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RESEARCH ARTICLE

Characterization of particulate polycyclic aromatic hydrocarbons in the east of France urban areas

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Abstract
Background Air samples collected on three different urban sites in East of France (Strasbourg, Besançon, and Spicheren), from April 2006 to January 2007, were characterized to measure the concentrations of polycyclic aromatic hydrocarbons (PAHs) in the particulate phase (PM_{10}) and to examine their seasonal variation, diurnal variations, and emission sources.
Results The average concentrations of ΣPAHs were 12.6, 9.5, and 8.9 ng m^{-3} for the Strasbourg, Besançon, and Spicheren sites, respectively. Strong seasonal variations of individual PAH concentrations were found at the three sampling sites, with higher levels in the winter that gradually decreased to the lowest levels in the summer. The diurnal variations of PAH concentrations in summer presented highest concentrations during the morning (04:00–10:00) and the evening (16:00–22:00) times, indicating the important contribution from vehicle emissions, in the three sampling sites. Furthermore, the ratio of BaP/BeP suggests that the photochemical degradation of PAHs can suppress their concentrations in the midday/afternoon (10:00–16:00), time interval of highest global irradiance. In winter, concentrations of PAH were highest during the evening (16:00–22:00) time, suggesting that domestic heating can potentially be an important source for particulate PAH, for the three sampling sites.
Conclusion Diagnostic ratios were used to identify potential sources of PAHs. Results showed that vehicle emissions may be the major source of PAHs, especially in summer, with a prevalent contribution of diesel engines rather than gasoline engines at the three sites studied, independently of the seasons.

Keywords PAHs · Atmospheric particles · Diurnal variation · Source identification

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of ubiquitous persistent organic pollutants, formed during incomplete combustion of organic materials. They are present in the ambient air, soil/sediment, water, and in food such as grilled meat (ATSDR 1995; IARC 1983). Atmospheric PAHs are present in both particulate and gas phases. PAHs with two to three aromatic rings exist predominantly in the gaseous phase, while compounds with four or more aromatic rings are primarily associated with the particulate fraction (Eiguren-Fernandez et al. 2004). Furthermore, the carcinogenic species are mainly associated with the particulate phase (Dickhut et al. 2000; Zhang et al. 2009). PAHs were widely studied with focus on their health-related impacts, and many of them were proven or possible mutagens and carcinogens (Ianistcki et al. 2009). The general population is exposed to PAHs primarily through inhalation of polluted air or cigarette smoke and through ingestion of PAH-containing foods (ATSDR 1995; Ramesh et al. 2004). Given their carcinogenic and mutagenic potential and their wide distribution that results in exposure in the general population, 16 PAHs have been included in the U.S. Environmental Protection Agency's as priority pollutants.

PAHs in the atmosphere can come from natural sources, such as forest fires and volcanic eruptions. However, their

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presence in densely populated areas is significantly increased by anthropogenic emissions, such as automobile exhaust, fossil fuel combustion, biomass burning, cigarette smoking, and industrial activities. The automobile exhaust 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 vehicle 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 that could either be 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).

Due to an increasing 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 Brazil (Fernandez et al. 2002; Dallarosa et al. 2005), Chile (Sienra et al. 2005), U.S.A. (Odabasi et al. 1999; Park et al. 2002; Hopke et al. 2003; Oros et al. 2007; Li et al. 2009a, b), Canada (Ngabé and Poissant 2003), China (Xinhui et al. 2003; Tan et al. 2006; Li et al. 2006; 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; Mastral et al. 2003), Greece (Mandalakis et al. 2002; Sitaras et al. 2004; Tsapakis and Stephanou 2005), UK (Halsall et al. 1994; Ciaparra et al. 2009), Italy (Caricchia et al. 1999), Belgium (Ravindra et al. 2006), and France (Besombes et al. 2001; Albinet et al. 2007). Most of these studies were based on integrated 24 h samples. In general, the variation of emission sources is not large from day-to-day, especially in the same season. However, the variation in emission sources in different time intervals of a day could be more distinct, and the chemical composition of aerosols would change rapidly when there are changes in source and meteorological conditions (Kuhlbusch et al. 2001). Therefore, samples collected in short time intervals are more conducive to source identification (Fine et al. 2004; Russell et al. 2004; Lammel et al. 2010a, b).

