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Article

Multivariate Optimization of Extraction Variables of PAH in Particulate Matter (PM_{10}) in Indoor/Outdoor Air at Campos dos Goytacazes, Brazil

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Polycyclic aromatic hydrocarbons (PAH) are products of incomplete combustion of biomass and fossil fuels, that are produced on a larger scale by anthropogenic sources. Burning sugarcane plantations can be a source of atmospheric PAH in regions where this culture predominates. Campos dos Goytacazes, Brazil, is surrounded by sugarcane crops that still use fire as a facilitating method for the harvesting process. This study aims to evaluate the presence of outdoor and indoor PAH in 10 µm particulate matter (PM_{10}) at one university in Campos dos Goytacazes. PM_{10} samples were collected from January to November 2018. Samples were extracted using an ultrasonic probe and analyzed by gas chromatography coupled to mass spectrometry (GC-MS). The ideal extraction conditions (3 min; 150 W; 50 mL) were defined by 2^3 full factorial design. The analysis showed a significant PM_{10} level increase (23.19 to 34.50 µg m^{-3} in outdoor, and 15.15 to 31.66 µg m^{-3} in indoor samples) and higher total PAH concentration in the harvesting season (outdoor: 0.73 ng m^{-3}; indoor 0.52 ng m^{-3}) than in non-harvesting season (outdoor: 0.49 ng m^{-3}; indoor: 0.28 ng m^{-3}), however, average PAH values found in outdoor samples in harvesting season did not show significant difference from non-harvesting season.

Keywords: polycyclic aromatic hydrocarbons, PM_{10}, atmospheric pollution, sugarcane, indoor air

Introduction

Polycyclic aromatic hydrocarbons (PAH) are semi-volatile organic compounds formed by two or more fused aromatic rings, known to be poorly soluble in water. Their hydrophobicity is defined by the number of rings that form the molecule, the higher the number of rings, the more hydrophobic is the PAH.[1,2] The primary concern in studying and quantifying PAH in the environment is due to their effects on human health. The United States Environmental Protection Agency (US EPA) and the International Agency for Research on Cancer (IARC) classify some PAH as probable carcinogens for humans.[3-6] PAH are distributed in the atmosphere according to their molecular weight. The lightest ones are found in higher concentration in the gaseous phase, and the heaviest ones adsorbed on particulate matter.[7] They are formed by the incomplete combustion of organic compounds such as fossil fuels and/or biomass.[8] Traffic and sugarcane crop burning are some examples of possible PAH sources that release them in the atmosphere.[9,10]

According to the Food and Agriculture Organization of the United Nations, Brazil is the largest sugarcane producer in the world, with approximately 747 million tons produced in 2018.[11] Part of the sugarcane harvesting process in Brazil is still carried out manually. The crop is burned to remove leaves and to scare off or kill venomous animals that may be on the plantation, making the manual harvesting process safer for workers. The heat also increases the sugar content in the sugarcane through water evaporation. These fires release vast amounts of smoke and particulate matter (PM) in the atmosphere, affecting air quality in nearby regions.[10,12] Particulate matter released from the burning of sugarcane plantations can carry adsorbed PAH on its surface

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formed in the incomplete burning process of biomass.[10,13-17] The city of Campos dos Goytacazes in the state of Rio de Janeiro, Brazil, has sugarcane as its primary agricultural product, representing, in 2018, approximately 55.7% of the planted area (30,000 ha) and 53.5% of production (1.2 ton) of the entire state of Rio de Janeiro.[18] Although there is state legislation aimed at the gradual elimination of sugarcane crops fires,[19] the practice of manual harvesting preceded by burning in the region is still prevalent.

