

1                   **Variation in particulate PAHs levels and their relation with the**  
2                   **transboundary movement of the air masses**

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12  
13                   **Abstract**

14                   The levels of particulate polycyclic aromatic hydrocarbons (PAHs) were determined  
15                   with a fast analytical approach to study their seasonal variations at Menen (Belgium) during  
16                   2003; they were noticed to be 5-7 times higher in January, February and December, in  
17                   comparison to May, June and August. The annual average concentration of sum of 16 US  
18                   Environmental Protection Agency (EPA) criteria PAHs was 6.7 ng/m<sup>3</sup> and around 63% of  
19                   it was found to be probably carcinogenic to humans. The application of diagnostic ratio and  
20                   principal component analysis showed vehicular emission as a major source. An increased  
21                   ratio of ‘combustion PAHs’ to ‘total EPA-PAHs’ during the winter season indicated  
22                   towards combustion activities. Further, the differences in PAHs concentration were  
23                   assessed with relation to backward air mass trajectories, which show that the levels of  
24                   PAHs increases when there is an air mass movement from Central and Western Europe and  
25                   a fall when the trajectories spend most of their 4-days time over the Atlantic Ocean or in  
26                   the Arctic region.

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29                   **Keywords:** *PAHs; Pressurized liquid extraction; nonalkylated PAHs; combustion emission;*  
30                   *air mass backward trajectories and long range transport.*

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## 1 **Introduction**

2           The polycyclic aromatic hydrocarbons (PAHs) are of major health concern, mainly  
3 due to their well-known carcinogenic and mutagenic properties. PAHs and their metabolites  
4 can form DNA adducts, which can induce mutation (Lewtas, 1993, 2007; Ravindra et al.,  
5 2001; Binkova et al., 1999, 2003; Sram et al., 2007a,b). These adverse properties demands  
6 to assess their concentration, trends and source profile in the atmosphere to provide an aid  
7 to manage regional as well as global air pollution control strategies (Ravindra et al., 2001,  
8 2008; Breivik et al., 2006). Atmospheric PAHs are partitioned between the particulate and  
9 the gaseous phases. However, the carcinogenic 5- and 6- ring species are predominantly  
10 associated with particles, especially those falling in the accumulation mode ( $0.5 \mu\text{m} < d < 1$   
11  $\mu\text{m}$ ) that deposit only slowly from the atmosphere and, depending on atmospheric  
12 conditions, may be airborne for days and be transported over long distances (Venkataraman  
13 et al., 1994; Manoli et al., 2004; Mantis et al., 2005). Ravindra et al. (2006a) studied PAH  
14 levels at various sites in Belgium and found that vapor phase PAHs represent more site  
15 specific characteristics than aerosol phase PAHs. However, the variations in aerosol phase  
16 (particle/droplet associated) PAHs levels also show their relation with local as well as the  
17 regional anthropogenic activities.

18           The occurrence of specific PAH compounds, or a group of PAHs, has been used to  
19 indicate the corresponding emission sources (Ravindra et al., 2008). Additionally, as PAHs  
20 associated with airborne particles vary significantly as a function of their emission sources,  
21 some PAH concentration ratios have been used to indicate vehicular emission sources  
22 (Rogge et al., 1993; Venkataraman et al., 1994; Khalili et al., 1995). In most of the studies,  
23 principal component analysis (PCA) was used to enhance the accuracy of emission source

1 identification (Ho et al., 2002; Park et al., 2002; Fang et al., 2004; Ravindra et al., 2006a,  
2 b).

3 Air mass backward trajectories provide a useful means of establishing source-  
4 receptor relationships of air pollutants (Stohl, 1998; Beverland et al., 2000). Pollutants  
5 emitted from various sources, can remain in the atmosphere sufficiently long to be  
6 transported thousands of kilometres and thus to spread over a large area, across national  
7 borders, far from the original sources of polluting emission. There are many studies, which  
8 confirm that the general atmospheric circulation leads to long-range transport of aerosol or  
9 suspended particulate matter (SPM) over various regions of the world (Buchanan et al.,  
10 2002; Graham et al., 2004; Grennfelt and Hov, 2005). These aerosols carry a complex  
11 mixture of various inorganic and organic species including PAHs, originating from  
12 different sources. As mentioned above, a number of studies investigate the origin and  
13 transboundary movement of inorganic constituents of aerosol but little attention has been  
14 given for organic constituents and specifically for PAHs.

15 In the present study, the concentrations of 16 US Environmental Protection Agency  
16 (EPA) priority listed particulate PAHs were assessed during different seasonal conditions at  
17 Menen, Belgium. Menen was selected considering its background nature and closeness to  
18 the French border. This site can reflect the influence of industrial activities and long range  
19 transport on particulate PAHs levels. Various multivariate techniques such as correlations,  
20 diagnostic ratio and PCA were applied to characterize and identify the possible dominant  
21 emission sources of PAHs. Furthermore the variations in PAHs levels were evaluated with  
22 relation to various emission sources and backward air mass trajectories to study the  
23 regional / global impact. The understanding of organic pollutants behavior across national  
24 borders provides an aid to manage regional/ global air pollution control strategies.

