

Gas–particle concentration and characterization of sources of PAHs in the atmosphere of a suburban area in Athens, Greece

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Received 10 March 2006; received in revised form 14 June 2006; accepted 15 June 2006

Available online 18 June 2006

Abstract

Atmospheric polycyclic aromatic hydrocarbons (PAH) were determined in two places in a suburban area of Athens greater area (AGA) during June and November 2003. Fourteen PAHs were quantified in the collected samples. The total concentration in the gas phase ranged between 6.89 and 124 ng m⁻³, while in the particulate phase between 0.44 and 13.2 ng m⁻³. Maximum concentrations of the total PAHs (gas and particulate phase) were observed during the cold period with an average of 40.7 ng m⁻³. PAHs were correlated with NO, NO₂ and O₃, wind speed, wind direction and temperature. Positive correlation was observed between PAHs and NO, NO₂, while negative correlation was detected between PAHs and O₃. The most abundant members were phenanthrene, anthracene, fluorene, fluoranthene and pyrene. Potential sources of PAHs in aerosols were investigated using molecular diagnostic ratios, which reflect sources such as diesel and gasoline engines, although other sources such as coal combustion and liquefied petroleum gas also contributed.

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Keywords: Ozone; Nitrogen oxides; Meteorology; Emissions; Ratios

1. Introduction

Atmospheric particulate matter is known to contain a number of organic species, including alkanes, alkenes, carboxylic acids, carbonyl compounds and aromatic compounds [1] such as polycyclic aromatic hydrocarbons or PAHs. PAHs have been recognized as a group of potentially hazardous chemicals and despite some natural sources (e.g. forest and prairie fires, volcanic eruptions), their occurrence is largely the result of human activity [2,3] and have deserved particular interest due to their global emissions [4].

PAHs in urban and industrial atmospheres are almost entirely anthropogenic in origin and are major products of the incomplete combustion or pyrolysis of all types of organic material containing carbon and hydrogen [5,6]. Organic compounds of

biogenic and anthropogenic origin often represent a large fraction up to 40% of aerosols with concentrations ranging between a few pg m⁻³ and hundreds of ng m⁻³ [7]. Major anthropogenic sources of PAHs include heating (coal, oil and wood), refuse burning, coke production, industrial processes and motor vehicles [8]. Concern about the occurrence of these compounds in the environment is well justified since they are ubiquitous in ambient air and many of them have proven carcinogenic and/or mutagenic properties [2]. The greater fraction of airborne organic particulate matter is present in the respirable size range [9]. In fact, epidemiological and experimental data have demonstrated the association between human respiratory problems and the ambient concentration of fine and ultrafine particles in urban air [10].

PAHs occur in both vapour and particulate phase in the atmosphere; both types can come into contact with living beings either externally (through the skin) or internally (through the lungs or ingestion) and this makes them hazardous or even toxic species [4,11]. The partitioning of a given compound between the par-

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ticulate and the gas-phase depends on the ambient temperature, the nature (i.e. origin, properties) of the aerosol, the interactions between the compound and the aerosol and the overall behaviour of the compound in the environment [12–14]. For example, low molecular weight PAHs tend to be more concentrated in the vapour phase while the higher molecular weight ones with four or more aromatic rings are often associated with particulates [6,15].

The objective of this work was to study the correlations between PAHs and both meteorological parameters and gaseous pollutants considering their gas/particle partitioning and to determine their emission sources using the ratios of individual PAHs. To do so, we perform environmental monitoring of PAH in urban areas and investigate public exposures to PAH and their associated health risks.

2. Experimental

2.1. Sampling area

Fifty-five air samples were collected during a warm and a cold period of 2003 at two suburban areas of the eastern part of AGA (Koropi and Spata). This area was chosen because it is located near the new Athens International Airport (AIA) as well as located near the Attiki Odos highway leading to the airport and connecting the Athens basin with the Mesogaia plain. Moreover, it is a rapidly developing suburban area with a number of industries.