Many techniques are used to extract the PAHs from the particulate matters.[8,20,21] Currently, there is a growth in the use of more robust and simpler technologies, such as microwave-assisted extraction (MAE) and accelerated solvent extraction (ASE).[21,22] Ultrasonic extraction is also fast and efficient, and various solvents (or combinations) can be used, such as dichloromethane,[16] hexane/acetone[23] and dichloromethane/methanol.[24]

Chemometric tools are used to improve the efficiency of the PAH extraction method adsorbed on particulate matter, without wasting laboratory resources and working time. The experimental domain, which encompasses the defined levels, varies according to the need of the method and should be established within the ideal working range. The answer may also depend on the process in which factorial design is applied.[25,26] Through the factorial design, it is possible to identify variables that interact with each other and save resources and time by knowing in advance the number and conditions of experiments to be performed. Identifying variables and defining their levels is one of the first steps to carry out the so-called complete factorial design.[27-30]

Therefore, this study aims to evaluate the presence of PAH in the PM_{10} (10 µm in diameter particulate matter) in outdoor and indoor environment in the university campus at Campos dos Goytacazes, during the year after the optimization of the extraction conditions using chemometric tools.

Experimental

Sampling details

Sampling sites were located in Universidade Estadual do Norte Fluminense Darcy Ribeiro (UENF) campus (21°45'42.5"S 41°17'32.3"W), in an urban area of Campos dos Goytacazes, Rio de Janeiro, Brazil. Outdoor samples were collected in the courtyard of Centro de Ciência e Tecnologia (CCT) building, a windy place with a constant movement of students. Indoor samples were collected in the first-floor hallway of the same building, close to the student's access ramp. CCT building is approximately 130 m away from a bustling avenue. Samples were collected in 2018 from January to November, with monthly frequency during the off-season (January to March) and biweekly during the sugarcane harvest period (May to November). No samples were collected in April due to a delay in the delivery of a new shipment of filters.

10 µm diameter particulate matter (PM_{10}) samples were collected on glass fiber filters (GFF) (25.4 × 20.3 cm, FHV 01, JCTM) using a PM_{10} high-volume sampler (ECO-HVS3000-02, Ecotech) with 67.8 m^3 h^{-1} sampling flow for 24 h, resulting in 1,627.2 m^3 of collected air *per* sample. GFFs were previously baked in an oven at 300 ºC with a heating ramp of 35 ºC min^{-1} for 5 h to remove organic contaminants and then kept in desiccator wrapped in aluminium foil in sealed plastic bags until sampling. PM_{10} measurement was performed by weighing the GFF before and after the samples. GFFs containing sampled particulate matter were wrapped in aluminium foil in sealed plastic bags and stored in a refrigerator until extraction.

Ultrasound probe operating parameters optimization: 2^3 full factorial design

The variables defined to optimize the process of PAH in particulate matter extraction in GFF using ultrasound probe were sonication time (T), equipment power (P) and volume of extracting solvent (V). After identifying the variables, high (+1) and low (–1) levels were defined for each one of them. A total of 2^k experiments were performed, where k equals the number of variables, in this case with three variables (k = 3), eight tests were defined, each one presented in duplicate, thus, 16 tests.

Chemical analysis

GFF containing particulate matter samples were cut into four equal parts (12.70 × 10.15 cm), and one of the pieces was extracted on an ultrasound probe (DESRUPTOR Eco-Sonics, Ultronique). The conditions were defined by factorial design (3 min of sonication; 150 W of power; 50 mL of solvent). A 1:1 mixture of *n*-hexane (Tedia®, Fairfield, USA):acetone (Tedia®, Fairfield, USA) (HEX:ACE) was used as an extractor solvent, and after extraction, the solution was concentrated on a rotary evaporator to near dryness. The flask was then rinsed with HEX:ACE and transferred to a 1.5 mL vial. The sample was then evaporated using an inert gas stream until dryness and resuspended in 250.0 µL of an 8.0 ng μL^{-1} *p*-terphenyl solution (internal standard).

Thirteen PAH were analyzed on a gas chromatograph (GC-2010, Shimadzu) coupled with a mass spectrometer

(GCMS-QP2010 Plus, Shimadzu) in a method based on Ratola *et al.*[8] Separation was performed on a DB-5MS column (30 m × 0.25 mm i.d., 0.25 µm film thickness, Agilent) using helium as a carrier gas. The initial furnace temperature was set to 100 °C, then to 190 °C at 10 °C min^{-1} and held for 3 min, then to 284, 260 and 285 ºC all at 6 °C min^{-1} and held for 3 min, then to 300 °C at 6 °C min^{-1} and held for 5 min, resulting in a 44.33 min run. 1.0 µL of the samples was injected in splitless mode, and the injector and ion source temperatures were set at 280 and 200 ºC, respectively. Data were obtained in SIM (selected ion monitoring) mode with quantification and confirmation ions[24,31,32] and retention time indicated in Table 1.