# 1 **Experimental**

## 2 **Site selection**

3           The emphasis of the study lies on the border area between Belgium and France to  
4 study the regional-global impact on PAHs levels. The selected sampling site was located at  
5 the Wervikstraat at the outskirts of the town of Menen and near the border of France  
6 (supplementary Figure S1). The sampling site at Menen may be influenced by emissions  
7 from the industrial activities in the conurbations Lille and Dunkerque in France. The town  
8 covers an area of 33.1 km<sup>2</sup> and has a population of 32,000 inhabitants. The sampling site is  
9 located in an open environment, in order to permit a good circulation of the air and is 8 km  
10 from the French city Tourcoing, in a northerly direction. The region between Tourcoing  
11 and Halluin can be classified as a suburban zone; the areas around Wervicq and Rollegem  
12 have a more rural character.

## 13 **Sampling**

14           Total suspended particulate samples (n = 63) were collected on quartz fiber filters  
15 (Ø 150mm) for the determination of EPA-PAHs using a Digital High Volume sampler  
16 DHA-80 (DIGITEL Elektronik AG, Switzerland). The average flow rate was 350 l/min  
17 with an approximate sampling time of 48 h. DHA-80 has a container of 15 filters stretched  
18 in filter holders and they are changed automatically to the flow position at the pre-set time.  
19 After the sampling, the filters were wrapped in aluminum foil separately and stored in a  
20 freezer at -20 °C, until they were extracted. During each month of 2003, 5 to 9 samples  
21 were collected except in July, when no sampling was possible due to instrument problems.  
22 Wind-speed (WS), wind direction (WD), relative humidity (RH), air temperature (T<sub>air</sub>), air

1 pressure (pair), and precipitation (PR) were recorded at meteorological stations of the  
2 Flemish Environmental Agency (VMM) nearby the sampling sites.

### 3 **Fast analytical approach**

4 The samples were extracted using pressurized liquid extraction (PLE) or  
5 Accelerated Solvent Extraction (Dionex, Titan Way, CA, USA), which offers a very fast  
6 extraction of PAHs i.e. in 30 minutes; with equal or even better efficiency than Soxhlet  
7 extraction and minimum consumption of the toxic solvents (Godoi et al., 2004; Ravindra et  
8 al., 2006a, b). The filters were loaded in the 34 ml extraction cell. The extractions were  
9 performed using a pressure of 10 MPa at an oven temperature of 100 °C. A solvent  
10 combination of 1:1 dichloromethane/acetone was used for extraction. The flush volume was  
11 60% of the volume of the extraction cell. The full cycle was repeated four times, and after  
12 the extraction, the instrument was purged at 1 MPa for 60 s with nitrogen. Pre-rinsed 60 ml  
13 screw cap I- Chem Vials were used to collect the extracts. Finally, the extracts were  
14 enriched in a Turbo Vap 500 (Zymark, Hopkinton, MA, USA) concentration workstation  
15 and recovered in 1 ml of acetonitrile. Blank filters were also extracted using the same  
16 procedure as the one mentioned above.

### 17 **Analytical procedure**

18 The extracts were analyzed by high performance liquid chromatography (HPLC;  
19 Waters, Milford, MA, USA) with programmed fluorescence detection (Perkin-Elmer  
20 LC240, Norwalk, CT, USA). Separation of the PAHs was accomplished using a Vydac  
21 201TP (250 mm x 4.6 mm) column, with a gradient elution ranging from a 50+50%  
22 acetonitrile-water mixture to 100% acetonitrile in 20 min. The fluorescence of PAH was  
23 monitored with an automatic adjustment of the wavelengths for each compound according  
24 to the retention time. The excitation wavelengths ranged between 260 and 300 nm, while

1 the emission wavelengths lay between 380 and 465 nm. Linear calibration graphs were  
2 obtained for every compound in the concentration ranges up to 800 ng/ml. The detected and  
3 quantified PAHs were: naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp),  
4 fluorene (Flu), anthracene (Ant), phenanthrene (PA), fluoranthene (Flut), pyrene (Pyr),  
5 benzo[a]anthracene (B[a]A), chrysene (Chr), benzo[b]fluoranthene (B[b]F),  
6 benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), dibenzo[a,h]anthracene (D[ah]A),  
7 benzo[g,h,i]perylene (B[ghi]P) and indeno[1,2,3-c,d]pyrene (Ind). The limit of quantitation  
8 varied from 0.001 to 0.014 ng/m<sup>3</sup> for various PAHs (see supplementary Table S1). As no  
9 gas phase back up filters were used during sampling, the concentrations of the most volatile  
10 compounds (the first 6 in the above list) do not reflect the real concentrations in air but  
11 report the amounts which remained sorbed/condensed on the particles collected on the  
12 quartz fibre filter.

### 13 **Quality assurance**

14 All analytical data were subjected to strict quality control. Blank and spiked  
15 samples were analyzed with each set of samples. The extraction recovery efficiencies were  
16 determined using a certified / standard reference material (SRM) of the National Institute of  
17 Standards and Technology (NIST): SRM1650a (Diesel Particulate Matter) and they were  
18 better than 80%. The NIST standard PAH (SRM 1647d) mixture (Schmidt, Amsterdam,  
19 The Netherlands) was used for calibration of the analytical method and the NIST SRM  
20 2260 was also used for the spiking of the test sample for the routine quality control. The  
21 standardized test method for PAHs was accredited by Beltest (<http://belac.ggov.be>) under  
22 the number 163- Test (norm ISO- 17025).

## 1 **Results and discussion**

### 2 **Potential carcinogenic fraction of particulate PAHs**

3           In the environment, individuals are most likely to be exposed to PAHs vapors or  
4 PAHs that are attached to dust or other particles in the air (Lewtas, 2007). Exposure to  
5 PAHs and SPM can results in cell mutation (Ravindra et al., 2001; Binkova et al., 2003;  
6 Sram et al., 2007a,b). The results of an experimental animal study on inhaled diesel soot-  
7 adsorbed B[a]P, a marker PAH, indicate that direct absorption through the alveolar  
8 epithelium is an important route of entry of unmetabolized PAHs (Gerde et al., 2001).