The first station (S1) was located on the outer area of the Health center of Koropi, 5 km Southwesterly from the AIA at Mesogaia plain, while the second one (S2) on the bypass road

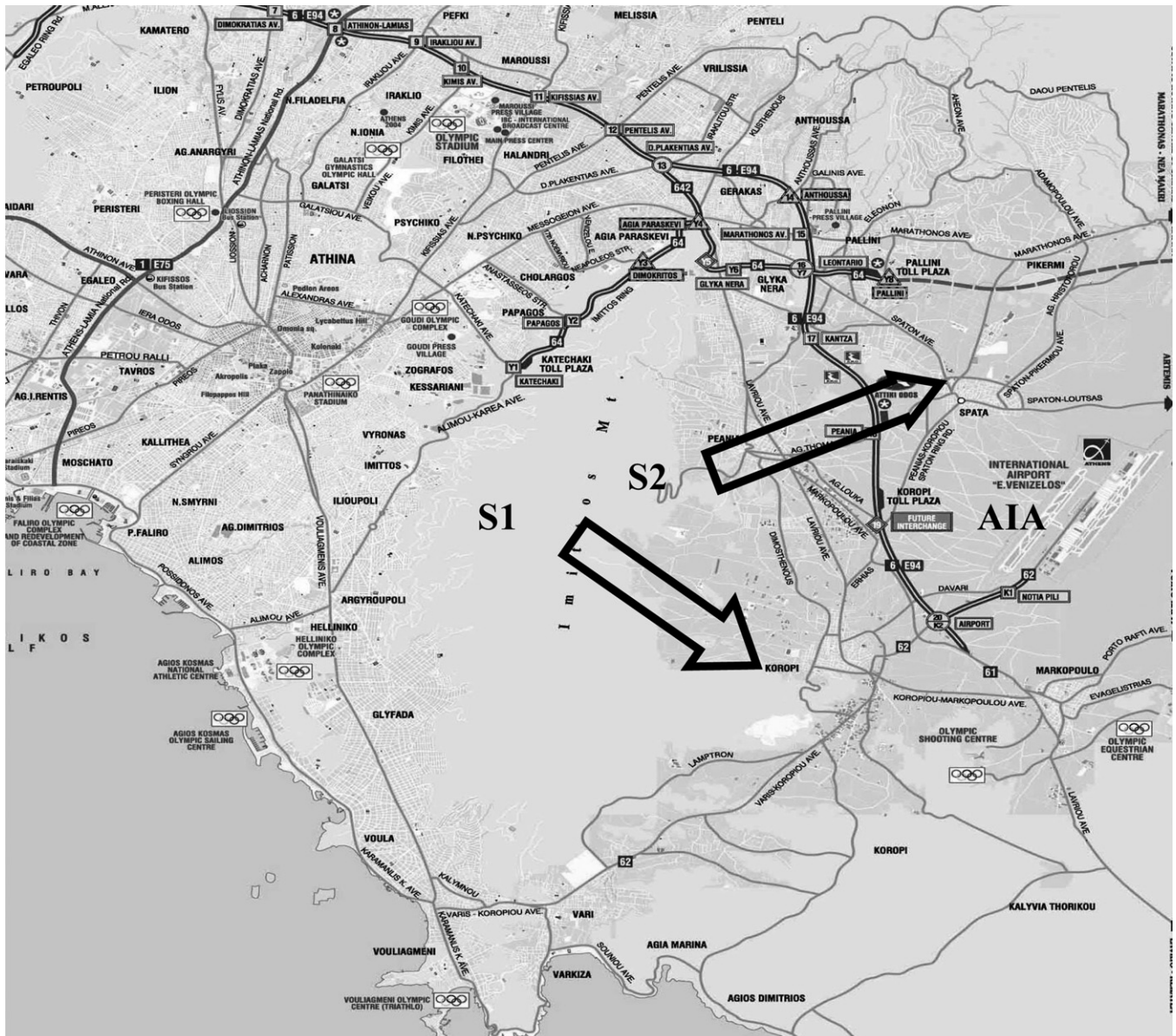


Fig. 1. AGA sampling sites.

of the Health centre of Spata, 3 km Northwesterly from AIA (Fig. 1).