PAH quantification

The analyzed PAH were quantified by constructing a curve using a standard mix containing the thirteen compounds (PAH Mix A 500 µg mL^{-1}, Supelco, Bellefonte, United States) with the addition of an internal standard (*p*-terphenyl). Quantification was performed by the ratio of the areas of each PAH and the area of the internal standard as a method of normalization. Addition/recovery tests were used to verify the accuracy of the determination of PAH, after ultrasonic extraction. The signals obtained in the gas chromatography coupled to mass spectrometry (GC-MS) for each PAH in the 10.0 ng μL^{-1} standard mixture solution were considered as being 100% recovery. These areas were compared with the analysis of the same concentration solution after all the ultrasonic extraction process. From the thirteen PAH analyzed, ten PAH recoveries ranged from 78-83%, only acenaphthylene (ACY), fluorene (FLU), phenanthrene (PHE) showed recoveries below 70% due to their high volatilities that may have caused the loss of part of these compounds in the extraction process. Laboratory blanks were prepared by baking GFF and going through the same extraction and analysis procedure as real samples. In the end, no PAH concentration was found in laboratory blanks. The limit of quantification of all compounds was defined by the visual method as 0.025 ng of injected mass (corresponding to 0.01 ng m^{-3} of sample concentration), a limit lower than some PAH GC-MS analysis studies.[21,33]

Results and Discussion

Ultrasound probe operating parameters optimization

From the 2^3 factorial design, a screening test was performed for the three selected variables of the PAH ultrasonic extraction (T; P; V). The experiments were performed at random order to avoid biased results. Eight experiments ($2^3 = 8$) were performed in duplicate, resulting in sixteen experiments. Level values for each variable tested are shown in Table 2.

Studies involving more than one response (e.g., 13 PAH areas) are established using a multiple response function (MR). The areas of each PAH were normalized, and the sum of the normalized areas was used as the response variable for each experimental condition studied, obtaining only one final response (called multiple response). The

Table 1. Retention times and selected ions for the analyzed PAH

Compound (abbreviation)	t_R / min	Quantification ion (*m/z*)	Confirmation ions (*m/z*)
Acenaphthylene (ACY)	7.17	152	76, 151
Fluorene (FLU)	8.79	166	164, 165
Phenanthrene (PHE)	11.70	178	89
Anthracene (ANT)	11.91	178	89
Pyrene (PYR)	17.96	202	101, 200
p-Terphenyl[a] (*p*TF)	18.95	230	115
Benzo[*a*]anthracene (B*a*A)	23.39	228	114, 226
Chrysene (CHR)	23.59	228	114, 226
Benzo[*b*]fluoranthene (B*b*F)	29.47	252	126, 250
Benzo[*k*]fluoranthene (B*k*F)	29.64	252	126, 250
Benzo[*a*]pyrene (B*a*P)	31.39	252	126, 250
Indeno[1,2,3-*cd*]pyrene (I*cd*P)	37.29	276	227, 138
Dibenz[*a*,*h*]anthracene (D*ah*A)	37.53	278	279, 139
Benzo[*ghi*]perylene (B*ghi*P)		276	138

[a]Internal standard. t_R: retention time.

Table 2. The experimental domain of the 2^3 full factorial design for determination of the most significant variables for extraction of PAH in particulate material in glass fiber filter

Variable	Level (–)	Level (+)
Sonication time (T) / min	3	9
Power (P) / W	150	350
Volume (V) / mL	30	70

multiple responses (MR1 and MR2) for each PAH were obtained by dividing the normalized area (A) of each PAH by the maximum normalized area (MaxA) obtained by the same PAH, as shown in equation 1. The multiple response functions (MR) were obtained by the average of MR1 and MR2. The areas of each PAH were normalized using the area of the internal standard *p*-terphenyl. Equation 1 presents the mathematical expression to obtain the multiple responses.

$$\mathrm{MR_i} = \frac{\mathrm{A_{PAH_1}}}{\mathrm{Max\ A_{PAH_1}}} + \frac{\mathrm{A_{PAH_2}}}{\mathrm{Max\ A_{PAH_2}}} + \ldots + \frac{\mathrm{A_{PAH_{13}}}}{\mathrm{Max\ A_{PAH_{13}}}} \quad (1)$$

where i = 1 represent the first 8 experiments and i = 2, the repetition of these experiments.

