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Polycyclic aromatic hydrocarbons in Tripuí River, Ouro Preto, MG, Brazil

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ABSTRACT

This paper reports the determination of 15 EPA-polycyclic aromatic hydrocarbons (PAHs) and benzo[e]pyrene in water samples collected in Tripuí River, Ouro Preto City, MG, Brazil. Samples were collected between September 2006 (dry season) and November 2006 (wet season) in the neighborhood of an aluminum smelter. Detection limits and quantification limits were sufficiently low to accomplish PAH determination below the maximum concentration levels established by the Brazilian and USEPA legislations. Recoveries from water spiked samples were always larger than 89%. Fluoranthene, pyrene, phenanthrene, chrysene and benzo[b]fluoranthene predominated in the studied samples. The concentrations of PAHs upstream the aluminum smelter were systematically lower than those found downstream indicating a possible role of the smelter in the local pollution by PAHs. Principal component analysis and cluster analysis also showed remarkable differences of the characteristics of samples collected upstream and downstream the aluminum smelter and also of samples from wet and dry seasons.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants of concern since many of them and many PAH mixtures exhibit mutagenic and/or pro-carcinogenic properties to humans and experimental animals [1–4]. PAHs are ubiquitous and their formation, sources and fate have been extensively reviewed [4,5]. There are three major PAH exposure pathways to human beings: (a) ingestion of contaminated food and/or water; (b) inhalation; (c) by dermal contact [3,4].

There is concern in the determination of PAHs in water since many natural water bodies are used as potable water supplies after treatment. Many environmental agencies have established very low maximum concentration levels (MCLs) of PAHs for potable and fresh waters. For example, USEPA [6] established a MCL of 0.2 μg/L for benzo[a]pyrene in drinking water while the Brazilian Health Ministry [7] established a MCL of 0.7 μg/L for benzo[a]pyrene in drinking water. The Brazilian Agency CONAMA [8] established a MCL of 0.05 μg/L for benzo[a]pyrene and other six PAHs (namely benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, indene[1,2,3-cd]pyrene and dibenz[ah]anthracene) in fresh water.

There are many sources of PAHs to natural waters that include: (a) wastewater from industrial activities; (b) petroleum spilling during transportation, refining and offshore oil-well drilling; (c) urban and rural runoff; (d) atmospheric deposition; (e) leacheate from solid waste disposal dumps [4,9,11–15].

Pollution of water bodies with PAHs may cause sediment contamination since PAHs are very hydrophobic compounds [4,9]. Aquatic biota may be affected by PAHs and it was demonstrated that phenanthrene, pyrene and fluoranthene were responsible for most of sediment toxicity [10]. Moreover the transport of PAHs associated with suspended sediments may contaminate large areas of hydrographic basins [9].

The determination of PAHs in water is usually performed by chromatographic techniques following PAH extraction. High resolution gas chromatography with mass spectrometry detection (HRGC–MS) or with flame ionization detection (FID) and high-performance liquid chromatography (HPLC) with fluorescence detection have been used for PAH determination following their extraction from water and other media. Liquid–liquid extraction (LLE) and solid phase extraction (SPE) are techniques of choice for PAH extraction from water and wastewater. However many different LLE conditions of PAHs from water are found in the literature [13–18]. Recently we have proposed a Doehlert optimization of LLE conditions for PAH extraction [19].

Present work describes the results of PAH determination in Tripuí River, Ouro Preto City, Minas Gerais State, Brazil. Minas Gerais State is located in the Brazilian Southeast and any minerals of economic value are found there. As a consequence many metallurgic

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and mining activities occur in the periphery of urban areas and in more isolated areas. However there are few data of environmental contamination and human exposure to environmental contaminants in these areas.

Tripuí River crosses both the Ecological Reserve of Tripuí and Ouro Preto City. An aluminum smelter is located in its margins between the reserve and the city. Since water samples were collected upstream and downstream the aluminum smelter, our results allow to assess its impact in PAH contamination of Tripuí River.

2. Experimental

2.1. Site description

Ouro Preto City is located in Minas Gerais State, in the Southeast of Brazil (20°23′13″S and 43°30′25″W) in altitudes varying between 1000 and 1300 m [20]. Tripuí River is the main affluent of Funil River that drains the urban area of Ouro Preto. According to the Brazilian Water Agency, Tripuí River is classified as Class 1 (fresh water) and it is not directly used for human consumption [20].

Tripuí River springs in the Ecological Reserve of Tripuí at an altitude of around 1500 m. Vegetation with mixed characteristics of both Cerrado and Mata Atlântica vegetations, beyond rupestral fields and humid areas occur in that area. The mean temperatures are 14 °C during winter and 19 °C in summer. The climate of the region is humid temperate with a dry winter and a rainy summer. Around 90% of rain precipitation occurs between October and March mainly between January and March. The altitude of the studied area is partly responsible for the high volumes of precipitation observed there. Local morphology exerts important influence on rains that are around 1800 mm/year characterizing a super humid regimen. Strong local declivities associated with intense precipitations result in fast superficial drainage that increases the processes of removal and transport of materials thus intensifying environmental impacts [20].

