



Polycyclic aromatic hydrocarbons in the bulk precipitation and surface waters of Northern Greece

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Abstract

Bulk (wet and dry) precipitation and surface water sampling was undertaken in the main plain of central Macedonia in Northern Greece. Fourteen polycyclic aromatic hydrocarbons (PAHs) included in the US EPA's priority pollutant list were analysed. The concentrations determined in bulk precipitation were in general within the range of values worldwide reported. Concentrations were highest in the cold months. Deposition fluxes of PAHs were of the same order of magnitude as reported data. The greatest values were found when high concentrations of PAHs in precipitation coincided with large precipitation amounts. The concentrations of PAHs in surface waters (main rivers, tributaries, ditches, etc) were in general lower than those in bulk precipitation, and among the lowest reported for European rivers, excepting Np and Ph. Bulk deposition and domestic effluents are suggested as being the main PAH sources into surface waters. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: PAHs; Bulk precipitation; Surface waters; Deposition fluxes

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds of great environmental concern because of the documented carcinogenicity in experimental animals and the widespread occurrence of several of its members (Moore and Ramamoorthy, 1984; IARC, 1991; USEPA, 1992). Sixteen unsubstituted PAHs, some of which are considered as being possible or probable human carcinogens, have been listed by the Environmental Protection Agency of the USA (USEPA) as priority pollutants, hence their distribution in the environment and potential human health risks have become

the focus of much attention (Keith and Telliard, 1979; Clean Water Act, 1993).

PAHs are introduced into the environment mainly via natural and anthropogenic combustion processes. Volcanic eruptions and forest and prairie fires are among the major natural sources of PAHs to the atmosphere. Anthropogenic sources include automobile exhaust and tire degradation, industrial emissions from catalytic cracking, air-blowing of asphalt, coking coal, domestic heating emissions from coal, oil, gas and wood, refuse incineration and biomass burning (Nikolaou et al., 1984; Baek et al., 1991).

Once in the atmosphere, the residence times and ultimate fates of these semivolatile chemicals depend upon their distributions among vapour, particle and droplet phases. This partitioning is in turn controlled by the vapour pressures, Henry's law constants and aqueous solubilities of the compounds, and by the concentrations

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and size distributions of particles and droplets in the atmosphere (Junge, 1977; Bidleman, 1988).

Despite their large source strength in urban/industrial sites, PAHs occur at relatively high concentrations in rural and remote areas due to their ability to be transported over long distances as gases or aerosols, and their apparent resistance to degradation on atmospheric particles.

Chemical transformations and atmospheric fallout remove gaseous and particle-associated PAHs from the atmosphere. Atmospheric fallout includes wet and dry deposition of particles and vapours. PAHs are subject to both vapour and particle washout from the atmosphere during precipitation events (Bidleman, 1988). Atmospheric fallout has been determined to be a prominent pathway for the loading of PAHs to many water bodies (Andren and Strand, 1981; McVeety and Hites, 1988; Dickhut and Gustafson, 1995; Golomb et al., 1997).

The major objectives of this paper were: (a) to investigate the spatial and temporal variability of the 16 EPA PAHs in the bulk (wet and dry) precipitation occurring in central Macedonia, Northern Greece, (b) to estimate PAH deposition fluxes and (c) to measure PAH concentrations in the local surface waters and identify major contributing sources. This paper is part of a wider research programme concerning the pollution of the environment in the main plain of central Macedonia (Albanis et al., 1998).

2. Materials and methods

2.1. Area description and sampling

The study was conducted in Imathia, a Greek province located in central Macedonia (Fig. 1). The area, consisting of two major mountainous volumes and an extended cultivated land (52,760 ha) is located to the east of the power “heart” of Greece, a basin where five lignite-burning power plants produce approximately 70% of the country’s electric power (total power 3663 MW in 1993) (Triantafyllou, 1994). The total suspended particulate (TSP) emissions from the power stations are roughly estimated to be 10^8 kg yr⁻¹. The prevailing winds above this basin are northwesterly, during the cold period, while southeasterly winds are also frequent during summer (Triantafyllou, 1994). The capital of Imathia province is the city of Veria with 60,000 population.

The study area is draining through two main rivers, Aliakmon and Loudias, into Thermaikos gulf (Fig. 1). The delta of these rivers are protected by the Convention of Ramsar (1971). Aliakmon river and the tributaries Tripotamos and Arapitsa comprise the main irrigation source for the plain. Significant pollution loadings are discharged into the lower part of Aliakmon river due to its confluence with Ditch-66. This ditch, which also receives water from smaller streams, is a major recipient