Table 3 presents the results of the experiments.

The goal of the factorial design is to find the effects of each variable: time (T), power (P) and volume (V). As well as the effects of their interactions: time and power (T/P), time and volume (T/V), power and volume (P/V) and time, power and volume (T/P/V) and determine the significance of each. For this, a contrast matrix is assembled with the levels of each variable/interaction in the experiments. Table 4 shows contrast coefficients from the variables and interactions which are calculated by multiplying the coefficients of the variables. It also presents the multiple response function (MR, which will be called "y" to simplify calculations).

The matrix (**x**) is then transposed ($\mathbf{x}^t$) and multiplied by the multiple response column (y), obtaining $\mathbf{x^ty}$:

$$\mathrm{x^t y} = \begin{bmatrix} 84.58 \\ 0.39 \\ 0.29 \\ 0.76 \\ 0.53 \\ 0.07 \\ 2.40 \\ 2.10 \end{bmatrix} = \begin{bmatrix} \mathrm{y} \\ \mathrm{x_1} \\ \mathrm{x_2} \\ \mathrm{x_3} \\ \mathrm{x_{12}} \\ \mathrm{x_{13}} \\ \mathrm{x_{23}} \\ \mathrm{x_{123}} \end{bmatrix}$$

The mean value is then divided by 2^k (where k equals the number of variables), where $2^3 = 8$. The values for the variables/interactions are divided by 2^{k-1}, so $2^2 = 4$. Dividing each value by its proper denominator, the results of the effects are obtained:

$$\begin{bmatrix} \mathrm{y} \\ \mathrm{T} \\ \mathrm{P} \\ \mathrm{V} \\ \mathrm{T/P} \\ \mathrm{T/V} \\ \mathrm{P/V} \\ \mathrm{T/P/V} \end{bmatrix} = \begin{bmatrix} 10.57 \\ 0.09 \\ 0.07 \\ 0.19 \\ 0.13 \\ 0.01 \\ 0.60 \\ 0.52 \end{bmatrix}$$

All effects and their experimental errors were then calculated from the responses generated in the complete 2^3 factorial design. Significant effects were analyzed at 95% confidence by replication at each point and the *t*-test with 8 degrees of freedom (Student's $t = 2.306$). The significance of each effect was calculated from the multiplication of Student's *t* value of 2.306 by the estimate of the standard error of the effect (0.547).[28,30] Figure 1 presents the

Table 3. Results of 2^3 factorial design for GFF total PAH extraction in an ultrasound probe for both replicates (R1, R2)

Experiment (R1, R2)	time (T)	Power (P)	Volume (V)	MR1	MR2	MR	Variance
1, 9	–	–	–	11.787	9.223	10.505	3.286
2, 10	+	–	–	11.763	10.191	10.977	1.236
3, 11	–	+	–	10.403	10.335	10.369	0.002
4, 12	+	+	–	10.694	9.421	10.057	0.810
5, 13	–	–	+	9.338	11.865	10.602	3.193
6, 14	+	–	+	10.317	9.802	10.059	0.132
7, 15	–	+	+	10.294	10.942	10.618	0.210
8, 16	+	+	+	11.994	10.795	11.394	0.719

MR: multiple response.

Table 4. 2^3 full factorial design contrast matrix

Average	T	P	V	T/P	T/V	P/V	T/P/V	y
+	−	−	−	+	+	+	−	10.505
+	+	−	−	−	−	+	+	10.977
+	−	+	−	−	+	−	+	10.369
+	+	+	−	+	−	−	−	10.057
+	−	−	+	+	−	−	+	10.602
+	+	−	+	−	+	−	−	10.059
+	−	+	+	−	−	+	−	10.618
+	+	+	+	+	+	+	+	11.394

T: time; P: power; V: volume; y: multiple response function.