Fig. 1 shows the localization of Ouro Preto City in Minas Gerais State and in Brazil, together with approximate localizations of sampling sites.

2.2. Glassware decontamination

All glassware was carefully decontaminated. Firstly, all glassware was rinsed with a solvent (ACS Analytical Grade acetone or methanol) to remove residues and organic contaminants. After organic solvent removal, glassware was rinsed with water and immersed for at least 12 h in a neutral Extran solution (Merck, Brazil) that was removed with distilled water. Glassware was rinsed several times with ultra-pure water and baked overnight at 250 °C.

2.3. Sample collection

River water samples were collected and stored as recommended by NBR 13895 [21]. Around 1000 mL of superficial water were sampled and transported to the laboratory under refrigeration ($T < 4$ °C) and kept at this temperature until analysis. Samples were collected and maintained in pre-cleaned amber 1 L flasks without headspace. They were always processed within 1 or 2 days after sampling.

2.4. Chemicals and reagents

A standard solution containing the 16 priority EPA PAHs (0.2 mg/mL—AccuStandard, CT, USA) and solid PAHs from Sigma

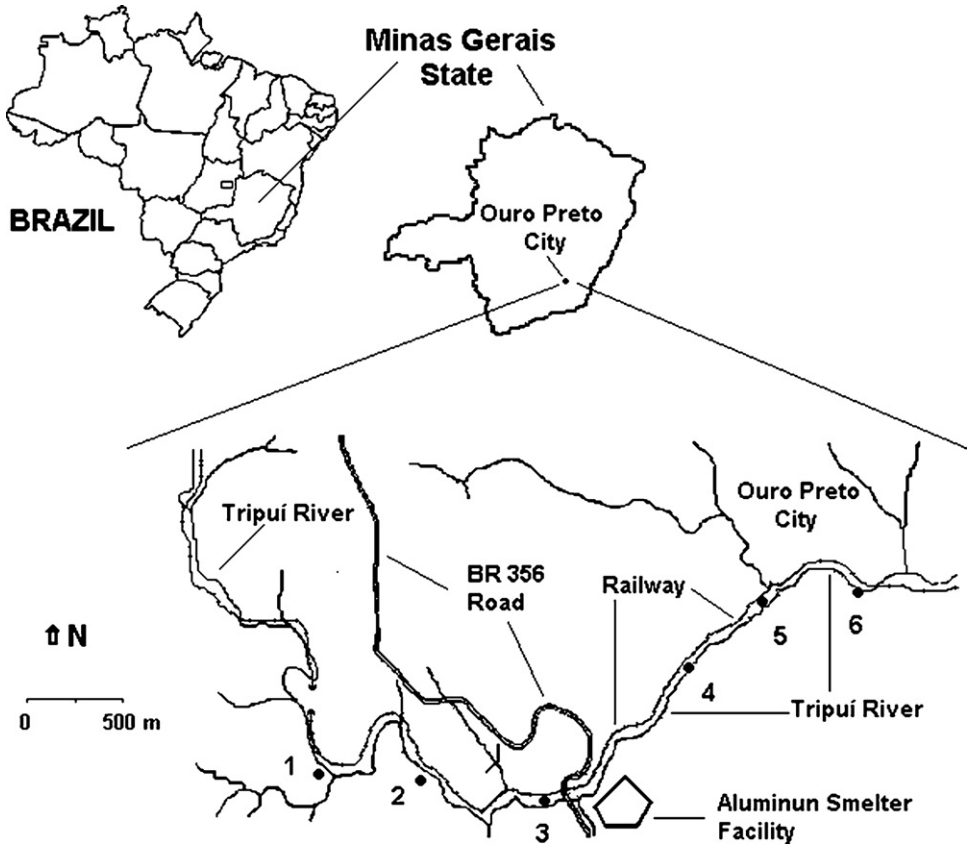

Fig. 1. Map indicating the localization of Ouro Preto in Minas Gerais State. Sampling sites are marked as black dots (IGA, 1998).

Table 1
Detection limit (ng/L), quantification limit (ng/L) and recoveries at 3 levels of the studied PAHs in the analytical methodology.