9           The carcinogenicity classifications verified by EPA Carcinogenicity Risk  
10 Assessment Endeavor Work Group (EPA, 1994) shows that B[a]A, B[b]F, B[k]F, B[a]P,  
11 Chr, D[ah]A and Ind are considered to be probable human carcinogens, whereas other  
12 PAHs such as AcPy, Ant, B[ghi]P, Flut, fluorene, PA and Pyr are not classified as  
13 promoters of the same health risk. According to a public health statement  
14 (<http://www.atsdr.cdc.gov/toxprofiles/phs69.html>) by Agency for Toxic Substances and  
15 Disease Registry (ATSDR), the International Agency for Research on Cancer (IARC) has  
16 determined that B[a]A and B[a]P are probably carcinogenic to humans; B[b]F,  
17 benzo[j]fluoranthene (B[j]F), B[k]F, and Ind are possibly carcinogenic to humans; whereas  
18 Ant, B[g,h,i]P, benzo[e]pyrene (B[e]P), Chr, Flut, Flu, PA, and Pyr are not classifiable as to  
19 their carcinogenicity to humans. The Department of Health and Human Services (DHHS)  
20 has determined that B[a]A, B[b]F, B[j]F, B[k]F, B[a]P, D[a,h]A, and Ind are known animal  
21 carcinogens. Acp has not been classified for carcinogenic effects by the DHHS, IARC, or  
22 EPA The potential carcinogenic fraction of PAHs, calculated based on the EPA (1994)  
23 criteria shows that around 63% of total particulate EPA-PAHs fraction determined in this

1 study is probably carcinogenic to human. During various months the carcinogenic fraction  
2 of PAHs varies from 44% (August) to 70% (November; December). Further estimation  
3 shows that the percentage of carcinogenic fraction of PAHs becomes higher with the  
4 increase in total ambient levels of EPA-PAHs and has maximum values in winter.

5 The World Health Organization (WHO, 2000) suggests that the unit risk of lung  
6 cancer is  $87 \times 10^{-6}$  per ng B[a]P per  $m^3$  for a life time exposure. Considering the upper limit  
7 of the additional lifetime risk should be less than  $1 \times 10^{-4}$  and health based evidence, a non-  
8 mandatory target value of  $1.0 \text{ ng}/m^3$  (yearly) is proposed for B[a]P in fourth daughter  
9 directive of European Union (PAHs position paper, 2001). Compared to this, the annual  
10 average value of B[a]P is somewhat lower, i.e.  $0.6 \text{ ng}/m^3$ , in Menen. Further the monthly  
11 average value exceeds this target value during December, January and February. This  
12 seasonal increase in PAHs levels may raise the concern as the direct effect of PAHs and  
13 other mutagens were considered to be a maximum of five lung cancer cases each year per  
14 one million individuals (Nielsen et al., 1996). Occupational exposures to PAHs are strongly  
15 suspected to increase lung cancer risk (Bruske-Hohlfeld et al., 2000).

### 16 **Temporal pattern of PAHs**

17 Sixteen US EPA criteria PAHs were determined at Menen because they are  
18 suspected to be more harmful than some of the others and exhibit adverse effects that are  
19 representative of the PAHs (ATSDR, 1995). Table 1 gives an overview of the temporal  
20 distribution of these PAHs concentration in aerosol samples during 2003 at Menen. PAHs  
21 have low vapor pressure and hence some PAHs are present at ambient temperature in air,  
22 both as gases and associated with particles. Although the lighter PAHs, such as PA, are  
23 found almost exclusively in gas phase, the heavier PAHs, such as B[a]P, are almost totally  
24 sorbed onto particles (Manahan, 1994). This is also evident from Table 1, which

1 demonstrates that the concentrations of lower molecular weight PAHs (<200) were found  
2 relatively very low in filter samples in comparison to high molecular weight PAHs  
3 fractions at Menen. Further only Nap (0.15 ng/m<sup>3</sup>) and PA (0.19 ng/m<sup>3</sup>) concentration were  
4 found noticeable in lighter molecular weight fraction of PAHs, whereas the high molecular  
5 weight species like, Flut (0.83 ng/m<sup>3</sup>), Chr (0.87 ng/m<sup>3</sup>), B[b]F (0.84 ng/m<sup>3</sup>), B[a]P (0.58  
6 ng/m<sup>3</sup>), B[ghi]P (0.73 ng/m<sup>3</sup>) and Ind (0.77 ng/m<sup>3</sup>), dominate the PAHs fraction of filter  
7 samples. The data also reveals that the daily PAHs concentration were also influenced by  
8 the prevailing wind directions during sampling days and the concentration was relatively  
9 high when the prevailing wind directions were SW at the sampling site (please see  
10 supplementary Table 1a,b,c).