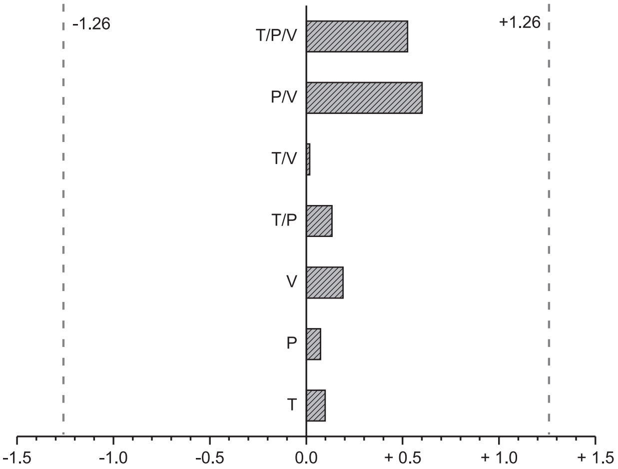

Figure 1. Graphical representation of the significance of the assessed variables: time (T), power (P) and volume (V) and their interactions for the PAH ultrasonic extraction (Student's *t* value × standard error estimate = ± 1.26).

significant effects of the assessed variables for each variable during GFF PAH extraction using an ultrasonic probe.

The variables or interactions that exceed the confidence interval are considered significant for the PAH ultrasonic extraction. The variables and their interactions were not considered significant, as none exceeded the confidence interval. These results indicate robustness in the extraction process by the ultrasound probe. Then, PAH extraction was defined for aiming at saving time and laboratory resources (T = 3 min; P = 150 W; V = 50 mL).

Atmospheric PAH concentrations

During the sampling period, only two samples presented daily PM$_{10}$ values above those recommended by the World Health Organization (50 µg m^{-3}).[34] The PM$_{10}$ values were of 63.30 and 51.75 µg m^{-3}, both in outdoor samples, in September 2018. The National Council of the Environment (CONAMA), responsible for Brazilian environmental policy, defines the average 24-hour concentration limit of 120 µg m^{-3} for inhalable particles (PM$_{10}$).[35] As can be seen from Table 5, no sampling has exceeded the CONAMA daily limit. The annual average obtained of 32.08 µg m^{-3} was above the recommended by the WHO (20 µg m^{-3}),[34] even when considering the relative standard deviation (RSD), and below the recommended by CONAMA (40 µg m^{-3}).[35]

The RSD also shows that PM$_{10}$ can vary less than total PAH concentration throughout the year. The highest

Table 5. PM$_{10}$ and total PAH concentrations in the sampling periods (2018) in both outdoor and indoor environments

		Sample period														Harvesting season avg.[a] (RSD / %)	Non-harvesting season avg.[a] (RSD / %)	Annual avg.[a] (RSD / %)	Calculated *t*[b]
		01/29	02/21	03/20	05/23	06/13	07/04	07/25	08/15	09/13	09/19	10/08	10/23	11/07	11/21				
PM$_{10}$ / (µg m^3)	outdoor	18.81	25.32	25.44	28.64	41.30	41.36	22.86	30.24	63.30	51.75	17.08	26.36	23.97	32.69	34.50 (39.85)	23.19 (16.39)	32.08 (40.76)	2.411
	indoor	7.01	15.75	22.68	38.16	24.46	43.76	35.64	25.75	24.65	40.56	27.78	38.78	19.30	29.44	31.66 (25.33)	15.15 (51.81)	28.12 (37.02)	3.172
Total PAH / (ng m^3)	outdoor	0.23	0.59	0.65	0.50	0.54	0.91	0.85	0.75	0.45	1.54	0.55	1.38	0.16	0.41	0.73 (57.53)	0.49 (46.94)	0.68 (57.64)	0.933
	indoor	0.22	0.28	0.34	0.58	0.27	0.98	0.75	0.40	0.56	0.55	0.59	0.45	0.28	0.31	0.52 (40.38)	0.28 (21.43)	0.47 (45.92)	3.325

[a]Avg: average of values during the year; [b]Student's t_{12} ($\alpha = 0.05$) = 2.179. RSD: relative standard deviation; PM$_{10}$: 10 µm particulate matter; PAH: polycyclic aromatic hydrocarbons.