PAHs	Detection limit[a,b] (ng/L)	Quantification limit[a,b] (ng/L)	Recoveries evaluations[c] (levels)		
			0.500 μg/L	0.0500 μg/L	0.0300 μg/L
Naphthalene	0.10	0.33	94 ± 9	100 ± 7	102 ± 4
Acenaphthene	0.033	0.11	106 ± 9	93 ± 12	100 ± 4
Fluorene	0.13	0.43	104 ± 9	101 ± 5	89 ± 8
Phenanthrene	0.033	0.11	116 ± 9	109 ± 9	104 ± 4
Anthracene	0.033	0.11	99 ± 6	97 ± 3	100 ± 3
Fluoranthene	0.033	0.11	110 ± 8	104 ± 6	92 ± 9
Pyrene	0.033	0.11	99 ± 2	93 ± 6	98 ± 4
Benz[a]anthracene	0.033	0.11	99 ± 5	97 ± 3	100 ± 3
Chrysene	0.067	0.22	97 ± 6	97 ± 3	100 ± 3
Benzo[e]pyrene	0.017	0.056	102 ± 4	96 ± 7	100 ± 4
Benzo[b]fluoranthene	0.13	0.43	105 ± 6	103 ± 3	105 ± 4
Benzo[k]fluoranthene	0.033	0.11	101 ± 6	98 ± 5	100 ± 5
Benzo[a]pyrene	0.033	0.11	102 ± 5	99 ± 4	102 ± 2
Dibenz[a,h]anthracene	0.033	0.11	95 ± 8	93 ± 3	98 ± 2
Benzo[g,h,i]perilene	0.067	0.22	100 ± 5	93 ± 7	96 ± 4
Indene[1,2,3-c,d]pyrene	0.067	0.22	94 ± 6	91 ± 7	98 ± 3

[a] See text for details for the calculation of detection limit and quantification limit.
[b] Considering the extraction of 300 mL of water with concentration to 1 mL.
[c] Mean ± standard deviation.

(MO, USA), Aldrich Chemical Co. (WI, USA) or AccuStandard (CT, USA) were used.

Hexane, methanol and acetonitrile (HPLC grade, Tedia, RJ, Brazil) were employed. Ultra-pure water was prepared in a Millipore Simplicity System (MA, USA).

2.5. PAH extraction

Water samples were homogenized prior to PAH extraction in order to resuspend all solids. Aliquots of 300 mL were extracted in Erlenmeyer flasks under magnetic stirring with four portions of 20 mL of hexane, during 20 min each. Due to the lowest density of the hexane layer and to the shape of extraction flasks, extracts were easily drawn and transferred into pear-shaped evaporation flasks. Combined extracts were concentrated in a rotary evaporator in temperatures below 40 °C. Concentrated extracts were made up to final volumes of 1 mL with acetonitrile, transferred to 2 mL vials and kept in a freezer until analysis. Samples were always extracted and analyzed in independent triplicates.

2.6. PAH determination

Qualitative and quantitative analysis of PAHs were performed by high-performance liquid chromatography with fluorescence detection (HPLC-FLUO). The maximum excitation and emission wavelengths were employed for PAH detection [19].

The HPLC consisted of a quaternary pump, an automated injector, a column oven and a fluorescence detector (all Agilent 1100 Series, USA). Chromatographic conditions (mobile phase composition and flow-rates) were evaluated and optimized using a reverse phase column (Vydac 201TP54, 250 mm × 4.6 mm; 5 μm) and a guard column of the same characteristics (10 mm).

Separation was achieved using a binary elution gradient consisting of acetonitrile (A) and water (B). The gradient was as follows: 50% of A held for 10 min, increased linearly to 85% of A during 10 min, held for 5 min, increased linearly to 95% A during 3.5 min, held for 5 min and decreased to 50% of A during 1.5 min to allow for equilibration before the subsequent injection.

It was possible to complete a chromatographic run in around 30 min with good resolution of benzo[e]pyrene and the 16 EPA-PAHs. Acenaphthylene that cannot be detected by fluorescence due to its low fluorescence intensity was not evaluated in the samples.

Calibration curves were built in between 0.5 and 15 μg/L with standard solutions containing all studied PAHs. Calibration curves were derived by least-squares regression. Equations of the calibration curves were also used to estimate the detection limits (DL) and the quantification limits (QL) of each PAH. DLs and QLs were obtained by dividing respectively 3 and 10 times the signal to noise ratios by the angular coefficients of the calibration curves. Signal to noise ratios were estimated by the standard deviations of peak areas obtained after 10 subsequent injections of the 0.5 μg/L standard [22]. DLs and QLs were both expressed in terms of sample volume by dividing the obtained values by the ratio of the extracted volume (300 mL) and the final volume of the concentrated extract (1.00 mL).

Concentrations that were below individual PAH QLs were assigned as not quantified (NQ).

2.7. Multivariate analysis of data

Principal component analysis (PCA) and cluster analysis (CA) were applied to evaluate data pattern and classification of data. The package Statistica® 7.0 was used. For PCA evaluation PAH concentrations that were below their QLs and assigned as not quantified were replaced by random values between the detection and quantification limits.

3. Results and discussion

Calibration curves presented excellent correlation coefficients ($r^2 \geq 0.999$) showing the good relationship between concentrations and fluorescence intensity in the studied range (Table 1). Quantification limits were sufficiently low (0.056–0.43 ng/L) (Table 1) to allow PAH determination below the MCLs established for drinking and fresh water by Brazilian agencies and USEPA [6–8]. Those results show the very good sensitivity of the method.

