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# Seasonal and diurnal variations of atmospheric PAH concentrations between rural, suburban and urban areas

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# ABSTRACT

Atmospheric sampling (gas and particle-phases) of 17 polycyclic aromatic hydrocarbons (PAHs) were performed between 2002 and 2004 in Strasbourg (east of France) and its vicinity. Sites were chosen to be representative of urban (Strasbourg), suburban (Schiltigheim) and rural (Erstein) conditions. Field campaigns were undertaken simultaneously in urban/suburban and urban/rural sites during three seasons. Moreover, air sampling has been performed in three 4–h time intervals per day (morning, midday/afternoon, and evening) to assess the diurnal variations in PAH concentrations.

Mean total PAH concentrations were 92 ng  $m^3$  for the rural site, 127 ng  $m^3$  for the urban site and 149 ng  $m^3$  for the suburban site. There is a significant difference in concentrations between the three sites, independently of the seasons considered. At the three sites, the most abundant compounds determined were naphthalene followed by phenanthrene and acenaphtene. Moreover, a variation between warm period (spring) and cold period (autumn and winter) for the three sites was observed with higher PAH concentrations during the cold periods.

The diurnal variations of PAH concentrations at the three sites, in warm period, have been observed in accordance with the intensity of the vehicle traffic, with highest concentrations during the morning and the evening. In cold period, there was no difference in concentrations between these two time intervals of high vehicle traffic in urban and suburban sites. It seems that the contribution of domestic heating influenced the diurnal variations of some compounds, especially in the rural site.

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# 1. Introduction

The atmosphere is well known to be a good pathway for the global dissemination of persistent organic pollutants like polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) (Baek et al., 1991). PAHs are ubiquitous contaminants of great environmental concern since some of the sixteen unsubstituted PAHs are considered as possible or probable human carcinogens and consequently listed by the U.S. Environmental Protection Agency (EPA) as priority pollutants.

The atmospheric origin of PAHs is very diverse: by-products from incomplete combustion of fossil fuels and wood, residential heating, coke production and vehicular exhausts. The latter can be considered as a major source in urban atmosphere (Baek et al., 1991; Velasco et al., 2004). For example, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene and coronene, along with fluoranthene, pyrene and phenanthrene, indicate direct vehicular emissions (Chiang et al., 1996; Caricchia et al., 1999). Diesel exhausts are believed to be enriched in fluoranthene, chrysene and pyrene relative to gasoline fuel exhausts (Larsen and Baker, 2003). Besides, an important natural source is the biomass burning, either from forest fires or from domestic heating (Cecinato et al., 1997; Masclet et al., 2000; Oros and Simoneit, 2001). However, PAH source signatures are not unique by source type and some PAH isomer ratios show substantial intra-source variability and intersource similarity, especially when grouped in coarse categories (Galarneau, 2008). Understanding the contributions of the various sources is critical to the appropriate management of PAH concentrations in the environment especially since certain PAHs are suspected to be carcinogens and some of them are associated with acute and chronic health effects (Fang et al., 2004).

Due to an increased concern about air quality and potential adverse effects to human health in large urban areas, many papers were recently published on PAHs in the atmosphere covering several countries including like Brazil (Fernandes et al., 2002; Dallarosa et al., 2005), Chile (Sienra et al., 2005), U.S.A. (Park et al., 2002; Hopke et al., 2003; Oros et al., 2007; Zheng et al., 2009), Canada (Ngabe and Poissant, 2003), China (Bi et al., 2003; Yang et al., 2010; Ma et al., 2010), Japan and Thailand (Chetwittayachan et al., 2002), Germany (Schnelle–Kreis et al., 2001), Spain (Lopez Cancio et al., 2002), Greece (Mandalakis et al., 2002; Sitaras et al., 2004), UK (Ciaparra et al., 2009) and France (Besombes et al., 2001; Albinet et al., 2007).

In this study, 17 PAHs (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[b]fluoranthene, benz[*a*]anthracene. chrysene, benzo[k]fluoranthene, benzo[*j*]fluoranthene, benzo[a]pyrene, dibenz[a,h] anthracene, indeno[1,2,3-cd]pyrene, benzo[*q*,*h*,*i*]perylene and coronene) were monitored in atmospheric samples (gas and particle-phases). Sampling campaigns have been performed between 2002 and 2004 in spring, autumn and winter seasons simultaneously on two sites

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(rural and urban; urban and suburban) during three 4–h time intervals (06:00–10:00; 11:30–15:30; 17:00–21:00) in order to compare the seasonal, diurnal and spatial variations.