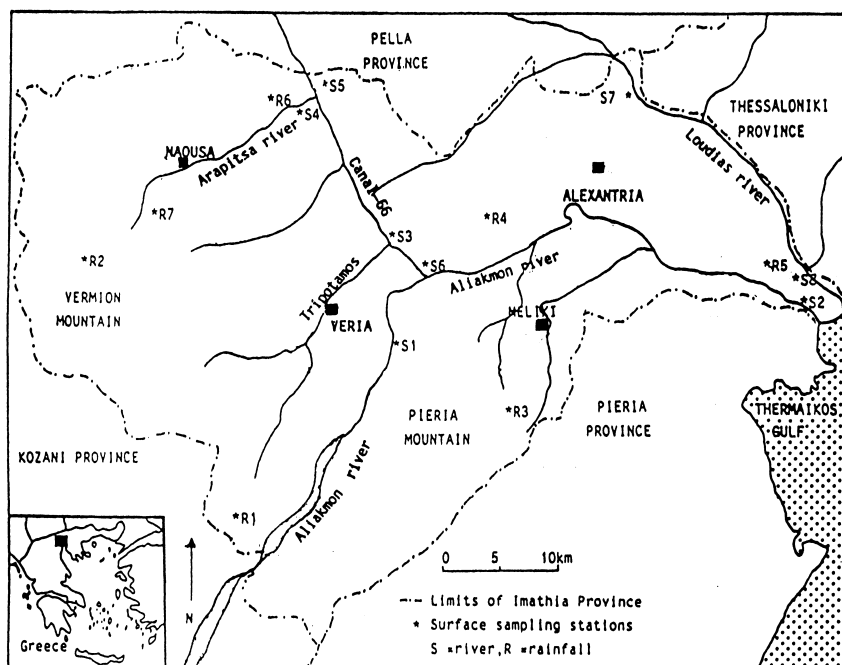


Fig. 1. Map of the sampling area.

for the effluents produced by a number of local industries, principally vegetable, fruit and juice canneries.

The major sources of PAHs in the precipitation occurring in the study area are considered to be urban activities taking place in the residential centres of the area (domestic heating, road traffic), industrial emissions (local or long-range transported), uncontrolled refuse burning, bush fire and stubble burning during late summer and early fall. Domestic effluents, surface runoff and atmospheric deposition are considered to be the major PAH sources into surface waters.

Bulk precipitation samples were collected from seven sampling sites (R₁–R₇ in Fig. 1) during the period September 1996–May 1997. The altitude of the sampling sites was in the range 6 and 1650 m (Table 1).

Bulk precipitation was collected in 1 l dark glass bottles open to wet and dry deposition through a 30 cm diameter-glass funnel. Samples were collected once a month, they were transferred to the laboratory within 1 day after sampling, and were stored at 4°C prior to extraction (normally within 48 h). Precipitation height was measured at two sites, one on Vermion mountain, near R₇, and the other in the plain, near R₄. Monthly precipitation heights were in the range 26.5–73.0 mm and 23.0–70.9 mm, at the two sites, respectively. PAHs were analysed in a total of 30 samples with minimum volume 500 ml.

Surface water samples were collected from eight sampling sites (S₁–S₈ in Fig. 1) located on the two main rivers (main flows and estuaries) as well as on tributaries and Ditch-66. Samples were collected twice in July and August 1996, using dark glass bottles with Teflon caps. Transport and storage conditions were the same as for precipitation samples.

2.2. Extraction and analysis

The extraction procedure performed on precipitation and surface water samples is briefly described in Fig. 2. Details have been reported elsewhere (Manoli and Samara, 1996).

PAHs were determined by HPLC with programmable fluorescence detection. The HPLC system consisted of a Perkin-Elmer LC-250 binary pump, a Perkin-Elmer LC-240 programmable fluorescence detector with 7 µl flow cell, and a Perkin-Elmer 1020 personal integrator. The NIST Standard Reference Material 1674c) (Promochem, Wesel, FRG) containing 16 EPA priority pollutants PAHs (naphthalene, Np; acenaphthylene, Acn; acenaphthene, Ace; fluorene, F; phenanthrene, Ph; anthracene, An; fluoranthene, Fl; pyrene, Py; benzo[*a*]anthracene, B[*a*]An; chrysene, Chry; benzo[*b*]fluoranthene, B[*b*]Fl; benzo[*k*]fluoranthene, B[*k*]Fl; benzo[*a*]pyrene, B[*a*]Py; dibenz[*a,h*]anthracene, dB[*a,h*]An; benzo[*ghi*]perylene, B[*ghi*]Pe and indeno[1,2,3-*cd*]pyrene, I[1,2,3-*cd*]Py), plus benzo[*e*]pyrene, B[*e*]Py externally

added was used as a test sample. Acenaphthylene, although contained in the standard is only weakly fluorescent and thus not determined. A 100 × 4.6 mm² Hypersil Green PAH column with a carbon loading of 13.5 ± 0.5% (5 µm particle size) and a guard column packed with the same material were used. Chromatography was performed at 30°C. The mobile phase was CH₃CN/H₂O gradient comprising 50% (v/v) CH₃CN from 0–5 min programmed to 100% CH₃CN between 5 and 20 min. The final composition was maintained for a further 10 min. The equilibration time between runs was 10 min. The mobile phase flow rate was 1.5 ml min⁻¹. During chromatography the mobile phase was degassed by passage of continuous flow of helium through the solvents. The injection volume was 20 µl. 3,6-dimethylphenanthrene (0.12 µg ml⁻¹) was used as internal standard (Lintelmann et al., 1993; Berset and Holer, 1995). The time programme of the fluorescence detector is presented below:

Time (min)	0	13.3	15.7	20.6	26.5
Excitation wavelength (nm)	250	240	265	290	300
Emission wavelength (nm)	345	425	380	430	500

Analysis of the PAH mixture and the samples was performed under identical conditions.

3. Results and discussion

Almost all 16 EPA PAHs were identified and quantified in the precipitation and surface water samples. Results for acenaphthene and fluorene are not given here because these compounds exhibited coelution problems in most of the samples. The recovery efficiency of the extraction procedure for the rest 14 PAHs was in the range 80–120%.