Recoveries were evaluated in three different levels (0.500, 0.0500 and 0.0300 μg/L) after spiking sufficient amounts of methanol solutions of PAHs to obtain the desired concentrations. The concentration of 0.05 μg/L corresponds to the MCLs of seven PAHs including benzo[a]pyrene in fresh water [8]. Very good recoveries (89–116%) were obtained in all cases showing the accuracy of the method and its robustness (Table 1).

Table 2
Ranges of PAH concentrations (μg/L) found in the different sampling sites.

PAHs	point 1	point 2	point 3	point 4	point 5	point 6
Naphthalene	0.004–0.034	0.004–0.012	0.002–0.016	0.001–0.206	0.002–0.124	0.001–0.108
Acenaphthene	0.002–0.006	0.002–0.017	0.001–0.006	0.003–0.073	0.002–0.051	0.002–0.054
Fluorene	0.004–0.020	0.005–0.001	0.003–0.012	0.003–0.101	0.001–0.052	0.002–0.072
Phenanthrene	0.003–0.040	0.003–0.025	0.003–0.028	0.007–0.590	0.011–0.258	0.010–0.533
Anthracene	NQ[a] to 0.002	NQ to 0.003	NQ to 0.009	NQ to 0.043	NQ to 0.020	NQ to 0.026
Fluoranthene	0.018–0.039	0.022–0.083	0.046–0.138	0.189–2.64	0.186–2.96	0.161–2.82
Pyrene	0.007–0.017	0.016–0.066	0.025–0.106	0.109–1.39	0.109–1.54	0.118–1.32
Benz[a]anthracene	NQ to 0.005	0.002–0.005	0.003–0.010	0.018–0.097	0.011–0.091	0.015–0.091
Chrysene	0.002–0.006	NQ to 0.012	0.009–0.019	0.033–0.381	0.030–0.426	0.029–0.329
Benzo[e]pyrene	NQ to 0.003	NQ to 0.019	0.004–0.007	0.037–0.189	0.024–0.154	0.022–0.112
Benzo[b]fluoranthene	NQ to 0.002	NQ to 0.013	0.009–0.025	0.040–0.296	0.033–0.244	0.032–0.250
Benzo[k]fluoranthene	NQ to 0.001	NQ to 0.002	0.002–0.012	0.008–0.084	0.006–0.064	0.006–0.046
Benzo[a]pyrene	NQ	NQ to 0.005	0.009–0.025	0.002–0.181	0.004–0.045	0.005–0.034
Dibenz[a]anthracene	NQ–0.001	NQ to 0.003	0.001–0.008	0.002–0.010	0.001–0.007	0.001–0.005
Benzo[ghi]perylene	NQ	NQ to 0.002	NQ to 0.008	0.002–0.093	0.001–0.038	0.001–0.029
Indene[1,2,3-cd]pyrene	NQ	NQ to 0.003	NQ to 0.013	0.004–0.153	0.005–0.050	0.005–0.032

[a] See text for details for the calculation of detection limit and quantification limit.

3.1. PAH concentrations in Tripuí River

Five campaigns were performed. The first one occurred in September 19th, 2006, by the end of the dry season while the other four campaigns occurred during the wet season (October 3rd, 2006, October 16th, 2006, November 6th, 2006 and November 21st, 2006).

The concentrations of individual PAHs in each campaign and site varied between not quantified and 2.96 μg/L (Table 2). The largest PAH concentrations were found in sites 4–6 in September 19th, 2006, in the dry season. The concentrations of all PAHs decreased from dry to wet season (September to November) possibly due to the rainy period and to the consequent increase of river water flow and volume that led to PAH dilution. The concentrations of fluoranthene and pyrene that were respectively 2.64 and 1.39 μg/L in site 4 in September 19th, 2006 (in the dry season) decreased to respectively 0.19 and 0.16 μg/L in November 21th, 2006 (during the wet season).

The predominant PAHs (namely phenanthrene, fluoranthene, pyrene, chrysene and benzo[b]fluoranthene) represented 53–90% of total PAH concentrations but the sum of fluoranthene, pyrene, phenanthrene concentrations represented 51–80% of total PAH concentrations. Both results agree well with previous published data of PAH emissions in aluminum smelting processes [23].

Besides risk of human exposure it must be considered that phenanthrene, pyrene and fluoranthene were previously found to be responsible for most of runoff toxicity to aquatic biota [10]. Into this perspective our data indicate that aquatic biota of the studied area may be affected by PAHs since these PAHs predominate in the studied area.

The concentrations of certain PAHs that have MCLs established for fresh water in Brazil [8] due to their carcinogenic potency (namely benz[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene, indene[1,2,3-cd]pyrene and dibenz[ah]anthracene) allow an evaluation of Tripuí River contamination. The concentrations of these PAHs in sites 4–6 were always higher than in sites 1 and 2, where they were always below their MCLs. For example, in September 19th, 2006, the concentration of benzo[a]pyrene in site 4 was 0.181 μg/L exceeding its MCL by a factor of almost four while in the same date, in site 2 it was only 0.002 μg/L.