#### 11 **Seasonal variation in PAHs levels**

12 Table 1 shows the monthly average concentration of individual PAHs at Menen,  
13 while Figure 1 shows the monthly average concentration of PAHs. It is evident from Figure  
14 1, that the PAHs concentrations were significantly higher during winter season in  
15 comparison to summer at Menen, the annual average concentration of PAHs being 6.7  
16 ng/m<sup>3</sup>. The monthly average PAHs concentrations were 5-7 times higher in January,  
17 February and December, in comparison to May, June and August. In contrast to Binkova et  
18 al. (2003), Manoli et al. (2004) and Sklorz et al., (2007); the present study shows higher  
19 levels of B[ghi]P during winter and likely suggest towards local/regional emission sources.  
20 However, following the trend of Sklorz et al. (2007); this study also obtained higher levels  
21 of B[a]A, B[b]F, B[k]F, and Ind during winter. Binkova et al. (2003) also reported 4-6 fold  
22 higher levels of B[a]P and Chr during winter than summer and they identified residential  
23 heating as an additional main emission source during winter. Similarly Lee et al. (2005)  
24 also suggested that additional emission of pollutants can be expected during winter from

1 various sources such as domestic heating, power plants etc. Further, the mixing height of  
2 pollutants also reduces with a fall in temperature and restricts the mixing of pollutants in  
3 the atmosphere.

4 The other possible reason of high concentration of PAHs during winter season  
5 seems to be related with the very low temperature during these periods, which made  
6 favorable conditions for the condensation/sorption of these species on suspended particles  
7 in air. However, condensation/sorption mainly influence PAH having a significant  
8 concentration in gas phase, not the PAH with 5 aromatic rings. Normally PAHs with 5 or  
9 more aromatic rings are found almost associated (more than 95%) with aerosol even at  
10 25°C. Interestingly, these PAHs also show some variation between summer and winter and  
11 hence can be used for source apportionment (Sklorz et al., 2007).

## 12 **Source apportionment**

### 13 *Correlations and diagnostic ratio*

14 The correlation of the PAHs data obtained from Menen was evaluated by regression  
15 analysis and their correlation coefficients, which show that Chr, B[b]F, B[k]F, B[a]P,  
16 D[ah]A, B[ghi]P and Ind, have a very strong correlation among them ( $R^2 \geq 0.8$ ;  $p < 0.01$ )  
17 and hence one of these PAHs can be used as an indication of other PAHs. Further this  
18 likely indicates towards a similar emission source of PAHs. There was no strong  
19 correlation found between low molecular weight PAHs and high molecular weight PAHs  
20 species. Previous studies also show that the concentrations of particulate sampled PAHs  
21 with equal or less than 4 aromatic rings are strongly influenced by the ambient temperature  
22 during sampling and mainly found in vapor phase (Yamasaki et al., 1982; Ligocki and  
23 Pankow, 1989).

1           The diversity in PAHs sources could also be characterized from diagnostic ratios.  
2   The concentration of specific PAH compounds, or a group of PAHs, have been used to  
3   identify the emission sources. In recent years many studies have used the diagnostic ratio  
4   and the following conclusions can be drawn from them. Grimmer et al. (1983) reported Ind/  
5   (Ind+B[ghi]P) values of 0.18, 0.37, 0.56 and 0.62, for gasoline, diesel, coal, and wood  
6   burning respectively. However other studies used a ratio between 0.35 and 0.70, towards  
7   diesel emission (Kavouras et al., 2001). A Flu/(Flu+Pyr) ratio higher than >0.5 indicates  
8   towards diesel emission, whereas a lower ratio (<0.5) indicates towards gasoline emission  
9   (Rogge et al., 1993; Mandalakis et al., 2002, Fang et al., 2004). The present study shows  
10   very low values of Flu/(Flu+Pyr) ratios and hence confirms the presence of gasoline  
11   emission in the region. Khalili et al. (1995) and Guo et al. (2003) proposed a value of  
12   B[a]P/(B[a]P+Chr) around 0.49 for diesel emission, and 0.73 for gasoline emission. Higher  
13   ratio of B[b]F/B[k]F and B[a]P/B[ghi]P indicate towards diesel emission and traffic  
14   emission (Pandey et al., 1999; Park et al., 2002); whereas a lower value (< 0.4) of  
15   Ind/BghiP has been reported for gasoline emission while the ratio for diesel engines  
16   approaches 1 (Caricchia et al., 1999). [Following to the initial studies of Prah \(1984\) and](#)  
17   [Takada et al. \(1996\); Gogou et al., \(1996\) suggested that](#) the ratio of the sum of 9 major  
18   nonalkylated            compounds            or            ‘combustion            PAHs’  
19   (Flu+Pyr+B[a]A+Chr+B[b]F+B[k]F+B[a]P+Ind+B[ghi]P) indicated as CPAHs, to the total  
20   concentration of EPA-PAHs (CPAHs/TPAHs) can be used to identify the combustion  
21   sources. However, in the above studies additional PAHs (e.g. retene, methylated  
22   phenanthrenes etc.) including most of the EPA- PAHs were analyzed. A CPAHs/TPAHs  
23   ratio towards unity has been suggested for PAHs produced by combustion activities  
24   (Manoli et al., 2004; Mantis et al., 2005; Ravindra et al., 2008).

1 Comparison of our data to the various diagnostic ratios (Table 2) shows that the  
2 emission from the diesel engines and combustion sources dominate the particulate PAHs  
3 emission in Menen. This is also expected as 60% of the traffic in Belgium is powered by  
4 diesel (MIRA, 2006). However the results also indicate that the emission from gasoline  
5 engines and stationary sources (industrial/coal/wood) also influences the PAHs levels.  
6 Further, it has to be noted that the CPAHs/TPAHs ratio varies significantly with the  
7 variation in monthly average concentration of PAHs and hence it can be concluded that  
8 increases in PAHs levels during winter seasons are likely to be associated with the  
9 combustion activities as it approaches towards unity.