2.2. Sample collection and implementation

The first sampling campaign was conducted between the 4th and 18th of June (warm period) at both sites. The second sampling campaign was conducted between the 11th of November and 8th of December for S1 and from the 11th to the 20th of November 2003 (cold period) for S2. All air samples were collected using a high-volume sampler TE-PUFF polyurethane foam with the opportunity of collecting particles and gas-phase compounds at the same time. The air was drawn through a 102-mm glass-fibre filter where the particles were collected and then through a polyurethane foam (PUF) plug to collect compounds present in the vapour phase. The duration of each sampling was approximately 24 h (from 8.30 until 8.00 of the next day) and the sample volume was approximately 300 m³. The nearby stations of the Environmental Department of Athens International Airport “Eleftherios Venizelos” provided meteorological data for both sampling areas.

2.3. PAH analysis

Before the sampling filters were loosely wrapped with aluminum foil and baked in a muffle furnace at 450 °C overnight. They were then allowed to cool to room temperature in a desiccator. PUF cartridges were cleaned by Soxhlet extraction using cyclohexane for 24 h. After the extraction the cartridges were also wrapped loosely with aluminum foil and dried in a desiccator under vacuum. The cleaned filters and PUF cartridges were transported in small air proof container, in order to avoid external exposure to ambient air before measurement. After sampling they were brought back to the laboratory and kept at constant temperature and humidity, in order to be conditioned. Before and after sampling the filters were weighted to obtain the total suspended particle concentrations (TSP).

PUF cartridges and filters were spiked with a solution containing a mixture of 4-perdeuterated PAHs; d₁₀-phenanthrene, d₁₀-pyrene, d₁₂-perylene and d₁₂-chrysene. Filters were cut into small pieces and extracted ultrasonically twice, each time with dichloromethane. The extracts were combined and evaporated in a rotary evaporator to near dryness and re-dissolved in 1 ml of hexane. PUF cartridges were extracted in a Soxhlet apparatus for 24 h with *n*-hexane and the extract was concentrated to 1 ml by the rotary evaporator. Both sample extracts were loaded onto

a 2 g activated silica gel (100–200 mesh) and eluted with 10 ml *n*-hexane and 10 ml *n*-hexane/ethyl acetate 90:10. PAHs were collected in the second fraction and each fraction was concentrated under a gentle steam of nitrogen.

GC–MS analysis was carried out on a Hewlett-Packard mass-detector (5972A) operating in SIM mode. The mass spectrometer was directly coupled with a GC Hewlett-Packard 6890 equipped with a 30 m × 25 mm, 0.25 μm film thickness, CP sil-8 MS fused silica column. In total 14 individual PAHs were quantified. The GC–MS was calibrated with a standard solution containing all of the 14 PAH compounds and the deuterated internal standards. All individual PAH and deuterated PAH compounds were purchased from Chemservice and both internal standard and calibration solutions were prepared in isoctane and contained 10 μg/ml of each compound. The quantification was based on the internal standards added in the beginning of the analytical procedure. The recoveries of the perdeuterated PAHs ranged between 81% and 91%. Blank filters and PUF cartridges transported in the field and treated in the lab as real samples were routinely analyzed as control. Blank levels of individual PAHs were not detectable.

3. Results and discussion

3.1. Variation of meteorological parameters and pollutants in the study areas

Table 1 presents the variation of each meteorological parameter and pollutant in the study areas for both seasons. As seen in Table 1 the concentrations of NO and NO₂ were higher in the cold period, while O₃ had the opposite behaviour which is expected since it is a photochemical pollutant. All pollutants concentrations were significantly lower in Koropi. This is probably due to the fact that Spata is located much closer to the road than the Koropi station.