3.1. PAHs in bulk precipitation

In general, the occurrence of PAHs in bulk precipitation could be hypothesized as being due to a combination of the following removal processes: particle scavenging by rain (within or below cloud), vapour dissolution in rain droplets, dry-gaseous deposition and dry-particle deposition. The relative contribution of each process to the total deposited amount of an individual PAH will be a function of several parameters, such as the compound's vapour pressure and Henry's law constant, its vapour-to-particle partitioning, the particle size distribution, prevailing meteorology, the size of raindrops, etc.

In general, the lower molecular weight PAHs which are predominantly present in the gaseous phase are

Table 1
Mean (min–max) concentrations of PAHs in bulk precipitation (ng l⁻¹)

PAH	R ₁ (1150 m) n = 4	R ₂ (540 m) n = 4	R ₃ (660 m) n = 4	R ₄ (15 m) n = 4	R ₅ (6 m) n = 4	R ₆ (35 m) n = 4	R ₇ (1650 m) n = 4
Np	126 (32–199)	307 (56–626)	129 (66–179)	426 (173–781)	268 (173–360)	238 (93–427)	317 (194–452)
Ph	38 (32–43)	50 (42–64)	45 (32–60)	67 (29–123)	58 (32–73)	65 (45–91)	200 (35–598)
An	2.3 (1.7–4.2)	1.8 (1.7 ^a –1.9)	2.0 (1.7 ^a –2.6)	3.0 (1.7–7.2)	1.8 (1.7 ^a –1.9)	2.0 (1.7 ^a –2.9)	30 (1.7 ^a –96)
Fl	14 ^a (14 ^a –14 ^a)	14 (14 ^a –14)	16 (14 ^a –20)	19 (14–30)	22 (14 ^a –32)	19 (14 ^a –32)	25 (14 ^a –54)
Py	4.1 (2.0–7.2)	5.3 (4.1–7.5)	9.6 (2.2–14)	15 (2.8–29)	15 (2.5–29)	11 (6.0–21)	27 (2.1–76)
B[α]An	2.1 (0.9–4.1)	5.0 (2.9–7.0)	4.9 (2.6–7.5)	3.2 (1.6–6.0)	5.7 (2.5–10)	4.4 (1.3–10)	5.7 (1.3–12)
Chry	3.9 (1.2–7.7)	16 (6.3–28)	8.4 (1.7–22)	6.9 (0.8–25)	9.4 (3.3–17)	4.5 (2.1–8.2)	13 (1.2–36)
B[e]Py	22 (15 ^a –44)	23 (15 ^a –31)	20 (15 ^a –30)	22 (15–54)	15 (15 ^a –15 ^b)	26 (15 ^a –40)	31 (15 ^a –63)
B[b]Fl	2.0 (1.0 ^a –3.8)	1.7 (1.2–2.0)	2.1 (1.6–2.3)	2.6 (1.0–4.3)	7.2 (2.1–11)	2.7 (1.1–4.4)	3.7 (1.3–9.5)
B[k]Fl	0.8 (0.3–1.4)	0.8 (0.6–0.9)	1.1 (0.8–1.8)	1.0 (0.4–1.7)	3.5 (0.8–5.4)	1.2 (0.7–1.7)	1.5 (0.5–3.5)
B[α]Py	1.5 (1.0–2.2)	1.3 (0.9–1.6)	2.0 (1.3–1.7)	1.6 (0.7–2.1)	3.0 (1.4–6.0)	1.8 (1.2–2.5)	4.4 (1.2–11)
dB[α,h]An	1.4 (1.3 ^a –1.7)	1.3 ^a (1.3 ^a –1.3 ^a)	1.4 (1.3–1.7)	1.4 (1.3–1.7)	2.1 (1.3 ^a –4.1)	1.6 (1.3 ^a –2.3)	1.6 (1.3–2.2)
B[ghi]Pe	4.5 (3.0–5.8)	2.7 (2.1 ^a –4.0)	4.0 (2.4–5.5)	3.9 (2.1–9.7)	8.9 (2.7–14)	4.4 (3.2–5.9)	7.1 (2.5–14)
I[1,2,3-cd]Py	2.9 (2.5 ^a –4.2)	3.5 (2.5 ^a –5.0)	4.0 (2.7–4.9)	3.0 (2.5–4.0)	6.2 (4.5–9.8)	3.9 (2.5 ^a –5.4)	4.7 (2.5–11)
∑PAH	225 (143–287)	423 (177–731)	249 (235–272)	575 (272–954)	427 (293–546)	385 (246–608)	672 (312–1397)
∑PAH _{CARC} ^b	11 (7.1–15)	13 (12–14)	16 (11–18)	13 (10–17)	29 (13–37)	15 (12–20)	22 (8.2–50)

^a Detection limits.

^b ∑PAH_{CARC} = B[α]An + B[β]Fl + B[k]Fl + B[α]Py + dB[α,h]An + I[1,2,3-cd]Py (IARC probable and possible human carcinogens).