Studies on the characteristics and sources of PAHs in particulate matter (PM_{10}) in East of France are very limited, and the diurnal variation of PAHs is not clear (Morville et al. 2011). The aim of this study was to investigate the PM_{10} concentrations of 12 selected PAHs in three different urban areas in East of France, for a period between April 2006 and January 2007, and to study their seasonal trends, their diurnal variations, and their main emission sources by diagnostic PAH ratios. The target PAHs include fluoranthene (FLU), pyrene (PYR), benz[*a*]anthracene (BaA), chrysene (CHR), benzo[*e*]pyrene (BeP), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), benzo[*g*,*h*,*i*]perylene (BghiP), dibenz[*a*,*h*]anthracene (DahA), indeno[1,2,3-*cd*]pyrene (IcdP) and coronene (COR).

2 Experiment

2.1 Chemicals

Methanol, methylene chloride, hexane, and acetonitrile of HPLC grade quality were purchased from VWR International (Fontenay-sous-Bois, France). Ultrapure water was obtained from a Milli-Q water system (Millipore, St. Quentin en Yvelines, France). The individual PAH standards were all supplied from Sigma-Aldrich (L'Isle d'Abeau, France). The purity was higher than 99% for benz[*a*]anthracene (BaA), benzo[*e*]pyrene (BeP), benzo[*k*]fluoranthene (BkF), indeno[1,2,3-*cd*]pyrene (IcdP) and coronene (COR); at higher than 98% for chrysene (CHR), benzo[*g*,*h*,*i*]perylene (BghiP) and benzo[*b*]fluoranthene (BbF); and at higher than 96% for benzo[*a*]pyrene (BaP) and dibenz[*a*,*h*]anthracene (DBaA). The 1,3,5-triphenylbenzene (97% purity) was also purchased from Sigma-Aldrich and was used as internal standard (IS). Stock solutions of each PAH at 1 gL^{-1} and calibration standard solutions were prepared in a mixture of methylene chloride/acetonitrile (50:50, *v*/*v*).

2.2 Sampling sites and method

Three sampling sites located in different regions in East of France (Alsace, Franche-Comté and Lorraine) were chosen to characterize particle-bound PAHs in urban conditions. The first sampling site was located in Alsace region on the roof of a building at the University of Strasbourg close to Strasbourg downtown (275,000 inhabitants). The building is about 25 m above ground level in a mixed institutional and residential area. The district is an urban area heavily impacted by traffic due to its location with some secondary roads present in quite the direction. Furthermore, three main roads (about 500 m in Northwest, 2 km in Southwest, and 1.5 km in South direction) and an intersection freeway (2 km in Northwest) which carries on average of over 50,000 vehicles per day (about 3,000 diesel trucks) are present around the sampling site. Moreover, there are several industrial activities close to the site, in particular the Kehl area, a Germany town to about 4 km in East direction. The second sampling site, in Franche-Comté region, was located on a platform (~3 m height) of a parking structure and was in a mixed institutional and residential area close to downtown Besançon (120,000 inhabitants). The district is also an urban area, surrounded by a main road with a moderate traffic compared to Strasbourg site. No important industrial area is present around the sampling site. The last sampling site, in Lorraine region, was located directly on the ground level, in the village of Spicheren (3,500 inhabitants), about 5 km between the urban area of Forbach and the urban area of Saarbrucken in Germany. This sampling point, in a residential area, was representative of background urban conditions but present less directly heavy emissions from traffic compared to Besançon. At the three sampling sites, there was also a meteorological station supplying temperature, wind speed and direction, and rainfall data.