3.2. PAHs concentrations and emission sources

The total (gas + particulate) concentrations varied between 15.6 and 127.6 ng m⁻³ in S1 and between 7.44 and 109 ng m⁻³ in S2 (see Table 2). The total average gaseous and particulate PAHs concentration was 23.71 and 3.21 in S1 and 26.4 and 3.08 ng m⁻³ in S2, respectively. The most abundant PAH in all samples was phenanthrene, while the lower concentrations were measured for PAHs with five or more aromatic rings (i.e. benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-

Table 1
Variation meteorological parameters and pollutants

	Temperature (°C)	Wind speed (m/s)	NO (μg/m ³)	NO ₂ (μg/m ³)	O ₃ (μg/m ³)
Cold period					
Koropi	8.04–17.7	0.03–1.25	1.72–15.7	10.2–38.9	18.4–56.3
Spata	9.32–16.8	0.86–2.78	2.09–34.6	9.56–47.8	22.5–68.8
Warm period					
Koropi	23.9–29.6	0.60–2.69	1.48–2.45	6.96–17.2	88.5–126
Spata	24.3–29.4	1.80–4.06	2.46–8.27	11.1–36.4	117–153

Table 2
Average total (gas + particulate) concentration in ng m^{-3} of the identified PAHs

PAH compounds	Gas S1	Gas S2	Particulate S1	Particulate S2	Total S1	Total S2
Fluorene, FL	2.55 (0.49–11.4)	2.67 (0.33–9.41)	0.02 (0.04–0.09)	0.02 (0.00–0.08)	2.59 (0.50–11.5)	2.69 (0.33–9.49)
Phenanthrene, PHE	13.1 (4.12–90.0)	15.6 (3.95–71.2)	0.12 (0.03–0.83)	0.13 (0.03–0.62)	13.4 (4.16–90.8)	15.7 (3.98–71.9)
Anthracene, ANTH	3.14 (0.58–12.1)	3.17 (0.47–10.7)	0.02 (0.00–0.09)	0.02 (0.00–0.08)	3.18 (0.58–12.2)	3.19 (0.47–10.8)
Fluoranthene, FLUO	2.33 (0.82–6.68)	2.41 (0.78–6.75)	0.17 (0.04–0.51)	0.18 (0.04–0.57)	2.52 (0.86–7.12)	2.59 (0.83–7.33)
Pyrene, PY	2.07 (0.83–6.08)	2.20 (0.70–6.69)	0.17 (0.04–0.53)	0.19 (0.04–0.80)	2.25 (0.87–6.59)	2.40 (0.74–7.48)
Benzo(a)-anthracene, B(a)ANTH	0.16 (0.01–0.82)	0.14 (0.01–0.64)	0.23 (0.01–1.74)	0.22 (0.01–1.29)	0.40 (0.03–2.55)	0.36 (0.02–1.91)
Chrysene, CHR	0.33 (0.05–1.28)	0.26 (0.04–1.07)	0.46 (0.04–2.81)	0.34 (0.04–1.42)	0.80 (0.08–4.09)	0.60 (0.08–2.49)
Benzo(b)-fluoranthene, B(b)FLUO	0.01 (0.00–0.04)	0.01 (0.01–0.03)	0.71 (0.06–2.44)	0.63 (0.05–2.67)	0.73 (0.06–2.46)	0.64 (0.06–2.69)
Benzo(e)-pyrene, B(e)P	0.03 (0.00–0.02)	0.00 (0.00–0.01)	0.35 (0.04–1.26)	0.30 (0.05–1.20)	0.36 (0.04–1.27)	0.30 (0.05–1.21)
Benzo(a)-pyrene, B(a)P	<0.01	0.00 (0.00–0.01)	0.21 (0.02–1.36)	0.25 (0.02–1.28)	0.22(0.02–1.36)	0.25 (0.02–1.29)
Perylene, PER	<0.01	<0.001	0.05 (0.00–0.14)	0.05 (0.00–0.28)	0.05 (0.00–0.14)	0.05 (0.00–0.28)
Indeno[1,2,3-cd]pyrene, IP	<0.01	<0.001	0.32 (0.03–1.05)	0.32 (0.03–1.30)	0.33 (0.03–1.05)	0.32 (0.03–1.30)
Dibenzo(a,h)-anthracene, DbA	<0.01	<0.001	0.07 (0.00–0.20)	0.04 (0.01–0.21)	0.06 (0.00–0.20)	0.04 (0.01–0.21)
Benzo(ghi)-perylene, BgP	<0.01	<0.001	0.34 (0.44–13.2)	0.38 (0.08–1.53)	0.34 (0.05–1.03)	0.38 (0.08–1.53)
Total	23.7 (7.46–124)	26.4 (6.89–104)	3.21 (0.44–13.2)	3.08 (0.51–12.7)	27.2 (7.90–128)	29.5 (7.44–109)