concentrations of PM_{10} were from May to October 2018 when sugarcane crops are harvested. In this period, the plantation is burned to facilitate harvesting, and this practice influences the particulate matter concentration in the atmosphere. This same situation was identified by de Andrade *et al.*[36] in Araraquara, Brazil, a city known for its large production of sugarcane (3.04 tons in 2018),[37] and by Mugica-Alvarez *et al.*[16] in Huixtla, Jojutla and Zacatepec, three of the most critical sugarcane cities in Mexico. A significant difference between PM_{10} concentrations in harvesting and non-harvesting seasons in both indoor and outdoor environments was also indicated by Student's *t* value (the null hypothesis is rejected), also shown in Table 5.

The calculated *t* value (Table 5) for outdoor total PAH was lower than the critical *t* value ($t_{12,\ \alpha = 0.05} = 2.179$), indicating that the harvesting season average does not have significant difference from the non-harvesting season average (the null hypothesis is not rejected). It means that the harvesting season does not significantly influence the concentration of total PAH in PM_{10}, even though concentrations slightly increase from May-Nov. A significant difference was expected due to various studies that observed such behavior. At Araraquara, Brazil, high concentrations of total PAH (ranging from 0.61 to 53.0 ng m^{-3}) was detected in sugarcane harvesting months.[12] Increase in the average total PAH concentration between harvest in/off-season was also identified in samples collected from Huixtla, Jojutla and Zacatepec, Mexico. The author found increases of 86% (2.82 to 5.26 ng m^{-3}) for the first city and 308% (1.50 to 6.12 ng m^{-3}) for the other two cities, for total PAH in PM_{10}.[16] Sugarcane harvesting season also affected Belle Glade, Florida, USA, increasing the concentration of total PAH in PM_{10} by nearly 15 times.[15] These studies analyzed not only the thirteen PAH in this study, but also naphthalene, fluoranthene, benzo[*e*]pyrene and eight other PAH.

Figure 2 shows a timeline of total PAH concentration in both indoor and outdoor environments in 2018 samples as well as the temperatures on sampling days. Even though low concentrations of PAH were found, at first sight, there is a slight increase in the mid-year months (Figure 2), which are within the sugarcane harvest period by the end of the fall, winter, and spring seasons when temperatures drop, and the sugarcane is harvested. However, the calculated *t* value showed no significant difference in outdoor samples.

The pollutants can be accumulated in indoor environments, depending on the air change rate (circulation) with the outdoor environments.[38] Indoor sampling site has a window that the students can keep open or closed and, altered the air change rate. The PAH identified in the indoor samples were considered from the outdoor due to the absence of possible indoor PAH sources, like heating systems, cooking, smoking and laser printing processes[39] in the sampling site. Total PAH concentrations in indoor samples showed a significant difference (Student's $t_{12} < t_{\text{calculated}}$) between harvesting and non-harvesting season (the null hypothesis is rejected). Individual PAH concentrations in both outdoor and indoor PM_{10} samples throughout the year of 2018 are available in Tables S1 and S2 (Supplementary Information section), respectively.

The PAH found in the samples may come from crop fires around Campos, but they do not significantly contribute to these concentrations. Some of the PAH found are commonly associated with biomass burning, like FLU, PHE and pyrene (PYR).[36,40] These PAH (including ACY and anthracene (ANT)) were linked to the burning of sugarcane dry leaves and stalks by Hall *et al.*[41] Some authors identified FLU, PHE and PYR (and also ANT) with