The low concentrations of PAHs found in sites 1 and 2 were comparable to background levels and possibly due to unspecific sources. However it was previously shown that certain PAHs (namely naphthalene, phenanthrene and perylene) may have also a biological origin in tropical areas [24–26].

Total PAH concentrations (μg/L) (ΣPAHs) in each date and sampling site are shown in Fig. 2. Upstream sites (1–3) showed ΣPAHs that were always lower than those found in downstream sites (4–6). ΣPAHs increased to a nearly constant value downstream site 4. Those results indicate that there is an important source or a set of sources of PAHs between sites 3 and 4.

Toxic equivalent quantities (TEQ) compare the individual carcinogenic potency of individual PAHs with that of benzo[a]pyrene [4,27]. TEQ were also applied to compare the sampling sites. This approach was successfully applied in the study of PAHs in total suspended particulate (TSP) [28] and in tree bark [29]. Individual PAH concentrations were multiplied by their TEQ and the results were summed up leading to total toxic equivalent quantities (TTEQ) of

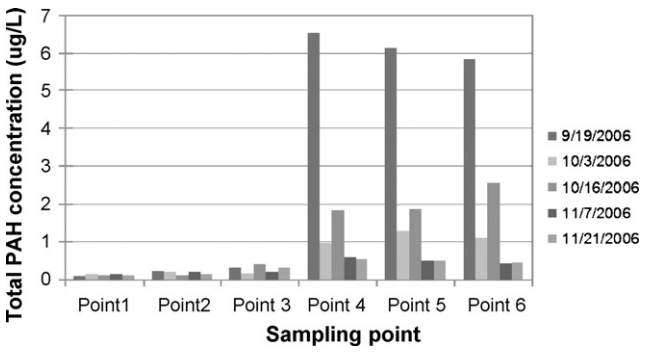

Fig. 2. Variation of total PAH concentrations (ΣPAH; μg/L) in the different sites and dates.

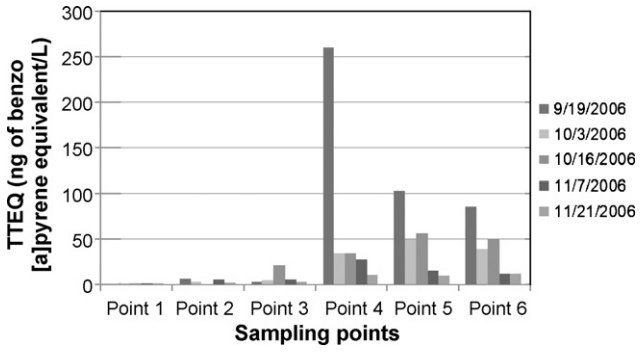

Fig. 3. Variation of total toxic equivalent quantities (TTEQ) expressed as ng of benzo[a]pyrene equivalent per liter of sample in the different sites and dates.

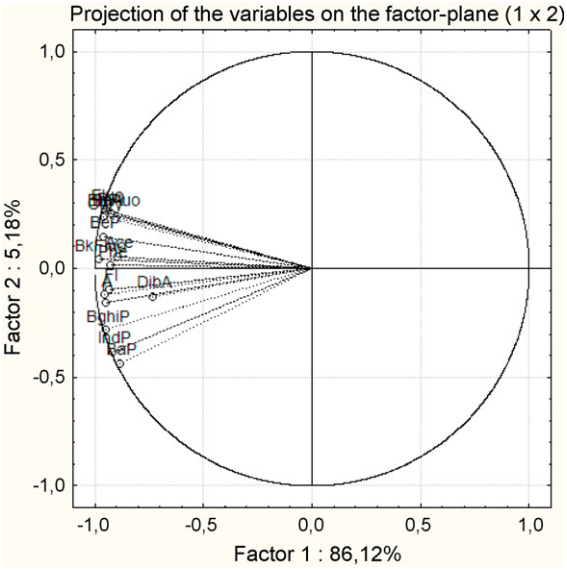

Fig. 4. Diagram of factor loadings (PC1 versus PC2) of PAHs.

the samples that are expressed as ng of benzo[a]pyrene equivalent per liter of sample (Fig. 3). TTEQ values ranged between 0.43 and 259 ng of benzo[a]pyrene equivalent/L (Fig. 3). Site 4 showed the largest TTEQ values and site 1 the lowest TTEQ values. These results indicate a reduction of water quality and an increase of its toxicity downstream site 4.

3.2. Multivariate analysis of data

PAH concentrations data were autoscaled before PCA by subtracting the mean concentration of each PAH from the observed concentration followed by division of the difference by the standard deviation of the concentrations of each PAH [30]. PCs1 and 2 were able to describe respectively 86.1% and 5.2% of total variance while PC3 described 4.5% of total variance.