cd)pyrene, benzo(b)fluoranthene, dibenzo(a,h)anthracene, benzo(ghi)perylene). Measured values of phenanthrene were often about two orders of magnitude higher than benzo(a)pyrene and three orders of magnitude higher than the perylene levels [3]. PAH concentrations have been measured in many different cities throughout the world. The sum of seven PAHs (fluorene, phenanthrene, fluoranthene, pyrene, chrysene, benzo(a)pyrene, indeno{1,2,3-cd]pyrene) was reported approximately 40 ng m^{-3} in the urban center of Heraklion, Greece [16], 15 ng m^{-3} in the suburbs of Athens [17] and 389 ng m^{-3} in Chicago [18]. In this study we found that the sum of these 7PAHs was 22.1 ng m^{-3} in S1 and 24.6 ng m^{-3} in S2. Nevertheless, a direct comparison of PAHs between various sites should be done with caution because PAHs concentration is affected by the location of the sampling site as well as by the sampling methodology.

Various molecular diagnostic ratios of PAH concentrations have been used for qualitative and quantitative characterization of sources in environmental samples [16,20–22]. Table 3 presents the diagnostic concentration ratios of isomeric PAHs, which were used to investigate their origin. The mean value of the ratio of fluoranthene to fluoranthene plus pyrene (Fluo/(Fluo + Py)) was found about 0.53, which is similar to vehicular emissions and especially for catalytic automobiles (0.44 was calculated by Rogge et al. [19]).

The ratio of benzo(a)anthracene to benzo(a)anthracene plus chrysene (B[a]A/(B[a]A + Chr)) was 0.49 for gasoline emis-

sions and 0.68 for diesel engines according to Khalili et al. [5], while Gogou et al. [20] mentioned the value of 0.33 for catalytic automobiles as the most important source of PAHs in urban samples. In the present study the corresponding value is 0.30 and 0.29 that is close to the value for catalytic vehicles. The concentration ratio of anthracene to anthracene plus phenanthrene Anth/(Anth + Phe) is used to estimate the presence of PAHs from fossil fuels inputs [21]. Thus, if the above ratio is lower than 0.1 this will be an indication of non-burned fossil fuel inputs, while if the ratio is higher than 0.1, combustion sources may prevail. In the present study the ratio reached 0.21 and 0.17 indicating combustion related emission sources.

The predominance of fossil fuel combustion over other anthropogenic PAH sources (e.g. wood combustion) is implied when the ratio of indeno[1,2,3-cd]pyrene to indeno[1,2,3-cd]pyrene plus benzo(ghi)perylene In/(B[g]P + In) ratio is higher than 0.5 [21]. The corresponding values for cars, diesel vehicles and coal are 0.18, 0.37 and 0.56 respectively [22]. In our case, the In/(B[g]P + In) ratio values were 0.46 for S1 and 0.41 for S2, indicating mixed combustion sources, including vehicular traffic as well as wood burning in the nearby agricultural area.

3.3. Seasonally variations of gas–particle phase of PAHs

The variation of PAHs concentration in gas and particulate phase during the two sampling periods is presented in Figs. 2 and 3. During the cold period PAH's concentrations were much higher than the summertime with the maximum value of 124 ng m^{-3} in S1 and 104 ng m^{-3} in S2 in the gas phase. It has been experimentally found [3,23] that during the winter the concentrations of PAHs are generally higher than the summertime probably due to the increased fossil fuel usage for central heating or/and more intense ground based temperature inversions that increase the pollutants' concentrations because of lower mixing heights [6,24]. Other factors known to contribute to lower summertime PAH concentrations include greater photolytic