## 2. Materials and Methods

## 2.1. Chemicals

Acetonitrile, methanol, methylene chloride and n-hexane of HPLC grade were obtained from VWR International (Fontenaysous-bois, France). Ultrapure water was obtained from a Milli–Q water system (Millipore, St. Quentin en Yvelines, France). The Standards of individual PAHs were supplied by Interchim (> 99% purity) for benz[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*j*]fluoranthene (BjF), benzo[*a*]pyrene (BaP), dibenz[*a*,*h*] anthracene (DBaA), indeno[*1*,*2*,*3*–*cd*]pyrene (IcdP), by Acros Organics (> 98% purity) for fluorene (FLU), anthracene (ANT), phenanthrene (PHE), fluoranthene (FLA), pyrene (PYR), chrysene (CHR), benzo[*k*]fluoranthene (BkF), benzo[*g*,*h*,*i*]perylene (BghiP), coronene (COR), and by Aldrich (> 98% purity) for naphthalene (NAPH) and acenaphthene (ACE). A stock solution of each PAH was prepared at 1g L<sup>-1</sup> in a mixture of methylene chloride/acetonitrile (50:50, v/v).

#### 2.2. Sampling site and procedure

Samples were collected on two sites simultaneously using two Digitel DA–80 high volume samplers (DIGITEL, Switzerland) equipped with a glass fiber filter (with a = 150 mm diameter) and 20 g of XAD–2 resin at a flow rate of 60 m<sup>3</sup> h<sup>-1</sup> for 4 h between 06:00 and 10:00; 11:30 and 15:30 and 17:00 and 21:00, sampling a total of 240 m<sup>3</sup> air.

Prior to sampling, the traps (filter and XAD-2 resin) were cleaned by Soxhlet extraction for 24 h with a solution of nhexane/methylene chloride (50:50, v/v). After cleaning, the traps were hermetically stored in new plastic bags and glass bottles in the freezer (-18°C). After sampling, the samples were stored in the freezer and were separately (gas and particle) extracted as soon as possible (no later than one week after sample collection) for 12 h in a Soxhlet apparatus with the same solvents used for cleaning. The liquid extract was concentrated using a rotary evaporator and evaporated to dryness under a gentle flow of nitrogen. Then 1 mL of acetonitrile and triphenylbenzene (internal standard) at 1 mg L were added. The blanks were evaluated by the extraction of traps after cleaning and storage procedure. No PAHs were detected in all cases. Recoveries of the 17 PAHs studied after sampling, extraction, evaporation to dryness, and refilling in acetonitrile varied between 50 % (NAPH) and 102 % (DBaA) with 10% of uncertainty as previously validated by Morville et al. (2004). These recoveries were taken into account in the calculation of concentrations.

The sites have been chosen in order to be representative of urban, suburban and rural conditions (Figure 1). The urban site was situated in downtown Strasbourg (250 000 inhabitants) far from direct emissions (i.e., industries, heavy roads) and the DA–80 sampler was located on the roof of the botanical institute of the University of Strasbourg (30 m above ground). The suburban site was situated in Schiltigheim (a mid–sized town with 29 000 inhabitants), a direct neighboring city, northwest of Strasbourg and the DA–80 was installed on the roof (10 m above ground) of the technological school of the University of Strasbourg. The rural site was situated in Erstein (small sized town of 8 000 inhabitants), situated 20 km in the south–east of Strasbourg. The DA Sampler was installed at ground level in a closed area.

In order to compare atmospheric PAH levels between sites, two kinds of sampling campaigns were performed: between urban and suburban sites and between urban and rural sites. Sites where sampling was conducted during each campaign are presented in Table 2. Sampling at the three sites was performed between 06:00 and 10:00, between 17:00 and 21:00 (two time intervals of high vehicle circulation) and between 11:30 and 15:30 (time interval of less vehicle circulation). Five campaigns were undertaken along three different seasons: spring 2002 (April and May), autumn 2002 (November), autumn 2003 (October/November) and winter 2004 (January/February).