10 The diagnostic ratios should be used with caution because it is often difficult to  
11 discriminate between some sources (Ravindra et al., 2008). The reactivity of some PAH  
12 species with other atmospheric species, such as ozone and/or oxides of nitrogen can change  
13 the diagnostic ratio (Robinson et al., 2006a,b). Liu et al. (2006) also reported that the  
14 concentration of 5- to 7- ring PAHs were underestimated in non-denuded samples, which  
15 are predominant in the aerosol phase. Further, Tsapakis and Stephanou, (2003) also  
16 reported that the degradation of PAHs may occur during the sampling process and can also  
17 modify their atmospheric levels. The difference in chemical reactivity, volatility and  
18 solubility of PAH species may introduce bias but to minimize this error, the diagnostic ratio  
19 with similar physico-chemical properties of PAHs should be used (Goriaux et al., 2006,  
20 Ravindra 2008).

### 21 *Principal component analysis*

22 In order to improve the accuracy of the emission source identification, the method  
23 of PCA was applied. The principle of PCA is to transform the original set of variables into  
24 a smaller set of linear combinations that accounts for most of the variance of the original

1 set. The primary function of this analysis is the reduction of the number of variables while  
2 retaining the original information as much as possible. Thus variables with similar  
3 characteristics can be grouped into factors. In the present study the source grouping were  
4 determined using PCA with varimax rotation and retention of principal components having  
5 an eigenvalue  $>1$  of the complete data set of PAHs concentrations. Factor analysis in this  
6 study was carried out using the statistical analysis SPSS 12.0 software package (Norusis,  
7 and SPSS Inc, 2002).

8 Table 3 provides the results of factor analysis of total EPA-PAHs concentrations at  
9 Menen. The PCA result shows that three factors explain the main part of the data variance.  
10 The factor loading correlates the variables and represents the most important information  
11 on which the interpretation of the factors is based. First factor is generally more correlated  
12 with the variables than the second factors because these factors are extracted successively,  
13 each one accounting for as much of remaining variables as possible. Factor 1 has a very  
14 high factor loading of B[a]A, B[a]P, B[b]F, B[ghi]P and Ind; which are identified as a  
15 marker of gasoline emissions (Duval and Friedlander, 1981; Khalili et al., 1995; Park et al  
16 al., 2002; Guo et al., 2003). A relatively high factor loading for Flut, PA, Ant and Pyr is an  
17 indication of diesel emission (Yang et al., 1998; Caricchia et al., 1999; Kulkarini and  
18 Venkataraman, 2000; Ho et al., 2002; Omar et al., 2002; Fang et al., 2004). Hence, it can be  
19 suggested that vehicular emissions form a major fraction of PAHs at Menen. The high  
20 factor loading of Chr and B[b]F indicates that stationary sources may also affect the PAHs  
21 levels at Menen (Yang et al., 1998; Kulkarini and Venkataraman, 2000; Fang et al., 2004).

22 For factor 2, AcPy, PA Ant and Pyr had a loading factor around 0.5 or more,  
23 indicating them to come from other sources than identified in factor 1. These PAHs have  
24 been identified in emission from incinerator (Smith and Harrison, 1998; Ravindra et al.,

1 2006), coal combustion, coke production and wood combustion (Duval and Friedlander,  
2 1981; Khalili et al., 1995, Lee et al., 2005). Van Lieshout et al. (2001) reported some open  
3 fires and incinerator activities in the vicinity of Menen. The closest coke-ovens or steel  
4 industry are situated in Sidmar (Zelzate) around 70 km in north of Menen and may not  
5 influence the PAHs levels. The third factor is comprised of the lighter PAHs (Nap, AcPy  
6 and Acp), which are prevalent in the vapor phase. Components related to the third factor  
7 are not attributed to 'identified sources'. Based on the PCA variance distribution, the data  
8 shows that vehicular sources contribute around 65% of total EPA-PAHs levels at Menen;  
9 whereas it account around 13% from combustion (e.g. incinerator, wood burning).

10 However, the source type identified in this study mainly results from PAHs source  
11 fingerprints in the literature, not from the local PAHs source profile. Up-to-date profiles of  
12 emissions from local source categories should be collected to identify more reliable PAHs  
13 source categories and to generate their quantitative source contribution.

#### 14 **Impact of regional-global activities on PAHs levels**

15 Long-range transport of various organic pollutants was demonstrated in the 1980s  
16 by Oehme and Mano (1984) but they mainly focus on vapor phase organic pollutants  
17 including only fluoranthene. After this, only few efforts have been made to study the long  
18 range transport of PAHs by measurement and use of various models. Some of the example  
19 studies includes Halsall et al., 1997, 2001; Lee et al., 1999; Prevedouros et al., 2004a,b;  
20 Jaward et al., 2004; Fenner et al., 2005; Park et al., 2006 etc. However, most of them were  
21 specific for a day or episode. In the present study the approach has been elaborated over a  
22 year period to study the influence of regional and global activities and emission sources on  
23 16 US EPA priority listed PAHs levels by backward air mass trajectories. The HYSPLIT-

1 v4 model from NOAA Air Resources Laboratory (ARL) was used for computing  
2 trajectories (Draxler and Hess, 1997). The trajectories were categorized based on their  
3 origin and where they spend most of their 4 days traveled routes.