Table 3
Diagnostic concentration ratios of selected PAHs

Diagnostic concentration ratio	Arithmetic mean \pm S.D. (S1)	Arithmetic mean \pm S.D. (S2)
Fluo/(Fluo + Py)	0.53 \pm 0.02	0.52 \pm 0.01
BaP/(BaP + Chr)	0.30 \pm 0.06	0.29 \pm 0.07
Anth(Phe + Anth)	0.21 \pm 0.11	0.17 \pm 0.07
In/(In + BgP)	0.46 \pm 0.08	0.41 \pm 0.07

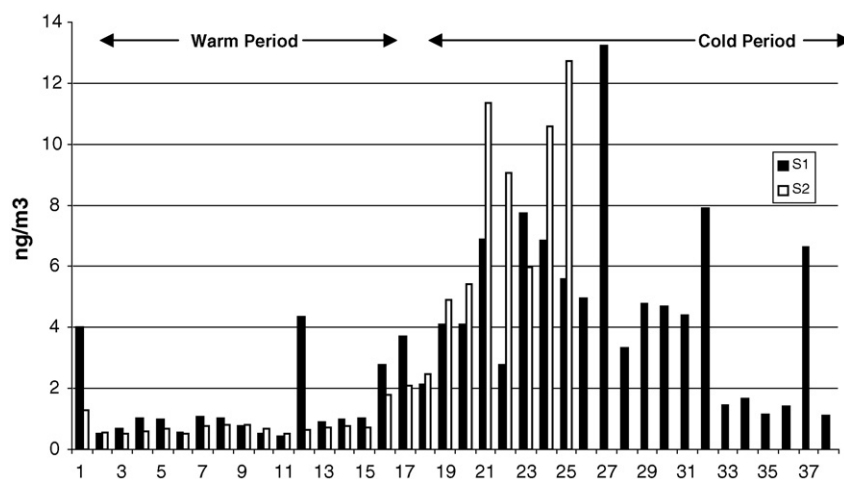


Fig. 2. Total PAH concentration in particulate phase.

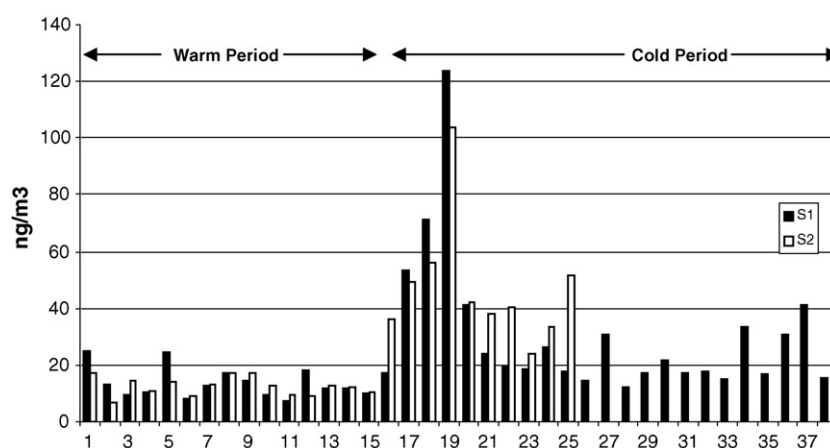


Fig. 3. Total PAH concentration in gas phase.

and thermal decomposition in the warmer summer months [2,6].

3.4. Correlations with meteorological parameters and measured pollutants

Pearson correlation was used in order to provide the correlation coefficients needed for the data analysis, with significant level $p < 0.05$. Table 4 presents the correlations between the total

Table 4
Correlations for PAHs and meteorological parameters and other pollutants

	Particle phase		Gas phase	
	S1	S2	S1	S2
NO	0.74	0.90	0.005	0.27
NO ₂	0.71	0.77	0.07	0.09
O ₃	-0.68	-0.83	-0.29	-0.68
T	-0.48	-0.62	-0.44	-0.79
RH	0.63	0.78	0.26	0.73
WS	-0.55	-0.71	-0.24	-0.50

particulate and gas concentration of the measured PAHs and the temperature (T), the relative humidity (RH), the wind speed (WS) and other pollutants.