Figure 1. Locations of the sampling sites.

### 2.3. Apparatus and analysis

The analysis was performed using a Kontron HPLC system coupled to a Jasco fluorescence detector FP–1520. Chromatographic conditions, the excitation/emission wavelengths and the detection limits of the method were presented elsewhere in detail (Morville et al., 2004). Limit of detection (LOD) for atmospheric samples, including blank correction, varied between 40 pg m<sup>-3</sup> to 400 pg m<sup>-3</sup> for 240 m<sup>3</sup> of air sampled.

# 3. Results and Discussion

#### 3.1. Mean concentrations

PAHs were determined between 2002 and 2004 during five sampling campaigns at the three sites. Mean total concentrations (gas and particle-phases) obtained for the three sites are presented in Table 1. As a first observation, it can be seen that most of the PAHs monitored were detected and sometimes at relatively high concentrations. Mean total concentrations varied between 92 ng m<sup>-3</sup> for the rural site (Erstein), 127 ng m<sup>-3</sup> for the urban site (Strasbourg) and 149  $\mathrm{ng}\,\mathrm{m}^{-3}$  for the suburban site (Schiltigheim). From these results it can be seen that the mean total concentrations of the rural site remains lower than the mean concentration of the two other sites. However, the mean total concentrations of the suburban site and the urban site are quite similar with a higher value for the suburban site. At the three sites, low molecular weight PAHs (MW <  $200 \text{ g mol}^{-1}$ ) present the highest concentrations and more abundant compounds are NAPH  $(> 53.7 \text{ ng m}^{-3})$ , PHE  $(> 26.2 \text{ ng m}^{-3})$ , ACE  $(> 25.9 \text{ ng m}^{-3})$  and FLU (>11.8 ng  $m^{-3}$ ). Lower concentrations were observed for PAHs with 5, 6 and 7 rings (i.e., COR, DBaA). These observations were consistent with the previous studies (Halsall et al., 1994; Caricchia et al., 1999; Prevedouros et al., 2004; Tsapakis and Stephanou, 2005). However, even if BaP presents lower concentrations than the other PAHs studied, mean concentrations of these compounds are not negligible since they are between 2.1, 3.0 and 1.1 ng m<sup>-3</sup> for the urban, suburban and rural sites respectively. A maximum value of 13.6 ng  $m^{-3}$  was observed for the suburban site in November 2002. These values for BaP are generally similar to those observed in other studies (Smith and Harrison, 1996; Park et al., 2002; Prevedouros et al., 2004; Tsapakis and Stephanou, 2005) and must be considered with attention knowing the toxicity of this compound. For example, values measured for this PAH are higher than of the mean annual concentration  $1 \text{ ng m}^{-3}$  set for EU members on their Air Quality Objectives.

Compound	Urban site			Suburban site			Rural site		
		(n = 36)			(n = 22)			(n = 14)	
-	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
NAP	43.9	< LOQ	210	53.7	< LOQ	231	38.1	< LOQ	137
ACE	20.3	< LOQ	68.9	25.9	< LOQ	59.3	11.4	< LOQ	38.1
FLU	9.7	0.8	20.9	11.8	1.6	38.0	7.4	1.9	14.9
PHE	24.5	6.1	78.3	26.2	8.0	95	17.3	7.0	40.0
ANT	2.3	0.1	13.7	1.8	0.1	7.3	1.3	0.1	4.1
FLA	9.1	2.5	28.5	7.5	3.8	17.6	6.1	2.7	13.8
PYR	4.8	1.8	15.2	4.7	1.9	14.7	3.2	1.5	6.7
BaA	1.5	0.1	5.6	2.3	0.1	7.6	0.8	< LOQ	2.4
CHR	1.2	< LOQ	3.5	1.5	< LOQ	5.5	0.6	< LOQ	1.9
BjF	1.2	n.d	4.6	1.4	n.d	5.6	0.7	n.d	2.7
BbF	1.6	0.1	7.0	2.2	0.3	8.6	1.0	0.1	3.1
BkF	0.7	< LOQ	2.9	0.9	0.1	3.5	0.4	< LOQ	1.4
BaP	2.1	0.1	10.2	3.0	0.2	13.6	1.1	0.1	3.5
BghiP	2.3	0.1	7.8	3.4	0.4	14.1	1.2	0.1	3.0
DahA	0.1	n.d	1.1	0.2	n.d	0.9	0.1	n.d	0.4
IcdP	1.1	n.d	4.1	1.5	n.d	4.4	0.7	n.d	1.8
COR	0.7	0.2	2.0	1.1	0.1	5.2	0.3	n.d	0.7
Σ PAHs	127			149			92		