4 In this study, 4-day trajectory were computed every 6 h at an arrival point in Menen  
5 ( $50^{\circ} 47' N, 3^{\circ} 6' W$ ) during the year 2003. The choice of a 4-day trajectory is a compromise  
6 between the several-day atmospheric residence time of suspended particles and especially  
7 of fine particles and the declining accuracy in calculation of the back trajectory (due to  
8 model assumptions and spatial and temporal resolution of the meteorological data). Any  
9 error associated with a single trajectory is reduced when daily trajectories are grouped  
10 together according to the common path the air masses followed (Stohl, 1998). Therefore,  
11 the 63 daily trajectories were assigned to ten categories: Benelux (BE), Atlantic (AT),  
12 Arctic (AR), United Kingdom (UK), Central Europe (CE), Western Europe (WE),  
13 Scandinavia (SC), Maritime (MT), Eastern Europe (EE) and Unclassified (UC); using the  
14 criteria as mentioned in Table 4. The representative day specific examples of these  
15 categories are shown in Figure 2, which shows that the levels of PAHs likely increase when  
16 there is an air mass movement from Central and Western Europe and fall when the  
17 trajectories spend most of their 4 days in the Arctic region or over the Atlantic Ocean  
18 (Table 4).

19 Jaward et al. (2004) reported that B[a]P inventory shows the highest loading in  
20 Eastern Europe (e.g. Poland, parts of Russia, and the Czech Republic), and the more  
21 populated and industrialized areas of western Europe (e.g. parts of United Kingdom and  
22 The Netherlands). These hotspots of PAH emissions are also evidenced from Figure 3,  
23 where predicted mean annual B[a]P concentrations are shown over Europe (EMEP, 2007).  
24 Furthermore, Figure 4 shows the predicted or modeled levels of PAHs in the air of Belgium

1 (EMEP, 2007). However, the modeled and measured levels varied significantly but the  
2 distribution pattern of PAHs seem in agreement with the present study (Table 4) and a  
3 study by Ravindra et al. (2006a). A study of Ravindra et al. (2006a) and an inventory  
4 studied done by Flemish Institute for Technological Research ([www.vito.be](http://www.vito.be)) under MIRA  
5 project (2006) found that transport and household emission were the major source of PAHs  
6 in Belgium during 2005 [transport (83 ton); household (74 ton); industries (15 ton); other (2  
7 ton)]. Further this report shows a decreasing emission trends from 1990 to 2005. However,  
8 a recent inventory by Breivik et al. (2006) suggest “residential heating plants” as a key  
9 source of PAHs in Europe and in contrary to MIRA report an increasing trend of PAHs for  
10 Belgium.

11 Only few countries in Europe have proposed a recommended (but non mandatory)  
12 value of PAHs using B[a]P as a surrogate for all PAHs (Ravindra et al., 2008). These  
13 proposed value ranged from 0.25 to 2 ng/m<sup>3</sup> on annual average basis (PAHs position paper,  
14 2001). These countries are Belgium (1.0 ng/m<sup>3</sup>), Croatia (2.0 ng/m<sup>3</sup>), France (0.7 ng/m<sup>3</sup>),  
15 Germany (1.3 ng/m<sup>3</sup>), Italy (1.0 ng/m<sup>3</sup>), Netherlands (1.0 ng/m<sup>3</sup>) and UK (0.25 ng/m<sup>3</sup>). As  
16 shown in this study, both regional and global activities influence the levels of PAHs and  
17 there is increasing evidence of their carcinogenic, mutagenic and or teratogenic nature  
18 (Ravindra et al., 2001; Lewtas et al., 2007; Sram et al., 2007a,b). Hence it is suggested to  
19 have a uniform policy (e.g. similar air quality standard of PAHs) for all European nations to  
20 curb PAHs pollution.

## 21 **Conclusions**

22 Particulate samples, collected during 2003, were extracted very fast by PLE and  
23 subsequently analyzed by HPLC for 16 US EPA criteria PAHs. The analytical results show

1 that the high molecular weight PAHs such as Flut, Chr, B[b]F, B[a]P, B[ghi]P and Ind,  
2 dominate the total fraction, whereas low molecular weight PAHs were found in relatively  
3 very low concentration and only Nap and PA show a significant presence. Further, the  
4 reported daily PAHs concentrations were relatively high when the prevailing wind direction  
5 were SW at Menen Seasonal and meteorological parameter also play a role to limit the  
6 PAHs concentration and generally a higher concentration of PAHs in the winter season was  
7 found. The higher concentration in winter mainly indicates its relation with increased  
8 emission from domestic heating and power plants with low temperature (i.e. different  
9 emission sources in winter and summer). Furthermore, enhanced sorption to particles at  
10 lower temperature (as a result of reduced vapor pressure) and reduced vertical dispersion  
11 due to inversion may also influence the PAHs levels. However the concentration of  
12 indicative PAHs i.e. B[a]P was found lower than its proposed maximum value ( $1 \text{ ng/m}^3$ ) at  
13 Menen, but the health risk associated with them can not be ignored, especially during  
14 winter.

15 The application of correlation coefficient calculation, diagnostics ratio and PCA  
16 allowed to find the possible sources of PAHs, which indicate towards vehicular emission as  
17 major source although other sources like [incinerator](#) and wood burning (specially during  
18 winter) may also exist. The variations in PAHs levels studied with relation to  
19 transboundary movement of air masses show a clear relation with the hotspots of PAH  
20 emissions, which were identified in EMEP studies. However the health risk studies  
21 conducted with relation to PAHs exposure urges to include these pollutants as top priority  
22 for air quality management but till date only few countries have proposed a (non-  
23 mandatory) limit for PAHs.

1

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10

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Table 1: Monthly average concentration (ng/m<sup>3</sup>) of individual PAHs at Menen.