The particulate PAHs were strongly positively correlated with NO and NO₂, while an insignificant positive correlation was observed between the gas phase PAHs and these two pollutants. NO and NO₂ are mainly released from vehicular emissions and therefore it can be assumed that both NO_x and PAHs arise from combustion sources and that low temperatures favor both high NO₂ concentrations and partitioning of PAHs in the particulate phase [6].

Furthermore a strong negative correlation was calculated for ozone concentration and PAHs particulate phase, which is expected taking into account the strong positive correlation between NO_x and PAHs particulate phase, due to the fact that NO₂ forms during the transportation away from the source and reacts with O₃. A negative correlation between O₃ and particulate PAHs was calculated also by Park et al. [6] (-0.52) and Tsapakis and Stephanou [16] (-0.81). A negative correlation was also observed between PAHs and temperature because of the higher concentrations of PAHs in win-

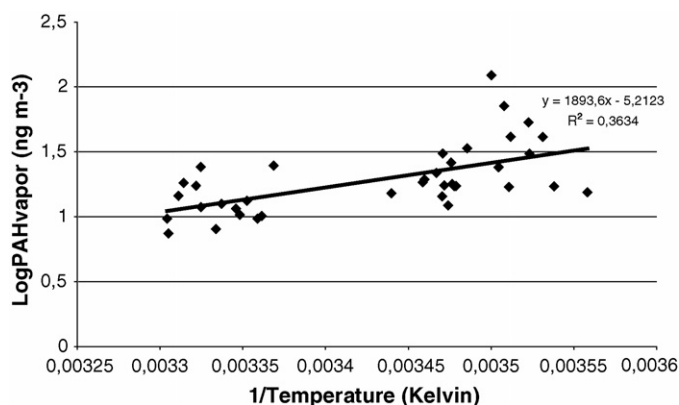


Fig. 4. $\log(\text{PAH})$ in gas phase with $1/\text{temperature}$ (K^{-1}).

tertime implying emissions by human activity such as central heating.

The relationship $\log(\text{PAH})_{\text{vapour}} (\text{ng m}^{-3}) = a + m/T$ (K) is illustrated in Fig. 4, where a and m are the intercept and slope obtained by a least-squares linear regression [6]. The positive slope ($m = 1894$) indicates that PAH concentrations increase with decreasing air temperature. Therefore, this supports the fact that central heating (oil fueled) is contributing to atmospheric PAH emissions during the wintertime. Finally, a negative correlation between PAHs and wind speed was observed probably due to the dilution of PAHs as the wind speed increases.

The mean wind pattern in the atmospheric boundary layer in the vicinity of the Mesogaia region can be characterised by

a predominantly northeastern flow. The area is exposed to the summer monsoon circulation driven by the Arabian heat low. The resulting northern winds in the Aegean, are occasionally interrupted by the passage of weak pressure troughs [25]. In this case, the surface wind flow at Koropi is a combined result between the Evoikos and the Saronikos Gulf sea breeze cells, where in most cases the first is reaching the Koropi area and the second is blocking the southern passage of Messogia Plain [24]. At Spata the surface wind flow is influenced mainly by the Evoikos Gulf sea breeze blowing from the E to NE directions, depending on the background flow [26]. Finally, under low background flow during the night, the Koropi area is under the influence of the Ymettus katabatic flow (NW–W flow), while the Spata area is influenced by the western land breeze flow [24]. Wind Direction seemed to influence PAH concentrations, since maximum observed values were strongly related to the prevailing wind direction observed during the experimental period. In particular, during the cold period maximum values of PAHs at Koropi were recorded during days with NW or NE prevailing winds, implying the predominance of sources from vehicular traffic in the NW direction and from Attiki Odos highway in the NE direction (see Fig. 5a). The corresponding maximums at Spata were detected during days with WNW or N prevailing winds due to the local streets located in close proximity with the experimental site and to the NW direction (see Fig. 5b). Respectively, during the summer period, maximum concentrations were observed during days with N, NE or NNE prevailing winds for both sites, strongly influenced by the Evoikos Gulf sea breeze blowing from the northeastern direction (see Fig. 5c and d).