Sampling of PM_{10} have been carried out over 15-day periods between April 2006 and January 2007 during two contrasted seasons (summer and winter) in the three sites and during all seasons in the site of Strasbourg in order to study the seasonal trend. Sampling has conducted during April 26 to May 10 in 2006 (spring), July 27 to August 10 in 2006 (summer), November 12 to 26 in 2006 (autumn), and January 15 to 29 in 2007 (winter). Samples were simultaneously collected on the three sampling sites, during four daily time intervals (04:00–10:00, 10:00–16:00, 16:00–22:00, and 22:00–04:00, local time), except the weekend days, to assess the diurnal variations in PAH concentrations. The time intervals were designed to capture the variation in emission sources such as the increasing of traffic emissions in rush hours. Filters resulting of each 3-day sampling period were composited according to the same daily time interval and climatic conditions, to increase the mass of particle by samples (540 m^3 by sample). PM_{10} samples were collected onto quartz fiber filters (QM-A, Whatman, Florhamn Park, NJ), 150 mm of diameter, by using a high volume air sampling system (Digitel DA80, Switzerland) at a flow rate of 30 $m^3\ h^{-1}$. Prior to sampling, quartz fiber filters were cleaned by Soxhlet extraction for 24 h with a mixture of hexane/dichloromethane (50:50, *v*/*v*) to remove organic impurities and stored in an aluminium foil in an oven at 80°C until the sampling step. After sampling, filters were individually wrapped in an aluminium foil and placed in individual opaque reclosable poly bags, and kept in a −20°C freezer until analysis.

2.3 Sample extraction and analysis

Filters resulting of each 3-day sampling period were composited according to the same daily time interval and climatic conditions, to increase the mass of particle by samples (540 m^3 by sample). The filters sampled during a precipitation event were not integrated to the combination. The new composites samples of three filters were spiked with 1,3,5-triphenylbenzene (IS) prior to extraction. Samples were Soxhlet extracted for 20 h in a mixture of hexane/methylene chloride (50:50, *v*/*v*). The extracted samples were concentrated to about 500 μL by rotary evaporation.

Analyses were performed using a Kontron HPLC system coupled to a Jasco fluorescence detector FP-1520. A detailed discussion on chromatographic conditions, excitation/emission wavelengths, and detection limits of the method were presented elsewhere (Morville et al. 2004), and a brief explanation will be given below. The analytical thermostated column was set to 25°C, the injection volume was 20 μL, and the separation of PAHs was performed by using a methanol/water mobile phase at a flow rate of 1 mL min^{-1} by using a Macherey-Nagel (MN, Hoerth, France) reversed phase chromatographic column (EC 250/8/4 Nucleosil 100-5C_{18} PAH, 250×4 mm i.d.) equipped with a MN guard column (CC 8/4 Nucleosil 100-5C_{18} PAH).

3 Results and discussion

3.1 Average concentration of PAHs

PAHs were analysed between April 2006 and January 2007 during two contrasted seasons (summer and winter) at three sites and during all seasons at the site of Strasbourg. The number of sample was the following: 64 samples for Strasbourg site, 32 samples for Spicheren site, and 32 samples for Besançon site. Among the 12 targeted PAHs, only fluoranthene and pyrene were never quantified independently of the sampling sites. These two compounds were mainly associated with the gas phase while the ten other PAHs were mainly associated with the particulate phase as observed in previous studies (Halsall et al. 1994; Odabasi et al. 1999; Poor et al. 2004; Tasdemir and Esen 2007). Figure 1 presents the average concentrations of individual PAHs at the three studied sampling sites. The average concentrations of all quantified PAH (ΣPAH concentrations) were 12.6 ng m^{-3} in Strasbourg, 9.5 ng m^{-3} in Besançon, and