**Table 1.** Mean, minimum and maximum total PAH concentrations (gas and particle-phases, ng  $m^{-3}$ ) for the three sites studied

n = number of samples

Min : minimum; Max : maximum

LOQ : limit of quantification; n.d : not detected

Note: see "Materials and Methods" for abbreviations of individual compounds

The mean PAH concentrations in this study were higher than those of many other urban areas reported around the world (Baek et al., 1991; Smith and Harrison, 1996; Mandalakis et al., 2002; Albinet et al., 2007), but were lower than that have been reported in Bursa (Turkey) during the heating season (Esen et al., 2008), in China (Li et al., 2006) and in London (Halsall et al., 1994). PAH concentrations determined at the urban and/or suburban sites, particularly in Seoul (Park et al., 2002), in Heraklion (Tsapakis and Stephanou, 2005) and in China (Yang et al., 2010) are similar. For the rural site, concentrations measured in Erstein were considerably higher than those observed in Wisconsin (Cotham and Bidleman, 1995), close to Birmingham during the summer (Smith and Harisson, 1996) and close to Atlanta (Li et al., 2009).

## 3.2. Seasonal variability

Mean total concentrations of the sum of the different PAHs at the three sites are summarized for all campaigns in Table 2. The average temperatures in Strasbourg are 17.0 °C during the spring, 7.7 °C during the autumn and 4.9 °C during the winter (the average temperatures are similar for the three sites, ±0.7 °C, independently from the seasons). Two periods according to this difference of temperature were considered, the warm period with spring sampling and the cold period with autumn and winter sampling. A high variation between warm period (April and May 2002) and cold period (November 2002, October/November 2003 and January/ February 2004) for the three sites was observed. For example, the total average concentrations at the urban site were 66.9 ng m<sup>-1</sup> during April, 2002 and 203 ng m<sup>-3</sup> during January/February 2004. The higher PAH concentrations during the cold period could be attributed by the increase in concentrations of high molecular weight PAHs (> 5 rings) in comparison to low molecular weight PAHs (2 to 4 rings) with the exception of naphthalene (2 rings) which its concentration increased strongly.

The variation of the total PAH concentrations were plotted as a function of the ambient air temperature for the urban site, in order to visualize the seasonal variations in more detail (Figure 2). It can be clearly seen that an increase of the PAH concentrations is observed when the temperature decreased (the Pearson correlation coefficient was 0.47), since concentrations were lower during the two first campaigns (April and May 2002) than during the three other campaigns (November 2002 and 2003, February 2004). A similar seasonal trend has been reported in a number of previously published studies (Baek et al., 1991; Caricchia et al., 1999; Sin et al., 2003; Sanderson et al., 2004; Tsapakis and Stephanou, 2005; Li et al., 2006; Esen et al., 2008).

**Table 2.** Mean total PAHs concentrations (ng  $m^{-3}$ ) during the five campaigns

Campaigns	Urban	Suburban	Rural	
	site	site	site	
April 2002 (1)	67	66		
May 2002 (2)	74		62	
November 2002 (3)	125	209		
October/November 2003 (4)	166	172		
January/February 2004 (5)	203		121	

The ratios of the total compound concentrations between cold and warm periods varied between 1.8 and 3.1 for the urban site, between 2.0 and 2.6 for the suburban site and had a value of 2.0 for the rural site. These ratios were similar to those observed in Hong Kong (1.4–2.4) by Sin et al. (2003) and in Napoli (1.5–4.5) by Caricchia et al. (1999) but significantly lower than those observed in Birmingham (5.4) by Smith and Harisson (1996). Several factors may contribute to the strong seasonal trend. During the cold period, PAH emissions from automobile exhaust are higher due to low ambient temperatures and increased effect of cold starts (Bjorseth and Ramdahl, 1985; Ludykar et al., 1999). Biomass burning is also likely to contribute to increase the PAH emissions in winter. Reduced atmospheric dispersion and atmospheric reaction can lead to higher PAH concentrations during the cold periods as well.