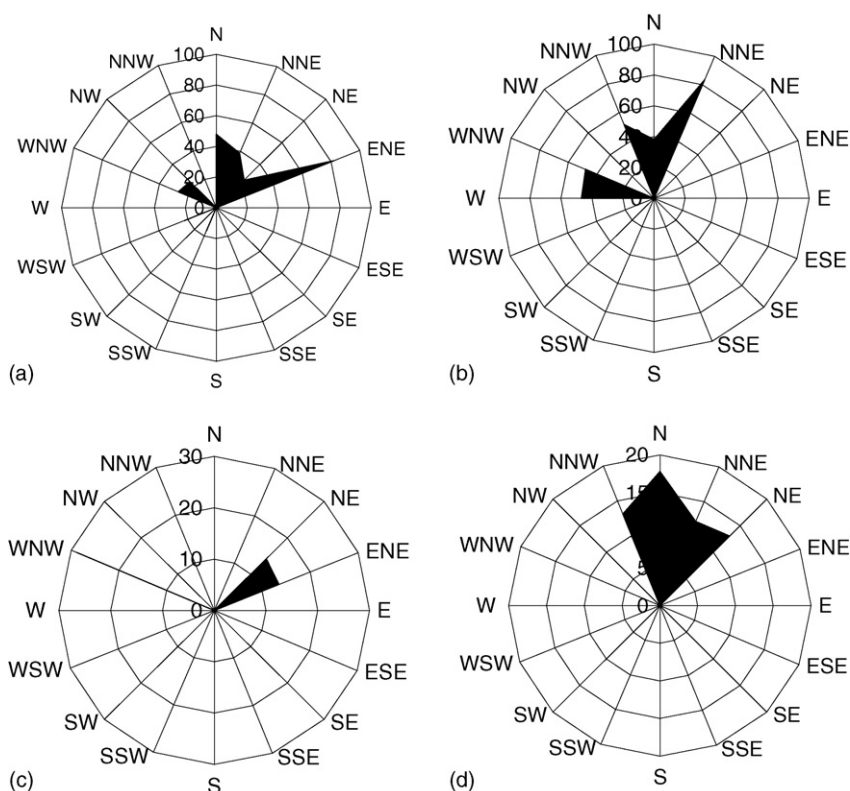


Fig. 5. (a) and (b) Arithmetic mean total PAH concentrations in each of the wind sectors for the cold period for Koropi (a) and Spata (b) site correspondingly. (c) and (d) Arithmetic mean total PAH concentrations in each of the wind sectors for the warm period for Koropi (c) and Spata (d) site correspondingly.

4. Conclusions

PAHs concentrations in ambient air samples collected during two periods in a suburban area of Athens were measured while their seasonal variations, their correlations with meteorological parameters and other pollutants and their sources were characterized. The results of the analysis showed that PAHs appeared mainly in the gas phase with concentrations ranging between 6.89 and 124 ng m⁻³ with a small fraction in the particulate phase (0.44–13.2), which constituted the 10% of the total arithmetic mean PAHs values, while higher total concentrations were observed in the cold period. In particular, mean summer total PAH concentration did not exceed the 24% of the winter value in Spata, while the corresponding summer concentration in Koropi reached the 43% of the winter value. Based on the diagnostic concentrations ratios it was concluded that fossil fuel combustion constituted the main source of PAHs in both areas during the studied periods (vehicular traffic as well as wood burning in the nearby agricultural area). Additionally, maximum values observed in both sites and during both periods were strongly related to the wind direction. Air masses were transported over the sites transferring PAHs from both Attiki Odos road and local streets, while the sea breeze from Evoikos Gulf was responsible for the respectively higher PAHs concentrations especially during the summer period. PAHs concentrations were higher during days with NW or NE prevailing winds in Koropi and during days with WNW or N prevailing winds in Spata and for the cold period. In general, the predominant wind sector was the northern one since it covered the 72% of the winter sampling period and 96% in the summer sampling period.

Acknowledgements

This work took place in the framework of a co-operation between the Environmental Research Laboratory, of Institute of Nuclear Technology—Radioprotection of NCSR “DEMOKRITOS” and the Environmental Department of Athens International Airport “Eleftherios Venizelos”.

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