The loading plot of PC2 versus PC1 (Fig. 4) shows that all PAHs are clustered in the same graphic area correspondent to negative loadings of PC1. PAH loadings varied between −0.735 (dibenz[a,h]anthracene) and −0.984 (benzo[k]fluoranthene). As a consequence samples were distributed along PC1 according to PAH concentrations with the most negative PC1 values corresponding to the samples that showed the largest ΣPAHs. The most positive values of PC1 corresponded to samples that showed the lowest ΣPAHs. PC2 loadings varied between −0.436 (benzo[a]pyrene) and +0.272 (fluoranthene).

A score plot of PC2 versus PC1 is shown in Fig. 5. Samples were coded as P*i*D*j* according to site localizations (*i* = 1–6) and campaign dates (*j* = 1–5; September 19 to November 21, 2006).

Fig. 5a shows that the samples are distributed along PC1 axis with a complex cluster of samples between PC1 values of 0 and 3. Downstream samples collected in sites 4, 5 and 6 in September 19th, 2006, during the dry season showed the most negative values of PC1 since these samples showed the largest ΣPAHs (6.5, 6.1 and 5.8 μg/L, respectively) (Fig. 2). PC2 allows a distinction between sites 5 and 6 (positive PC2 values) and site 4 (negative PC2 value). This negative value of PC2 is certainly due to benzo[a]pyrene concentration (0.181 μg/L) shown by this sample that was the largest concentration of this PAH found among all samples. In fact this sample showed the largest TTEQ (Fig. 3) among all samples reflecting the large concentration of benzo[a]pyrene.

Samples of sites 4–6 collected in October (during the beginning of the wet season) showed intermediate ΣPAHs (Fig. 2) and are situated in higher but still negative values of PC1. All other samples that showed low ΣPAHs that is all samples from sites 1 to 3 and samples from sites 4 to 6 collected in November, 2006 (Fig. 2) showed positive values of PC1.

Fig. 5b shows an expansion of PC1 and PC2 scales and allows a clear evaluation of this cluster of samples. This way, samples collected in sites 4–6 in November, 2006 show low positive PC1 values associated with positive values of PC2. All remaining samples—those collected in upstream sites—were clustered in the same area of Fig. 5b with positive values of PC1 and low negative values of PC2. It is remarkable that except for the samples collected in September 19, 2006 and in October 3rd, 2006 in site 4 (P4D1 and P4D2) all other downstream samples are characterized by low PC1 values (negative or low positive values) and positive PC2 values.

In order to further evaluate the similarities among samples, our results were also evaluated by cluster analysis. PAH concentrations were used as descriptors of sites and dates. Euclidian distances were employed for data matrix treatment and Ward's method was employed for clustering. The results of cluster analysis are shown in Fig. 6.

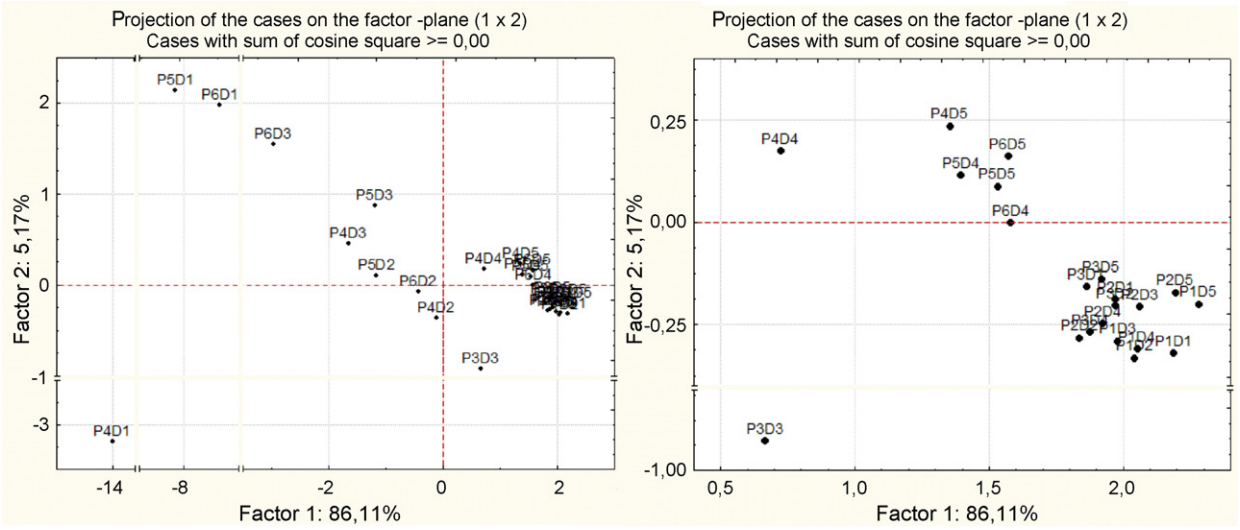

Fig. 5. Diagram of principal component scores (PC1 versus PC2) of samples (a, left) and scale expansion (b, right). Sites and dates were coded as explained in the text.