Nevertheless, evolution of the concentration with temperature is not identical for each PAH. Indeed, as previously observed by Halsall et al. (1994), Prevedouros et al. (2004) and more recently by Li et al. (2009), light PAHs present a very low seasonal variation while concentrations of heavy PAHs (predominantly in the particle–phase, like BaP) increase highly during cold periods when domestic heating increases. On the other hand, concentrations of the light PAHs can be maintained during colder periods by the decrease of their volatilization from surface soil or leaves (Wild and Jones, 1995). The ratio between BaP concentrations measured in cold period and in warm period was 6.7 for the suburban site, 8.4 for the urban site and 9.7 for the rural site.



Figure 2. Variation of the total PAH concentrations (gas and particle-phases) in the urban site as a function of the temperature.

This observation can be explained by a more important degradation during warm period and by an important reactivity of BaP (Hoyau, 1997). FLA presents lower ratio which is in accordance with its weak reactivity. For light PAHs like FLU the ratio between cold and warm periods reaches to a maximum of 2.5 in the suburban site.

In order to compare the concentrations between the three sites according to the seasons (warm or cold), the ratios of the mean total PAH concentrations between the urban and the rural sites  $(C_{\text{urban}}/C_{\text{rural}})$  or between the urban and the suburban sites (C<sub>urban</sub>/C<sub>suburban</sub>) were calculated. In the warm period, C<sub>urban</sub>/C<sub>rural</sub> is 1.2 indicating a very slight increase of the PAH concentrations in urban site. In the cold period, the ratio  $C_{urban}/C_{rural}$  is higher with a value of 1.7. It seems that there is a contribution of other sources (i.e., domestic heating and industrial) in urban site during cold period in comparison to warm period. On the other hand, similar levels of contamination between the urban site and the suburban site during the two periods were observed  $(C_{urban}/C_{suburban} = 1$  for the two periods). In terms of total concentrations, there is no significant difference between the two sites, regardless the seasons. The monitoring site in the suburban area is impacted by a nearby major freeway that could explain the similarity between the measured concentrations. Hayakawa et al. (2002) have observed a significant difference in concentrations between urban and suburban sites, while Mastral et al. (2003) and Li et al. (2009) have not observed significant variations.

PAHs with molecular weight of 202 are commonly used for the distinction between combustion and petrogenic sources. A ratio FLA/(FLA+PYR) > 0.5 indicates a predominance of combustion (Yunker et al., 2002). Ratios calculated for the three sites during the 5 campaigns were similar and always higher than 0.6 indicating the predominance of combustion sources. However, a petrol harbor located near the urban site on the Rhine River (approximately 3 km) may be a potential source.

## 3.3. Diurnal variability

As air sampling has been performed during 4-h time intervals during the same day to make the comparison possible for the variations in concentrations between the morning, afternoon and evening hours. This comparison was performed between cold and warm periods.

**Warm period.** The diurnal variation of the total concentration of compounds considered during campaigns 1 and 2 (April and May 2002), is presented in Figures 3a and 3b respectively, for a specific day. This specific day has been chosen since the meteorological conditions between the two sites and between the three time intervals were comparable.

At the three sites, the concentrations profiles observed for six PAHs were similar and were in accordance with the intensity of the vehicle circulation, with highest concentrations during the morning and the evening, the time interval corresponding to an important flux of vehicles. In fact, the urban and suburban sites are both heavily impacted by traffic due to their proximity to busy city streets and intersections of several freeways (approximately 3 km). The rural site is less impacted by traffic than the two other sites but the very close presence of a freeway to the sampling point (about 2 km) induces a high concentration of PAHs in the morning and in the evening. Indeed, in rural site the concentration difference between the two time intervals (06:00-10:00 and 17:00-21:00) corresponding to a high vehicle circulation is higher than for the two other sites. One hypothesis to explain this difference between morning and evening is that the returning home after the working day takes longer during the evening than during the morning.