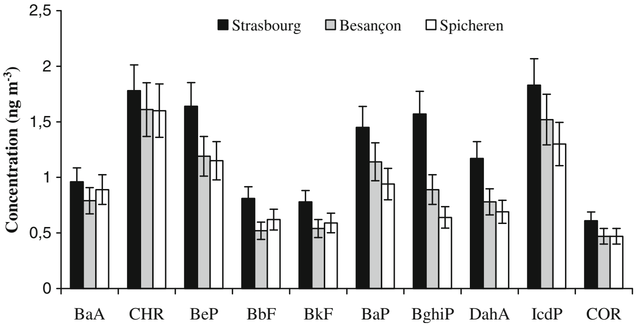

Fig. 1 Average concentrations of individual PAHs at the three sampling sites. Note: see "Materials and methods" for abbreviations of individual compounds

8.9 ng m^{-3} in Spicheren. It can be observed that there was no significant difference in PAH concentrations between the Besançon and Spicheren sites. Higher concentrations in Strasbourg than the two other sites were not surprising. This is consistent with the sampling location in densely populated and heavily trafficked areas with a high PAH contribution from traffic emission and anthropogenic input. However, the individual PAH concentrations are not quite significantly higher at the site of Strasbourg. Indeed, the concentrations of BaA and CHR are similar at the three sampling sites. Furthermore, the concentrations for all the PAHs quantified were similar between the Besançon site and the Spicheren site. This result is more surprising; in fact, Spicheren site presents less directly heavy emissions, as vehicle traffic, compared to Besançon site. The dominant wind direction may provoke a significant influence on concentrations in Spicheren area with an additional source, being able to result from the industrial area of Forbach (city situated in approximately 5 km in the east direction).

At the three sampling sites, CHR, IcdP, and BeP were found as the most abundant PAHs whereas coronene was the less abundant compound. These observations were not in accordance with the study of Morville et al. (2011) relative to atmospheric sample (gas and particulate phases) collected at the same site of Strasbourg. These authors found 2.3 ng m^{-3} for BghiP, 2.1 ng m^{-3} for BaP, 1.6 ng m^{-3} for BbF, 1.5 ng m^{-3} for BaA, and 1.2 ng m^{-3} for CHR. However, by considering the ΣPAH concentrations, a very similar value can be found of 12.5 ng m^{-3}. The light difference profile of PAH distribution at the Strasbourg site between the two studies can be explained by a change of the meteorological parameters, especially the dominant wind direction.

The ΣPAH concentrations in this study, at the Strasbourg area (the most polluted area), were lower than those of many other urban areas reported around the world, in particular, in Chicago (Odabasi et al. 1999), in Italy (Caricchia et al. 1999), in Turkey (Tasdemir and Esen 2007; Esen et al. 2008), in China (Tan et al. 2006; Li et al. 2006; Yang et al. 2010; Li et al. 2011), and in Hong Kong (Guo et al. 2003). They were higher than those already reported in Atlanta (Li et al. 2009a, b), in Japan (Hien et al. 2007), in Belgium (Ravindra et al. 2006), and in France (Albinet et al. 2007), and they were similar with those reported in Seoul (Park et al. 2002), in Greece (Tsapakis and Stephanou 2005), and in London (Halsall et al. 1994).

3.2 Seasonal variability

Concentrations of individual PAHs in PM$_{10}$ during each sampling season were plotted in Figs. 2 and 3. Strong seasonal variability was found for individual PAH concentrations at the three sampling sites with a maximum in the winter and a minimum in the summer, except for BghiP and DahA in Strasbourg, which present no significant difference between the autumn and the winter seasons. The seasonal concentration for the ΣPAH at the Strasbourg site were 5.95, 3.21, 16.28, and 24.85 ng m^{-3} for spring, summer, autumn, and winter seasons, respectively. At the Besançon and Spicheren sites, the values were 1.38 and 1.65 ng m^{-3} for summer season, and 17.51 and 16.13 ng m^{-3} for winter season, respectively. The winter to summer ratios of ΣPAH concentrations were 7.8, 12.6, and 9.8, respectively, in Strasbourg, Besançon, and Spicheren sites. The average temperatures in Strasbourg were 15.1°C in spring, 21.9°C in summer, 6.6°C in autumn, and 1.0°C in winter. In Besançon, the average temperatures were 20.7°C in summer and −0.4°C in winter, and in Spicheren, the average temperatures were 18.6°C in summer and 0.2°C in winter. Pearson correlations coefficients of ΣPAH with the average temperature were calculated. The coefficient value was −0.83 in Strasbourg, −0.87 in Besançon, and −0.69 in Spicheren. These strong negative correlation show further evidence that the particle-bound PAH concentrations varied inversely with temperature: higher concentrations in the cold season and lower ones in the warm season.