Months	Monthly Average Concentration of Individual PAHs															
	Nap	AcPy	AcP	Flu	PA	Ant	Flut	Pyr	B[a]A	Chr	B[b]F	B[k]F	B[a]P	D[ah]A	B[ghi]P	Ind
January	0.13 ±0.07	0.03 ±0.02	0.04 ±0.03	0.04 ±0.03	0.08 ±0.06	0.01 ±0.01	2.28 ±3.34	0.31 ±0.29	0.81 ±1.29	2.20 ±3.20	1.79 ±2.46	0.80 ±1.10	1.35 ±2.11	0.37 ±0.50	1.49 ±2.23	1.51 ±2.08
February	0.20 ±0.14	0.17 ±0.27	0.09 ±0.03	0.03 ±0.02	0.73 ±0.93	0.10 ±0.10	2.30 ±2.23	1.32 ±1.46	0.97 ±0.72	2.33 ±1.83	1.76 ±1.27	0.81 ±0.59	1.40 ±1.28	0.52 ±0.57	1.77 ±1.44	1.72 ±1.22
March	0.22 ±0.18	0.04 ±0.02	0.07 ±0.03	0.03 ±0.02	0.22 ±0.20	0.04 ±0.03	0.28 ±0.18	0.44 ±0.23	0.48 ±0.25	0.67 ±0.24	0.82 ±0.28	0.36 ±0.14	0.43 ±0.19	0.38 ±0.32	0.92 ±0.40	0.77 ±0.33
April	0.19 ±0.18	0.03 ±0.02	0.03 ±0.02	0.03 ±0.02	0.29 ±0.23	0.05 ±0.06	0.63 ±0.24	0.19 ±0.23	0.22 ±0.26	0.52 ±0.28	0.57 ±0.30	0.24 ±0.13	0.32 ±0.16	0.10 ±0.09	0.44 ±0.32	0.59 ±0.33
May	0.14 ±0.05	0.10 ±0.15	0.09 ±0.07	0.02 ±0.01	0.09 ±0.05	0.03 ±0.02	0.21 ±0.18	0.16 ±0.15	0.30 ±0.17	0.25 ±0.12	0.30 ±0.17	0.14 ±0.08	0.15 ±0.10	0.10 ±0.11	0.28 ±0.21	0.27 ±0.26
June	0.10 ±0.02	0.02 ±0.01	0.10 ±0.07	0.02 ±0.01	0.14 ±0.11	0.05 ±0.04	0.17 ±0.01	0.04 ±0.00	0.03 ±0.00	0.23 ±0.04	0.27 ±0.06	0.11 ±0.04	0.12 ±0.01	0.08 ±0.01	0.16 ±0.06	0.21 ±0.08
August	0.08 ±0.04	0.02 ±0.01	0.11 ±0.06	0.02 ±0.01	0.07 ±0.09	0.01 ±0.01	0.26 ±0.27	0.07 ±0.03	0.02 ±0.02	0.11 ±0.05	0.15 ±0.12	0.06 ±0.04	0.06 ±0.04	0.06 ±0.03	0.05 ±0.03	0.08 ±0.06
September	0.20 ±0.14	0.03 ±0.03	0.07 ±0.04	0.03 ±0.01	0.18 ±0.16	0.06 ±0.05	0.29 ±0.18	0.15 ±0.07	0.28 ±0.15	0.32 ±0.15	0.38 ±0.18	0.18 ±0.08	0.20 ±0.12	0.17 ±0.16	0.37 ±0.18	0.36 ±0.21
October	0.09 ±0.04	0.12 ±0.11	0.10 ±0.05	0.03 ±0.02	0.14 ±0.14	0.02 ±0.01	0.82 ±0.52	0.24 ±0.18	0.27 ±0.10	0.63 ±0.33	0.70 ±0.26	0.33 ±0.12	0.53 ±0.22	0.29 ±0.16	0.65 ±0.27	0.70 ±0.31
November	0.10 ±0.01	0.03 ±0.03	0.05 ±0.04	0.02 ±0.01	0.06 ±0.04	0.05 ±0.01	0.66 ±0.29	0.17 ±0.01	0.19 ±0.01	0.86 ±0.06	1.05 ±0.05	0.46 ±0.02	0.62 ±0.08	0.30 ±0.07	0.78 ±0.11	1.06 ±0.02
December	0.19 ±0.22	0.05 ±0.07	0.07 ±0.04	0.02 ±0.02	0.06 ±0.06	0.04 ±0.06	1.27 ±2.05	0.33 ±0.53	0.62 ±1.16	1.45 ±2.31	1.40 ±1.98	0.64 ±0.92	1.25 ±2.15	0.55 ±1.03	1.17 ±2.05	1.27 ±1.91
<b>Average</b>	<b>0.17</b> ±0.05	<b>0.06</b> ±0.05	<b>0.07</b> ±0.03	<b>0.03</b> ±0.01	<b>0.20</b> ±0.19	<b>0.04</b> ±0.02	<b>0.84</b> ±0.79	<b>0.34</b> ±0.35	<b>0.42</b> ±0.31	<b>0.89</b> ±0.78	<b>0.85</b> ±0.59	<b>0.38</b> ±0.27	<b>0.60</b> ±0.51	<b>0.28</b> ±0.18	<b>0.77</b> ±0.56	<b>0.79</b> ±0.55

[For daily variations, prevailing WD and other details see supplementary Table S-2a,b,c]