The concentration profiles observed during the two campaigns performed in spring 2002 are in accordance with those obtained by Chetwittayachan et al. (2002). Two factors could explain these variations of concentrations during the day: a high correlation exist between the atmospheric levels of PAHs and the vehicle circulation (in particular heavy trucks) and the photochemical reactions. Indeed, the 11:30–15:30 time interval has high photochemical activity where PAHs can react with OH radicals (Reisen and Arey, 2005). This hypothesis can be confirmed in this study by the value of the global irradiance which can reach 284.4 joule cm<sup>-2</sup> in the morning (73.8 joule cm<sup>-2</sup>) and evening (98.4 joule cm<sup>-2</sup>). Some reactive PAHs like BaP could be degraded and consequently a decrease in their concentrations can be observed during the 11:30–15:30 time interval.



Figure 3. (a) Diurnal variations of the total concentrations for the six selected compounds during the Campaign 1 (warm period) between urban and suburban sites, and (b) during the Campaign 2 (warm period) between urban and rural sites.

**Cold period.** The diurnal variations of the total concentrations of the six selected compounds are illustrated in Figure 4a for the campaign 4, and in Figure 4b for the campaign 5. These figures were plotted according to the criteria defined for the warm period.

Concentrations measured during campaigns 4 and 5 are higher than those observed in warm period and this observation can be attributed to lower degradation processes and an increase in direct emissions, especially from vehicles. At the three sites, for the PYR and FLU, there is no significant difference between the concentrations measured during the three 4–h time intervals.

The diurnal concentration profiles determined for BaP, BaA and BghiP in urban and in suburban sites were similar, with high concentrations during the time intervals of high vehicle circulation (06:00–10:00 and 17:00–21:00). Contrary to the warm period there was no difference in concentrations between these two time intervals. Although, there is an increase of emissions from vehicles (Bjorseth and Ramdahl, 1985) during low air temperatures, this cannot explain the highest concentrations during the 17:00–21:00 time interval. Indeed, the intensity of the vehicle circulation in these sites does not vary between warm and cold periods. Thus, there is a new emission source of PAHs in cold period which can be domestic heating. In fact, the emissions from domestic heating are more important during the day and the evening in comparison to the night and early morning. In the rural site, a maximum of these three PAH concentrations were observed during the 17:00–21:00 time interval. This tendency can also be explained by the contribution of domestic heating.



Figure 4. (a) Diurnal variations of the total concentrations for the six selected compounds during the Campaign 4 (cold period) between urban and suburban sites, and (b) during the Campaign 5 (cold period) between urban and rural sites.

For phenanthrene, in urban site, the maximum concentration was measured between 11:30 and 15:30 and in suburban site this interval time corresponds to the minimum concentration. Moreover, the concentrations of other PAHs in urban and suburban sites were very similar during the three time intervals. It was very difficult to explain this phenomenon but the multiple sources for phenanthrene must be taken into account. In fact, the presence of an industrial area (about 2 km in the East) to the urban sampling point in contrary to the suburban sampling point can be the reason of the higher concentrations of phenanthrene during the 11:30–15:30 time interval. The mean wind direction (East)

during the campaign is in accordance with a possible contribution of sources from the industrial area.

## 4. Conclusions

The analysis of atmospheric samples in both particle and gasphases shows the presence of PAHs at the three different studied sites. At the three sites, independent from the campaigns, the most abundant compounds of those measured were naphthalene followed by phenanthrene and acenaphtene. The seasonal variability of these compounds in urban, suburban and rural atmosphere show that the concentration increases when the temperature decreases. For cold period, increase of concentrations can be explained by the contribution of new PAH sources like domestic heating, in addition to vehicle traffic. There was no difference in concentrations between the urban and suburban sites, contrary to the urban and rural site, with C<sub>urban</sub> ( $\Sigma$ PAH) > C<sub>rural</sub> ( $\Sigma$ PAH) especially during the cold period.

The diurnal variation, in warm period, observed for the six selected PAHs was in accordance with the vehicle circulation, with highest concentrations during the morning and the evening hours. In cold period, the diurnal variation for BaP, BaA and BghiP was also consistent with the vehicle circulation, but an additional source, the domestic heating, influenced the concentration profiles of these compounds. FLU and PYR presented no diurnal variations. The presence of an industrial area close to the urban sampling site influences the concentrations of phenanthrene.

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