proceedings of the National Academy of Sciences of the U.S.A* 106, 21063–21067.