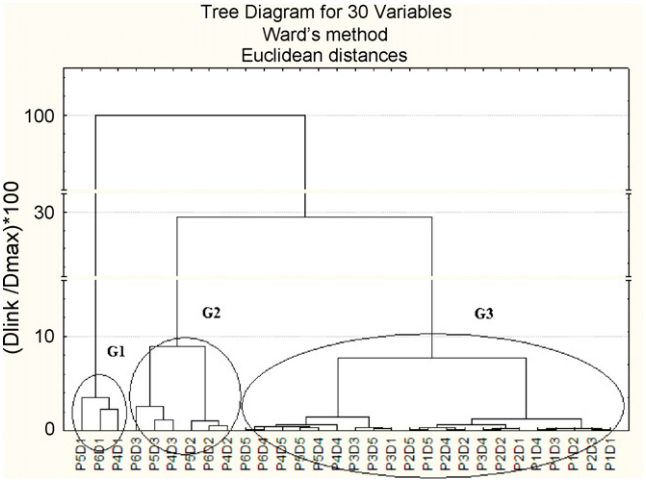

Fig. 6. Dendogram of samples using PAH concentrations as descriptors after cluster analysis. The Euclidian distance axis was cut to allow better visualization of sample distribution.

Three distinct groups of samples can be observed in Fig. 6. G1 represents the samples collected in sites 4, 5 and 6 in September 19th, 2006, in the dry season that showed the largest ΣPAHs (6.5, 6.1 and 5.8 μg/L, respectively) (Fig. 2). In opposition to G1, G3 represents the samples that showed the lowest ΣPAHs (Fig. 2) that is, all upstream samples (from sites 1 to 3) and downstream samples collected in November, 2006, during the wet season. G2 represents the samples containing intermediate ΣPAHs (Fig. 2) that is, downstream samples collected in the beginning of the wet season (October, 2006). The classification of the samples by CA is in very good agreement with that of PCA.

An overall interpretation of all data (individual PAH and ΣPAHs concentrations, TTEQ, PCA and CA) shows that sites 1–3 showed lower levels of PAH contamination than sites 4–6 except during the rainy season when both groups of sites tended to show similar concentrations of PAHs and contamination thus indicating an important dilution of the samples due to the rain and a remarkable reduction of PAH concentrations in sites 4–6 in this period.

4. Conclusions

Water samples collected in Tripuí River showed different concentrations of PAHs depending on sampling site localization and season (dry or wet). The concentrations decreased during the rainy period possible due to dilution.

The concentrations of carcinogenic PAHs such as benzo[a]pyrene found in certain samples collected downstream the plant were higher than the Brazilian MCL showing the contamination of Tripuí River. Moreover PAHs such as phenanthrene, fluoranthene and pyrene that were considered to be toxic to aquatic biota were found in relatively high concentrations in certain samples.

The evaluation of the samples by principal component analysis and cluster analysis showed that downstream and upstream samples can be classified in groups that depended also on sampling site localization and rain volume (dry and wet seasons).

An overall interpretation of data (individual PAH and ΣPAHs concentrations, TTEQ, PCA and CA) indicates that different levels of environmental contamination by PAHs are found in the neighborhood of the aluminum smelter. Upstream sites presented lower levels of PAHs than downstream sites except during the rainy season when both groups of sites showed similar PAH concentrations thus indicating an important dilution due to the rain that allowed a remarkable reduction of downstream PAH concentrations in this period.