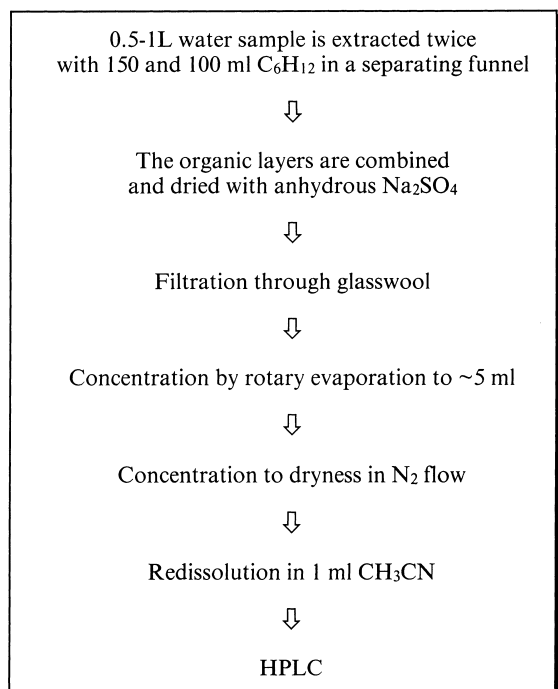


Fig. 2. Extraction procedure for the analysis of PAHs in precipitation and river water samples.

expected to be removed either by vapour washout or by dry gaseous deposition (Bidleman, 1988). The heavier species which are predominantly bound to particles are removed by particle washout, a mechanism that has been found to be very efficient (Ligocki et al., 1985b; McVeety and Hites, 1988; Dickhut and Gustafson, 1995; Poster and Baker, 1996) and by dry-particle deposition. Since PAHs are associated with particles of the accumulation size range that have minimal dry deposition velocities, the latter mechanism could be considered as less important (Bidleman, 1988).

The distribution of PAHs between the particulate and dissolved phases of rain is a result of at least two processes, gas and particle scavenging and partitioning between the particulate phase in the hydrometer and the hydrometer itself. Both processes can be explained quite well by equilibrium based models, in which particle and gas scavenging is strongly correlated to the compound aqueous solubility, while partitioning is strongly correlated to the compound K_{ow} (Hart et al., 1993).

Mean PAH concentrations found in this study in bulk precipitation at each sampling site are given in Table 1.

As shown, Np was the most prominent PAH followed by Ph, B(e)Py and Py. The mean contribution of Np to \sum PAH was 62% and could be attributed to its distinct water solubility (31 mg l⁻¹ vs 1.1 mg l⁻¹ of Ph, 0.13 mg l⁻¹ of Py, and even lower for the heavier PAHs)

as well as to increased dry gaseous deposition. Contributions up to 58% and 45% have been reported for Np and substituted naphthalenes in the wet and dry precipitation onto Massachusetts Bay (Golomb et al., 1997). Phenanthrene, Fl, Py and B(ghi)Pe were also major contributors, however, with much lower percentages (~5–10%). Bulk deposition in the UK urban centres of Manchester and Cardiff was also found to be dominated by Ph (17% and 22%, respectively), Fl/1-methyl-phenanthrene (27% and 21%) and Py (12% and 8.6%) (Halsall et al., 1997).

A breakdown of PAH concentrations found in precipitation occurring in Europe and the USA is given in Table 2. In general, our results are within the range of reported values, although differences in sampling and analytical methods do not permit a direct comparison among data. Nevertheless, it would be probably worth to note the high concentrations of Ph and An found in our study at R₇. This sampling site is a recreation place where open barbeque cooking is very often taking place. Open barbeque cooking using wood or coal has been reported as important PAH emission source (Freeman and Cattell, 1990). B[α]Py and the sum of the six carcinogenic PAHs (\sum PAH_{CARC}) were highest at R₇ and R₅ (Table 1).

Temporal and spatial variabilities of the concentrations of PAHs in bulk precipitation were examined using two-way ANOVA with interaction. Precipitation samples were classified into two time periods, cold with ambient temperature below 15°C (samples of October, December, January, March) and warm with ambient temperature over 19°C (samples of September and May). Results obtained are presented in Table 3. Sampling site R₅ was excluded from ANOVA since no samples were collected from this site during the warm period. Results of Table 3 show that variations due to the sampling period were significant only for B[α]An and B[ghi]Pe. At the majority of sampling sites, these compounds exhibited highest concentrations in the cold period. The effect of sampling site was significant only for B[ghi]Pe that exhibited highest mean concentrations at R₇ while minimum at R₂. The significant interaction found for B[ghi]Pe suggests that the effect of one factor is not independent of the presence of a particular level of the other factor.

Higher wet deposition of PAHs in winter compared to summer has been reported by several investigators. It was attributed to greater emissions of PAHs in winter months from residential and commercial space heating, as well as to the lower mixing heights prevailing during the cold period (Gardner and Hewitt, 1993; Golomb et al., 1997). Hart et al. (1993) found the winter:spring:summer ratio of total PAH concentrations in rain occurring in Dübendorf, Switzerland to be about 5:2:1. Oil burning for residential heating was hypothesized to be responsible for this distribution.