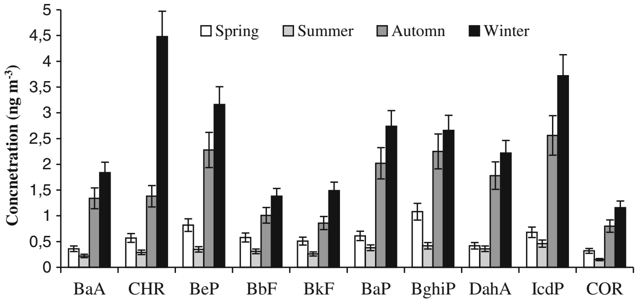

Fig. 2 Seasonal concentrations of individual PAHs at Strasbourg sampling site. Note: see "Materials and methods" for abbreviations of individual compounds

The increase in particulate PAH concentration during the winter and the dependence of PAH concentration on

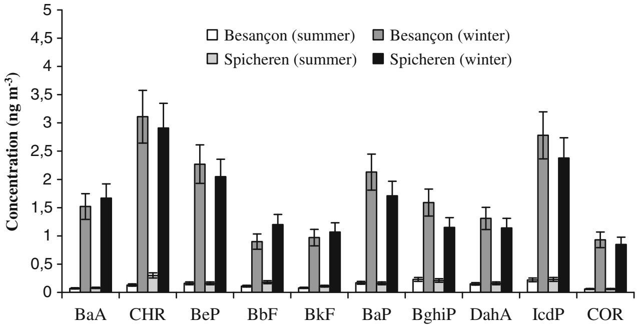

Fig. 3 Seasonal concentrations of individual PAHs at Besançon and at Spicheren sampling sites. Note: see "Materials and methods" for abbreviations of individual compounds

atmospheric temperature have 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). Several factors may contribute to the strong seasonal trend. During the winter season, PAH emissions from automobile exhaust are higher due to low ambient temperatures and increased cold start impacts (Bjorseth and Ramdahl 1985; Ludykar et al. 1999). Increased emissions from heating sources are also likely to contribute to increase PAH concentrations in winter. In addition to anthropogenic factors, reduced atmospheric dispersion resulting from lower mixing height and atmospheric reaction can lead to higher PAH concentrations during the cold periods as well. Pearson correlation coefficient of ΣPAH with the average global irradiance have been calculated. The relatively strong correlations, at the three sampling sites (−0.61 in Strasbourg, −0.63 in Besançon, and −0.65 in Spicheren), show further evidence that the photochemical reaction can also be an origin of the seasonal trend observed in this study. Furthermore, low atmospheric temperature can affect the distribution of PAHs between the gas and particulate phases and results in a relatively larger portion of PAH partitioning to the particulate phase. However, PAH quantified in this study, were principally present in the particulate phase independently of the seasons (Tasdemir and Esen 2007), and consequently, this partitioning between the gas and particulate phases was mainly not affected by the seasonal trend.