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References

[1] P. Boffetta, N. Jourenkova, P. Gustavsson, Cancer risk from occupational and environmental exposure to polycyclic aromatic hydrocarbons, Cancer Causes Control 8 (1997) 444–472.
[2] IARC—International Agency for Research on Cancer. Complete list of agents, mixtures and exposures evaluated and their classification, 2007, http://www.iarc.fr.
[3] A.D. Pereira Netto, J.C. Moreira, A.E.X.O. Dias, G. Arbilla, L.F.V. Ferreira, A.S. Oliveira, J. Barek, Avaliação da contaminação humana por hidrocarbonetos policíclicos aromáticos (HPAs) e seus derivados nitrados (NHPAs): uma revisão metodológica, Química Nova 23 (2000) 765–773.
[4] IPCS—International Programme on Chemical Safety, Selected Non-Heterocyclic Polycyclic Aromatic Hydrocarbons, World Health Organization, Geneva, 1998.
[5] T. Vo Dinh, J. Fetzer, A.D. Campiglia, Monitoring and characterization of polyaromatic compounds in the environment, Talanta 47 (1998) 943–969.
[6] USEPA—United States Environmental Protection Agency. National Primary Drinking Water Standards, 2003, http://www.epa.gov/safewater.
[7] Brazilian Health Ministry. Portaria MS 518. Brasília, Brazil, 2004.
[8] Brazilian Environment Ministry. Resolução CONAMA 357. Brasília, Brazil, 2005.
[9] M.B. Yunker, R.W. Macdonald, R. Vingarzan, R.H. Mitchell, D. Goyette, S. Sylvestre, PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition, Org. Geochem. 33 (2002) 489–515.
[10] A.B.A. Boxall, L. Maltby, The effects of motorway runoff on freshwater ecosystems. 3. Toxicant confirmation, Arch. Environ. Contam. Toxicol. 33 (1997) 9–16.
[11] A.D. Pereira Netto, T.M. Krauss, I.F. Cunha, E.C.P. Rego, Polycyclic aromatic hydrocarbons levels in street dust in the Central Area of Niterói City, RJ, Brazil, Water Air Soil Pollut. 176 (2006) 57–67.
[12] A.D. Pereira Netto, F.C. Muniz, E.C.P.R. Laurentino, Identification of polycyclic aromatic hydrocarbons in street dust of Niterói City, RJ, Brazil, Bull. Environ. Contam. Toxicol. 68 (2002) 831–838.
[13] A.D. Pereira Netto, I.F. Cunha, F.C. Muniz, E.C.P. Rego, Polycyclic aromatic hydrocarbons in street dust of Niterói City, RJ, Brazil, Bull. Environ. Contam. Toxicol. 72 (2004) 829–835.
[14] E. Manoli, C. Samara, Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis, Trends Anal. Chem. 18 (1999) 417–428.
[15] A.D. Pereira Netto, C.L.S. Sisinno, J.C. Moreira, G. Arbilla, M. Dufrayer, Polycyclic aromatic hydrocarbons in leachate from a municipal solid waste dump of Niterói City, RJ, Brazil, Bull. Environ. Contam. Toxicol. 68 (2002) 148–154.
[16] E. Manoli, C. Samara, Polycyclic aromatic hydrocarbons in waste waters and sewage sludge: extraction and clean-up for HPLC analysis with fluorescence detection, Chromatographia 43 (1996) 135–142.
[17] D.A. Azevedo, E. Gerchon, E.O. Reis, Monitoring of pesticides and polycyclic aromatic hydrocarbons in water from Paraíba do Sul River, Brazil, J. Braz. Chem. Soc. 15 (2004) 292–299.
[18] G.M. Titato, F.M. Lancas, Comparison between different extraction (LLE and SPE) and determination (HPLC and capillary-LC) techniques in the analysis of selected PAHs in water samples, J. Liquid. Chromatogr. Relat. Technol. 28 (2005) 3045–3056.
[19] D.M. Brum, R.J. Cassella, A.D. Pereira Netto, Multivariate optimization of a liquid–liquid extraction of the EPA-PAHs from natural contaminated waters prior to determination by liquid chromatography with fluorescence detection, Talanta 74 (2008) 1392–1399.
[20] IGA—Instituto de Geociências Aplicadas. Desenvolvimento Ambiental de Ouro Preto–Microbacia do Ribeirão do Funil. Secretaria de Estado de Ciência e Tecnologia e Meio Ambiente; Belo Horizonte, 1998.
[21] ABNT—Associação Brasileira de Normas Técnicas. NBR 13895. Rio de Janeiro, Brazil, 1997.
[22] G.R. Ramos, M.C.G. Álvarez-Coque, Quimiometria, Editorial Sintesis, Madrid, Spain, 2001.
[23] P. Booth, K. Gribben, A review of the formation, environmental fate and forensic methods for PAHs from aluminum smelting process, Environ. Forensic 6 (2005) 133–142.
[24] W. Wilcke, W. Amelung, M. Krauss, C. Martius, A. Bandeira, M. Garcia, Polycyclic aromatic hydrocarbon (PAH) patterns in climatically different ecological zones of Brazil, Org. Geochem. 34 (2003) 1405–1417.

[25] W. Wilcke, M. Krauss, J. Lilienfein, W. Amelung, Polycyclic aromatic hydrocarbon storage in a typical Cerrado of the Brazilian Savanna, J. Environ. Qual. 33 (2005) 946–955.
[26] M. Krauss, W. Wilcke, C. Martius, A.G. Bandeira, M.V.B. Garcia, W. Amelung, Atmospheric versus biological sources of polycyclic aromatic hydrocarbons (PAHs) in a tropical rain forest environment, Environ. Pollut. 135 (2005) 143–154.
[27] C. Nisbet, P. LaGoy, Toxic Equivalency Factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs), Regul. Toxicol. Pharm. 16 (1992) 290–300.
[28] A.V. Castellano, J.L. Cancio, P.S. Aleman, J.S. Rodriguez, Polycyclic aromatic hydrocarbons in ambient air particles in the city of Las Palmas de Gran Canaria, Environ. Int. 29 (2003) 475–480.
[29] A.D. Pereira Netto, R.P. Barreto, J.C. Moreira, G. Arbilla, Spatial distribution of polycyclic aromatic hydrocarbons in *Terminalia catappa* L. (Combretaceae) bark from a selected heavy road traffic area of Rio de Janeiro City, Brazil, J. Hazard. Mater. 142 (2007) 389–396.
[30] M. Otto, Chemometrics: Statistics and Computer Application in Analytical Chemistry, Wiley–VCH, Weinheim, 1999.