Table 2
Literature data of PAH concentrations in precipitation (ng l⁻¹)

PAH	Ligocki et al., 1985a Portland ^{a,b}	Ligocki, et al., 1985b Portland ^{a,c}	McVeety and Hites, 1988 Isle Royale ^{a,d}	Levsen et al., 1991 Germany ^a	Dickhut and Gustafson, 1995 Chesapeake Bay ^{a,d}	Hoff et al., 1996 Great Lakes ^a	Berg and Hjell-brekke, 1988 Germany ^{a,c}	Berg and Hjell-brekke, 1988 Finland ^{f,e}
Ph	90	4.1 ^g	1.6		2.0–8.0	3.2–11	12.2–36	9.0
An	5.1		0.2				0.7–1.82	0.2
Fl	48	4.4	1.3	149	2.0–3.0		16.4–56	8.4
Py	39	4.1	1.0	84		2.7–8.2	11.6–29	6.0
B[z]An	3.3	1.5	0.3	20			3.0–12.6	1.6
Chry	7.9	3.6	0.6 ^h	49			6.2–13.8	4.0 ^h
B[e]Py	0.37	3.0	1.0	46	0.5–10			
B[b]Fl	1.6 ⁱ	9.2 ⁱ		52			6.1–11.9	4.3
B[k]Fl				25			2.7–5.6	1.5
B[z]Py		2.8	0.5	29		2.6–8.2	3.8–6.9	2.2
dB[z,h]An				4.0		2.9–5.1	1.2–2.3	
B[ghi]Pe		6.0	1.0	33			1.8–8.2	2.7
I[1,2,3-cd]Py			1.0	33			2.9–7.4	5.5

^a Wet precipitation.

^b Rain-dissolved phase.

^c Rain-particulate phase.

^d Roughly estimated from other papers.

^e Volume weighted mean concentrations.

^f Bulk precipitation.

^g Ph + An.

^h Chry + Triphenylene.

ⁱ B(b + j + k)Fl.

Table 3
Analysis of variance of PAHs concentrations in bulk precipitation and surface waters^a

	Np	Ph	An	Fl	Py	B[z]An	Chry	B[e]Py	B[b]Fl	B[k]Fl	B[z]Py	dB[z,h]An	B[ghi]Pe	IPy
<i>Precipitation</i>														
Sampling period	-	-	-	-	-	++	-	-	-	-	-	-	++	-
Sampling site	-	-	-	-	-	-	-	-	-	-	-	-	+	-
Interaction	-	-	-	-	-	-	-	-	-	-	-	-	++	-
<i>Surface waters</i>														
Sampling site	-	-	-	-	-	-	-	-	-	++	++	-	-	-

^a ++ : significant effect at the 99% confidence level; +: significant effect at the 95% confidence level; -: insignificant. effect at the 95% confidence level.

Halsall et al. (1997) also found higher bulk deposition of PAHs in Manchester and Cardiff during winter. At both sites this was largely attributable to a decline in the deposition of Ph and Fl/1-methylphenanthrene during summer, whereas the heavier PAHs (B(b)Fl and above) did not show a similar decrease. Particle washout was found to vary seasonally also in the Chesapeake Bay watershed, however with higher particle scavenging occurring in spring/summer compared to fall/winter. The same authors observed an exponential increase in the gas scavenging coefficient with temperature decrease. Both processes were found to be affected by precipitation intensity (Dickhut and Gustafson, 1995).

3.2. PAH deposition fluxes

Bulk deposition fluxes of PAHs (i.e. the amounts monthly deposited on a 1 m² surface) were estimated for the two sampling sites, R₄ on the mountain and R₇ in the plain, for which precipitation data were available. Deposition calculation was possible for two cold and two warm months only and should be considered as an order of magnitude. Monthly deposition fluxes of \sum PAH and \sum PAH_{CARC} are shown in Fig. 3, while Fig. 4 illustrates mean deposition fluxes for individual PAHs.

Monthly deposition fluxes of total PAHs were in range 6.3–32.8 $\mu\text{g m}^{-2}$ (i.e. 0.21–1.1 $\mu\text{g m}^{-2} \text{d}^{-1}$)

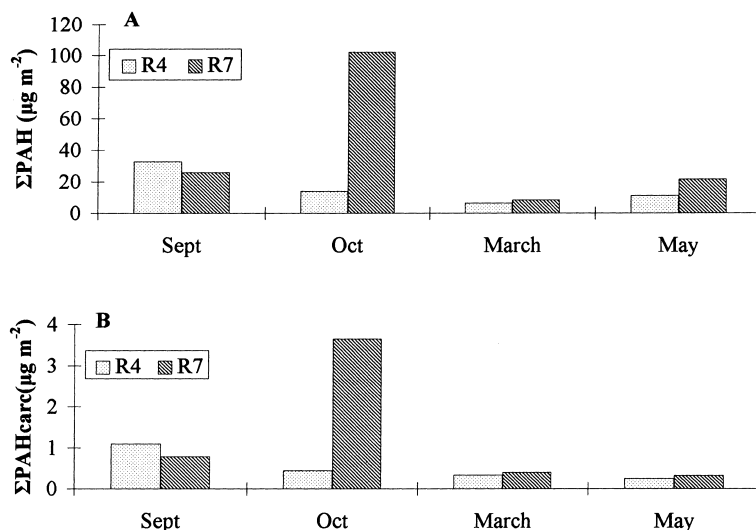


Fig. 3. Monthly deposition fluxes of ΣPAH (A) and $\Sigma\text{PAH}_{\text{CARC}}$ (B).