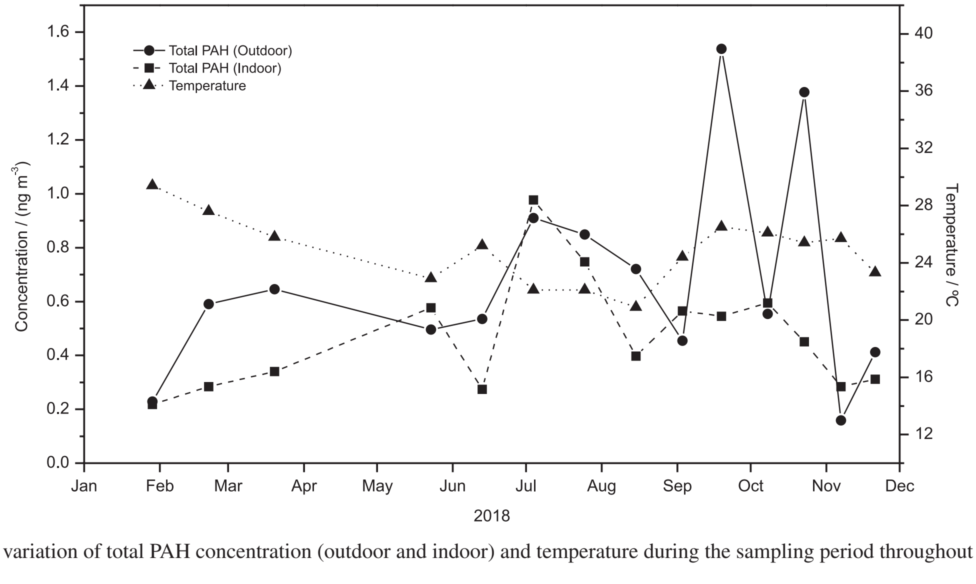

Figure 2. Seasonal variation of total PAH concentration (outdoor and indoor) and temperature during the sampling period throughout the year of 2018.

coal-burning.[42] This activity is not common in the Campos dos Goytacazes region, so they probably have been formed by a different source.

Studies in regions without the influence of sugarcane burning show that traffic is also a contributor to atmospheric PAH concentrations.[43] Sites like the Universidade Estadual do Rio de Janeiro (UERJ) campus (commercial area), Tijuca forest (research, leisure and tourist area) and Jardim Botânico street (access to the Andre Rebouças Tunnel) showed total PAH concentrations of 1.38, 0.34 and 3.80 ng m^{-3}, respectively.[44,45] All the PAH found in the 2.5 µm particulate matter ($PM_{2.5}$) fraction is due to heavy traffic, especially in the Jardim Botânico street that has a constant and heavy traffic flow.[44] The PAH found in the Tijuca Forest are linked by the authors to the increased traffic flow during the sampling period performed in vacation season, when the area attracts many tourists.[45]

The UENF campus is located nearby the Alberto Lamego Avenue, a busy avenue with a continuous flow of vehicles all year long, including heavy vehicles (trucks), especially during business hours. This avenue is one of the access roads to the Açu Harbor in the neighbor city of São João da Barra, a coastal town that also attracts a massive flow of tourist vehicles. Other PAH found in this study such as chrysene (CHR), benzo[*a*]anthracene (B*a*A), benzo[*a*]pyrene (B*a*P), indeno[1,2,3-*cd*]pyrene (I*cd*P) and benzo[*ghi*]perylene (B*ghi*P) are also mostly related to vehicle emissions.[43,46]

Conclusions

A robust and easy procedure for extracting PAH from PM_{10} in glass fiber filters was proposed and optimized in this work, using an ultrasound probe, which saves time and solvent. The optimization was performed using factorial design experiments which defined the following extraction conditions: 3 min of sonication; 150 W of equipment power; 50 mL of HEX:ACE solvent. The levels of particulate matter and thirteen atmospheric polycyclic aromatic hydrocarbons, compounds that are formed mainly by incomplete combustion of carbon-containing materials, were evaluated. PM_{10} levels increase in sugarcane harvesting season in outdoor (from 23.19 to 34.50 µg m^{-3}) and indoor (from 15.15 to 31.66 µg m^{-3}) samples, linking this increase to sugarcane crop fires. The annual average and two daily PM_{10} outdoor levels exceeded the recommendations by the WHO, and none exceeded the national limits by CONAMA. This study showed that PAH is present in the indoor and outdoor atmosphere of UENF in low concentrations. Total PAH in outdoor samples show a slight increase in concentration in the harvesting months, but through statistical tests, this increase was proved not significant. However, some PAH found are commonly associated with biomass burning.

Supplementary Information

Supplementary information (Tables S1 and S2) is available free of charge at http://jbcs.sbq.org.br as PDF file.

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