The profiles of the relative distribution of individual PAHs at the three sampling sites were studied. In Strasbourg, during the spring, the summer, and the autumn seasons, BghiP, IcdP, BeP, and BaP were the four most abundant PAHs. These compounds were source markers of motor vehicle emissions (Khalili et al. 1995; Smith and Harrison 1996; Guo et al. 2003), showing that the profiles in these seasons were principally influenced by the vehicle traffic. In contrast, CHR was the most abundant PAH followed by IcdP, BeP, BaP, and BghiP in the winter season. Rogge et al. (1993) found that fluoranthene, PYR, BaA, and CHR are the major emission components from domestic heating of fossil fuel such as natural gas. Furthermore, Simcik et al. (1999) indicate that BaA and CHR were typical markers for coal combustion. So, the increase of CHR concentration in our study may be explained by the contribution of domestic heating to Strasbourg area, as well as by the contribution of industrial emission. In fact, the mean wind direction (East) during the winter was in accordance with a possible contribution of source from the industrial area of Kehl. The distribution profiles of PAHs were quite similar at the two sites, Strasbourg and Besançon, during summer and winter seasons. However, in contrast to Strasbourg, the increase of CHR during the winter results only by the contribution of domestic heating, because the mean wind direction at the Besançon site was not in accordance with an industrial area. In Spicheren, during the summer, CHR was the most abundant PAH followed by BghiP, IcdP, BbF, BeP, and BaP. The different profiles of PAHs between Spicheren and the two others sites results to an additional source, other than the vehicle traffic, and could originate from the combustion of coal or garbage incineration. Finally, the PAH profiles during the winter season were also quite similar at the two sites, Strasbourg and Besançon, suggesting a similarity in PAH sources.

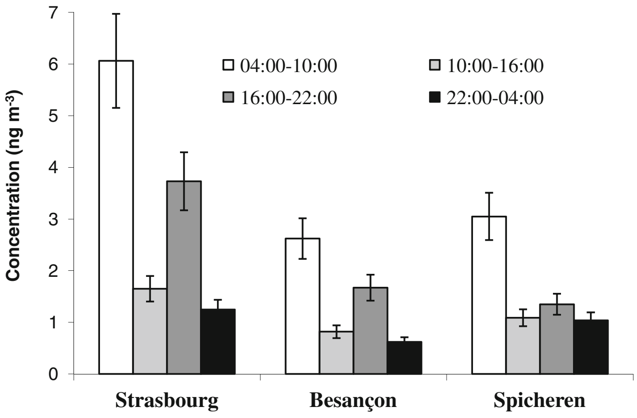

Fig. 4 Diurnal variations of total PAH concentrations in summer at the three sampling sites

3.3 Diurnal variability

As air sampling has been performed during 6 h time intervals during the same day, the comparison of the variations of concentrations between the morning, midday/afternoon, evening, and night hours was possible. The diurnal variation

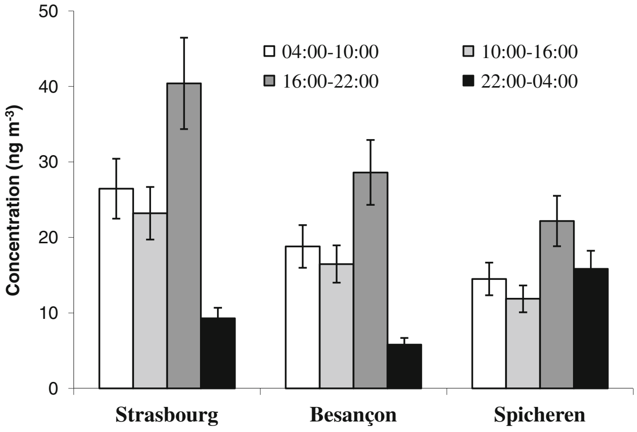

Fig. 5 Diurnal variations of total PAH concentrations in winter at the three sampling sites

Table 1 Daily variations of BaP/BeP ratio in summer period

Location	04:00–10:00	10:00–16:00	16:00–22:00	22:00–04:00
Strasbourg	0.86	0.54	0.81	1.08
Besançon	0.71	0.46	0.74	0.94
Spicheren	0.78	0.61	0.76	1.12

was performed between summer and winter seasons at the three sampling sites (Figs. 4 and 5).