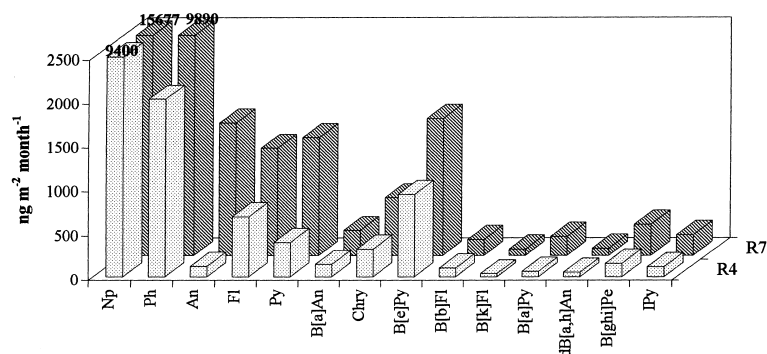


Fig. 4. Mean deposition fluxes for individual PAHs.

excepting the high value ($3.4 \mu\text{g m}^{-2} \text{ d}^{-1}$) observed at R₇ in October. This was due to the higher concentrations of PAHs in the local precipitation in that month, as well as to the larger precipitation amount (73 mm vs 39 at R₄). The deposition fluxes of $\Sigma\text{PAH}_{\text{CARC}}$ exhibited a similar pattern. At both sampling sites, deposition was highest primarily for the lower molecular weight PAHs (Np, Ph, Fl, etc) and secondarily for B(α)Py.

The deposition fluxes calculated in this study are in general agreement with the bulk deposition fluxes of PAHs estimated for other locations. Bulk deposition fluxes of $\Sigma 13$ PAHs (the same as in our study except Np) in the Swedish west coast were in the range 0.30 – $2.0 \mu\text{g m}^{-2} \text{ d}^{-1}$ with a mean value $0.9 \mu\text{g m}^{-2} \text{ d}^{-1}$. Deposition varied markedly among individual compounds with highest values being observed for Fl, Py and Chry. The authors also reported that deposition of PAHs took place continuously, but the greatest amounts were measured when atmospheric concentrations of PAHs

coincided with large precipitation amounts (Brorström-Lunden et al., 1994).

Halsall et al. (1997) estimated relatively higher bulk deposition fluxes of PAHs in Manchester and Cardiff. Median and range values reported for $\Sigma 13$ PAHs were 5.2 (1.0 – 24.2) and 4.1 (0.8 – 19.6) $\mu\text{g m}^{-2} \text{ d}^{-1}$, respectively. At both cities, deposition was dominated by Fl, Ph and Py.

The majority of literature data concern wet-only or dry deposition fluxes of PAHs. Generally, reported data are of the same order of magnitude as those found in this study (Hart et al., 1993; Leister and Baker, 1994; Pirrone et al., 1995; Franz et al., 1998).

3.3. Surface waters

The concentrations of PAHs determined in surface waters are presented in Table 4. As in the precipitation samples, Np was the most prominent compound

Table 4
Concentrations of PAHs in surface waters (ng l⁻¹)

PAH	S1	S2	S3	S4	S5	S6	S7	S8
Np	494	108	419	530	677	158	119	367
Ph	33	31	70	34	51	45	30	48
An	3.6	1.7 ^a	1.6	1.7	1.7	3.8	1.7	1.7
Fl ^b	14	14 ^a	14 ^a	14 ^a	14 ^a	14 ^a	14 ^a	14 ^a
Py	3.5	3.7	19.6	11.7	11.7	7.9	3.3	9.5
B[α]An	9.4	0.9 ^a	7.5	9.1	9.1	4.5	5.3	11.3
Chry	1.2	0.9	7.4	4.5	4.5	2.8	1.2	2.3
B[e]Fl ^b	23	15	75	78	78	53	36	68
B[b]Fl	1.0 ^a	1.6	3.1	1.3	1.3	1.4	1.0 ^a	1.0 ^a
B[k]Fl ^b	0.2	0.4	1.0	0.4	0.4	0.3	0.2	0.3
B[α]Py ^b	0.9	0.9	1.7	0.7	0.7	1.1	0.6	0.7
dB[α ,h]An	1.3 ^a	1.4 ^a	1.3 ^a	1.3 ^a	1.3 ^a	1.6	1.3 ^a	1.3 ^a
α [ghi]Pe ^b	2.1 ^a	2.1 ^a	3.1	2.1 ^a	2.1 ^a	2.2	2.2	2.1 ^a
I[1,2,3-cd]Py ^b	3.3	2.7	2.7	2.5 ^a	3.7	2.7	2.5 ^a	2.5 ^a
Σ PAH	591	184	627	419	856	297	218	530
Σ PAH _{CARC}	16	7.9	17	11	16	12	11	17
Σ PAH _{EC}	22	22	26	21	22	22	21	21

^a Detection limits.

^b PAHs mentioned in the European Community Directive for drinking water (80/778/EEC).

followed by Ph and B(e)Py. On the other hand, many PAHs (An, Fl, B[b]Fl, dB[a,h]An, B[ghi]Pe and I[1,2,3-cd]Py) exhibited high frequency of occurrence (50–100%) at concentrations below detection limits. The concentrations of these PAHs in surface waters were in general lower than those in bulk precipitation. In contrast, surface waters had higher B[e]Py and B[a]An content.