Table 2: Diagnostic ratio of various PAHs at Menen

Months	Diagnostic ratios							
	Ind/(Ind+B[ghi]P)	Flu/(Flu+Pyr)	B[a]P/(B[a]P+Chr)	PA/(PA+Ant)	B[b]F/B[k]F	B[a]P/B[ghi]P	Ind/B[ghi]P	CPAHs/TPAHs
January	0.47 ±0.15	0.13 ±0.05	0.35 ±0.04	0.82 ±0.24	2.26 ±0.09	0.81 ±0.20	1.00 ±0.45	0.88 ±0.06
February	0.49 ±0.05	0.06 ±0.07	0.36 ±0.04	0.86 ±0.06	2.19 ±0.09	0.75 ±0.17	0.99 ±0.20	0.83 ±0.05
March	0.46 ±0.08	0.07 ±0.07	0.39 ±0.05	0.79 ±0.11	2.39 ±0.50	0.48 ±0.13	0.89 ±0.33	0.78 ±0.06
April	0.59 ±0.08	0.19 ±0.12	0.39 ±0.04	0.87 ±0.06	2.49 ±0.25	0.82 ±0.35	1.52 ±0.53	0.81 ±0.06
May	0.40 ±0.17	0.15 ±0.06	0.36 ±0.07	0.76 ±0.14	2.20 ±0.11	0.64 ±0.47	0.77 ±0.41	0.72 ±0.07
June	0.56 ±0.13	0.32 ±0.11	0.35 ±0.01	0.74 ±0.01	2.55 ±0.18	0.77 ±0.13	1.40 ±0.72	0.72 ±0.01
August	0.59 ±0.15	0.22 ±0.05	0.35 ±0.05	0.92 ±0.08	2.44 ±0.43	1.35 ±0.69	1.66 ±0.74	0.64 ±0.13
September	0.47 ±0.08	0.18 ±0.08	0.37 ±0.04	0.74 ±0.09	2.19 ±0.11	0.52 ±0.12	0.93 ±0.24	0.73 ±0.05
October	0.51 ±0.02	0.12 ±0.08	0.47 ±0.03	0.84 ±0.10	2.13 ±0.03	0.82 ±0.14	1.06 ±0.10	0.82 ±0.06
November	0.58 ±0.02	0.08 ±0.02	0.42 ±0.03	0.53 ±0.09	2.30 ±0.00	0.80 ±0.15	1.37 ±0.11	0.88 ±0.01
December	0.55 ±0.09	0.11 ±0.06	0.43 ±0.07	0.61 ±0.16	2.37 ±0.28	1.15 ±0.58	1.35 ±0.60	0.84 ±0.06
<b>Average</b>	<b>0.52 ±0.06</b>	<b>0.15 ±0.08</b>	<b>0.38 ±0.04</b>	<b>0.77 ±0.12</b>	<b>2.32 ±0.14</b>	<b>0.81 ±0.25</b>	<b>1.18 ±0.29</b>	<b>0.79 ±0.08</b>
Source	Diesel/coal /wood	Gasoline	Diesel	-	Diesel	Traffic	Diesel	Combustion

Table 3: Factor analysis of total EPA-PAHs data of Menen.

<b>PAH</b>	<b>Factor 1</b>	<b>Factor 2</b>	<b>Factor 3</b>
Nap	0.24	0.26	-0.62
Acpy	0.46	0.69	0.37
Acp	-0.04	0.41	0.68
Flu	0.57	0.08	-0.28
PA	0.53	0.75	-0.13
Ant	0.61	0.52	-0.41
Flut	0.94	-0.14	0.11
Pyr	0.78	0.46	0.06
B[a]A	0.97	-0.16	0.02
Chr	0.97	-0.18	0.09
B[b]F	0.97	-0.22	0.06
B[k]F	0.97	-0.21	0.05
B[a]P	0.97	-0.20	0.07
D[ah]A	0.89	-0.09	-0.02
B[ghi]P	0.98	-0.15	0.05
Ind	0.97	-0.19	0.02
<b>Eigen value</b>	10.13	2.05	1.28
<b>Variance (%)</b>	63.3	12.8	8.01
<b>Cumulative (%)</b>	63.3	76.1	84.1
<b>Origin</b>	Vehicular	Combustion	?

Table 4: Criteria used to classify air mass back trajectory atmospheric transport pattern and corresponding average PAHs levels (ng/m<sup>3</sup>).

<b>Category</b>	<b>Description of trajectory categories</b>	<b>n</b>	<b>Average PAHs Levels</b>
BE	Trajectory stagnating over, or spending most of 4-day period in the vicinity of the Belgium and Netherlands.	8	4.2 ±2.6
AT	Trajectory spending most of 4-day period over the Atlantic ocean.	8	3.7 ±3.7
AR	Trajectory spending most of 4-day period in the Arctic region, including those originating in or near Greenland.	7	2.8 ±1.7
UK	Trajectories originating from or spending most of 4-days period crossing the United Kingdom.	3	3.6 ±1.5
CE	The trajectory originating from and spending most of the time over Central Europe.	4	17.5 ±15.5
WE	Trajectory originating from or spending most of 4-day period crossing Western Europe.	20	9.2 ±12.6
SC	Trajectory originating from or spending most of 4-day period crossing Scandinavia or Northern Baltic areas.	3	6.8 ±2.4
MT	Trajectory spending most of 4-day period crossing maritime regions close to the Belgium.	5	3.7 ±3.2
EE	Trajectory originating from or spending most of the 4-day period crossing Eastern Europe.	2	4.2 ±0.3
UC	Trajectory unable to be unambiguously classified into any one trajectory category.	3	6.3 ±5.2