In summer, concentrations profiles observed for the PAH compounds were similar between the three sites. The highest PAHs levels occurred in the morning hours (06:00–10:00) and in the evening hours (16:00–22:00), time interval corresponding to rush hours, indicated the important contribution from vehicle emissions. The concentration profile observed in Strasbourg area is in accordance with the study obtained by Morville et al. (2011), at the same sampling site, and the study of Gu et al. (2010) in an urban site in China. Indeed, Morville et al. (2011) studied the profiles of six PAHs (fluorene, phenanthrene, pyrene, BaA, BaP, and BghiP), and they observed highest concentrations during the morning and the evening, time interval corresponding to an important flux of vehicle around the urban site considered.

In Spicheren, there is not a significant difference in concentration between midday/afternoon (10:00–16:00), evening, and night (22:00–04:00) time intervals. One hypothesis to explain the phenomenon is that the site is less impacted by vehicle emission, and the traffic density is not typical of a French town in contrary to the two other sites.

Two factors could mainly explain these variations of concentrations during the day: a high correlation exist between the atmospheric levels of PAHs and the vehicle traffic and the photochemical reactions. Indeed, the 10:00–16:00 time interval has high photochemical activity where PAH 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 187.8 Jcm^{-2} in the midday/afternoon, a value higher than those observed in the morning (39.7 Jcm^{-2}), evening (67.5 Jcm^{-2}), and night (0 Jcm^{-2}). Some reactive PAH like BaP, COR, BaA, and BghiP could be degraded, and consequently, a decrease of their concentrations can be observed during the 10:00–16:00 time interval. Panther et al. (1999) reported that BaP is a high-reactive compound with a half-life of 5.3 h under simulated sunlight conditions, whereas BeP is more stable with a half-life of 21.1 h. These authors indicated that the ratio of BaP/BeP can give further insight on the negative correlation between total PAHs and sunshine hours. As shown in Table 1, BaP/BeP ratio ranged from 0.46 to 1.12, and the ratio was lower during the midday/afternoon than at the three other time interval for the three sampling sites. These results suggest that the photochemical degradation of PAHs apparently suppresses their concentrations in the midday/afternoon, time interval of high global irradiance.

In the winter, the PAH concentration profiles in Strasbourg site and in Besançon site were similar but were different to their concentration profiles in the summer season. Indeed, the concentrations were highest during the evening, followed by the morning and the midday/afternoon. Also, there is no difference of concentration between the morning and the midday/afternoon. Although, there is an increase of emissions from vehicles (Bjorseth and Ramdahl 1985) during low air temperature, which cannot explain the highest concentrations during the 16:00–22:00 time interval. Indeed, the intensity of the vehicle traffic in the sites does not evolve between summer and winter seasons. The effect of photochemical reaction was reduced because of the global irradiance and the decreasing of temperature in winter. Furthermore, besides emissions from vehicles, stagnant atmospheric condition was another reason for high PAHs levels in the morning during winter (Fine et al. 2004), and this phenomenon was in contradiction with highest concentration in the evening hours. There is thus a new emission source of PAHs which can be the domestic heating, with an important emission during the day and the evening. 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 Spicheren site, a maximum of PAH concentrations were also observed during the 16:00–22:00 time interval, but contrary to the two other sites, there is no difference of concentration between the morning, the midday/afternoon,

Table 2 The diagnostic ratios of PAHs at the three sampling sites

Location	Seasons	BaP/BghiP	IcdP/(IcdP+BghiP)	IcdP/BghiP	BghiP/BeP	BaP/(BaP+Chr)
Strasbourg	Spring	0.63	0.42	0.66	1.38	0.52
	Summer	0.88	0.49	1.08	1.26	0.57
	Autumn	0.91	0.51	1.10	0.94	0.59
	Winter	1.01	0.54	1.31	0.86	0.40
Besançon	Summer	0.75	0.47	0.97	1.41	0.56
	Winter	1.29	0.59	1.62	0.74	0.42
Spicheren	Summer	0.77	0.51	1.07	1.28	0.38
	Winter	1.44	0.64	1.90	0.65	0.41

and the night. Furthermore, in the Spicheren area, the concentration of PAHs during the night was higher than in Strabourg area and Besançon area. These tendencies can also be explained by the addition of domestic heating. In Spicheren, the heating more frequently used wood, being able to engender consequent emissions during the night.