Naphthalene exhibited large differences between the two months at most sampling sites, with higher concentrations shown in August. Higher concentrations in August compared to those in July were also exhibited by B(e)Py and Py at S₃, S₅ and S₆ which are located on Ditch-66. Spatial variabilities of the concentrations of PAHs in surface waters were examined using one-way ANOVA and the results are given in Table 3. As shown, variations due to the sampling site were significant only for B(k)Fl and B(α)Py, which exhibited highest concentrations at S₃, a sampling site that usually shows high BOD and COD pollution (Voutsas et al., 1999).

The concentrations of PAHs reported for European rivers have been reviewed recently (Manoli and Samara, 1999a). Although a direct comparison of literature data is difficult due to differences in the phases analysed (dissolved, particulate or both), the analytical methods used, and the compounds considered in each study, it is apparent that PAH concentrations found in this work are among the lowest reported for Europe, excepting Np and Ph. Several reasons would be hypothesized: (a) PAH emissions during summer are normally lower than those during winter, (b) rain events are very seldom in Greece during summer, (c) it could be assumed that

surface waters do not receive effluents which are heavily contaminated with PAHs. A greater number of samples throughout the year are necessary to give a representative view of the PAH levels in the local surface waters. At all sampling sites, the sum of the six PAH mentioned in the European Community directive 80/778/EEC was below the 200 ng l⁻¹ limit for drinking water. Maximum levels for the sum of these PAHs in surface waters can reach 1 μ g l⁻¹, depending on the surface water treatment processes.

3.4. PAH signatures

The PAH signatures in bulk deposition, surface water, TSP and domestic effluents were compared to investigate source/sink relationships. Domestic effluent PAH data were taken from Manoli and Samara (1999b) while TSP data were taken from Papageorgopoulou et al. (1999). Fig. 5 shows this average signature of the concentrations of all PAHs normalized to Σ PAH concentrations of the four sample types. The PAH signature in surface waters was correlated at the 99% confidence level with the signature of bulk precipitation ($r = 0.90$) and the signature of domestic effluents ($r = 0.83$), supporting the hypothesis that atmospheric deposition and domestic effluents are among the major PAH sources into surface waters. The different PAH distribution found for TSP, especially for the heavier PAHs, could be attributed to the fact that these compounds are mainly associated with particles of the accumulation size range that have minimal