3.4 Source identification by diagnostic ratios of PAHs

The PAH contents of urban air samples can be considered to be a composite of the emission products of various local sources combined with a contribution from outside areas. Diagnostic ratios of specific PAHs in the particulate phase have been successively used in previous work to characterize the PAH emission source in the atmosphere (Harrison et al. 1996; Caricchia et al. 1999; Kavouras et al. 2001; Park et al. 2002; Guo et al. 2003; Ding et al. 2007; Liu et al. 2007; Vardar et al. 2008; Yang et al. 2010).

Table 2 provides the five diagnostic ratios between total concentrations of PAHs at the three sampling sites studied. The BaP/BghiP ratio higher than 0.6 refers to the presence of traffic emission (Park et al. 2002). A similar value of this ratio was found at the three sampling sites. A value of 0.35–0.7 of IcdP/(IcdP+BghiP) ratio has been used for diesel emissions (Kavouras et al. 2001). The corresponding values have been noticed in the range of 0.42–0.64 at the three sampling sites. Furthermore, Caricchia et al. (1999) reported that the IcdP/BghiP ratio for gasoline engines is about 0.4, while the ratio for diesel engines approaches 1.0. All the values for this ratio were higher than 0.66 with a maximum ratio at 1.90. These two last ratios indicate the prevalent contribution of diesel engines rather than gasoline engines at the three sampling sites studied, independent of the seasons.

The BghiP/BeP ratio was used as an indicator for traffic, with higher ratios indicating a higher traffic contribution (Nielsen et al. 1996). The BghiP/BeP ratio was >1.26 during the warm period (spring and summer) and was <0.94 during the cold period (autumn and winter), which suggested that vehicle emissions have a higher contribution at the warm period, at the three sampling sites. Furthermore, Khalili et al. (1995) reported that BghiP/BeP ratios have a value of 2.9±0.9 for gasoline emissions and 1.3±0.8 for diesel emissions. In this study, the values of this ratio were in the range 0.65–1.41, confirming the prevalent contribution of diesel engines at the three sampling sites.

4 Conclusion

To characterize the atmospheric PAHs associated with PM_{10}, campaigns were performed between April 2006 and January 2007 at three urban sites located in the East Region of France. The ΣPAH concentrations at the Strasbourg site were 5.95, 3.21, 16.28, and 24.85 ng m^{-3} for spring, summer, autumn, and winter seasons, respectively. The ΣPAH concentrations at the Besançon and Spicheren sites were 1.38 and 1.65 ng m^{-3} for summer season, and 17.51 and 16.13 ng m^{-3} for winter season, respectively. Higher concentrations in Strasbourg area were observed, site located in densely populated and heavily trafficked areas with a high PAH contribution from traffic emission and anthropogenic input. A clear seasonal pattern was observed for all PAHs, with the maximum concentrations in the winter and the minimum in the summer. Significant diurnal variations of PAH concentrations were found at the three sampling sites. In the summer, the PAH concentration were highest during the morning (04:00–10:00) and the evening (16:00–22:00), indicating the important contribution of vehicle emissions in the rush hours. In the winter, the high atmospheric loading for PAHs pollutants was observed during the evening (16:00–22:00) because one important incidence is the increase of large amount of pollutant emission from domestic heating at the three sampling sites. Different diagnostic ratios of PAHs indicated that the vehicle emission may be the major source of PAHs, especially in summer, with a prevalent contribution of diesel engines rather than gasoline engines at the three sampling sites, independently the seasons.

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