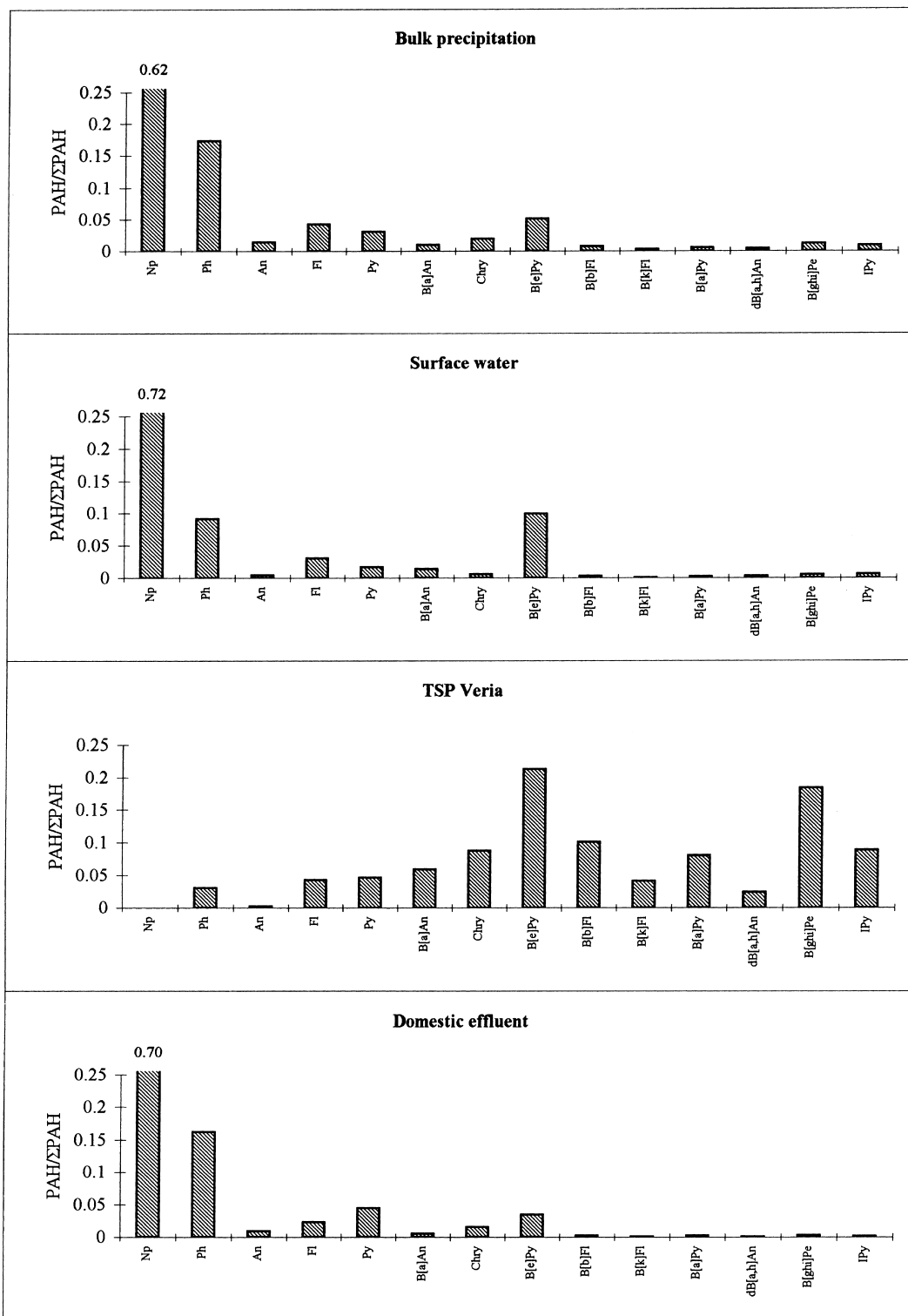


Fig. 5. Average signatures of the concentrations of PAHs normalized to \sum PAH concentrations.

dry deposition velocities and rain-scavenging efficiency. Thus, heavier PAHs are most prominent in TSP than in bulk precipitation samples.

4. Conclusions

The concentrations of PAHs determined in bulk precipitation that occurs in Northern Greece were in general within the range of values reported worldwide. Concentrations were highest in the cold months. Transport from the neighbouring lignite-burning power plants was not identified. Deposition fluxes of PAHs were of the same order of magnitude with reported data. The greatest values were found when high concentrations of PAHs in precipitation coincided with large precipitation amounts. The concentrations of PAHs found in the local surface waters were in general lower than those in bulk precipitation, and among the lowest reported for European rivers, excepting Np and Ph. The comparison of PAH signatures in bulk deposition, surface waters, atmospheric particulates and domestic effluents suggested that atmospheric deposition and domestic effluents are major PAH sources into surface waters.

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References

- Albanis, T.A., Hela, D.G., Sakellarides, T.M., Konstantinou, I.K., 1998. Monitoring of pesticide residues and their metabolites in surface and underground waters of Imathia (N. Greece) by means of solid-phase extraction disks and gas chromatography. *J. Chromatogr. A*, 823, 59–71.
- Andren, A.W., Strand, J.W., 1981. Atmospheric deposition of particulate organic carbon and polyaromatic hydrocarbons to Lake Michigan. In: Eisenreich, S.J. (Ed.), *Atmospheric Pollutants in Natural Waters*. Ann Arbor Science, Ann Arbor, MI.
- Baek, S.O., Field, R.A., Goldstone, M.E., Kirk, P.W., Lester, J.N., Perry, R., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behaviour. *Wat. Soil Pollut.* 60, 279–300.
- Berg, T., Hjellbrekke, A.G., 1988. Heavy metals and POPs within the ECE region. Supplementary data for 1989–1996 EMEP Co-operative Programme for Monitoring and Evaluation of the Long range Transmission of Air Pollutants in Europe. EMEP/CCC-Report 7/98, O-95038.
- Berset, J.D., Holer, R., 1995. Organic micropollutants in Swiss agriculture: distribution of polynuclear aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in soil, liquid manure, sewage sludge and compost samples: a comparative study. *Int. J. Environ. Anal. Chem.* 59, 145–165.
- Bidleman, T.F., 1988. Atmospheric processes. *Environ. Sci. Technol.* 22, 361–367.
- Brorström-Lunden, E., Lindscock, A., Mowrer, J., 1994. Concentrations and fluxes of organic compounds in the atmosphere of the Swedish west coast. *Atmos. Environ.* 28, 3605–3615.
- Clean Water Act, 1993. Suspect Chemicals Source book. In: Clansky, K.B., Bethesda, M.D. (Eds.), *Source List 3B, Clean Water Act Section 307, Priority Pollutants*, first ed., Roytech Publications, Inc., USA.
- Dickhut, R.M., Gustafson, K.E., 1995. Atmospheric washout of polycyclic aromatic hydrocarbons in the southern Chesapeake bay region. *Environ. Sci. Technol.* 29, 1518–1525.
- Franz, T.P., Eisenreich, S.J., Holsen, T.M., 1998. Dry deposition of particulate polychlorinated biphenyls and polycyclic aromatic hydrocarbons to Lake Michigan. *Environ. Sci. Technol.* 32, 3681–3688.
- Freeman, D.J., Cattell, F.C.R., 1990. Woodburning as a source of atmospheric polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* 24, 1581–1585.
- Gardner, B., Hewitt, C.N., 1993. The design and application of a novel automated sampler for wet and dry deposition to water surfaces. *Sci. Total Environ.* 135, 135–245.
- Golomb, D., Ryan, D., Underhill, J., Wade, T., Zemba, S., 1997. Atmospheric deposition of toxics onto Massachusetts bay – II. Polycyclic aromatic hydrocarbons. *Atmos. Environ.* 31, 1361–1368.
- Halsall, C.J., Coleman, P.J., Jones, K.C., 1997. Atmospheric deposition of polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) and polycyclic aromatic hydrocarbons (PAHs) in two UK cities. *Chemosphere* 35, 1919–1931.
- Hart, K.M., Tremp, J., Molnar, E., Giger, W., 1993. The occurrence and the fate of organic pollutants in the atmosphere. *Wat. Air Soil Pollut.* 68, 91–112.
- Hoff, R.M., Strachan, W.M.J., Sweet, C.W., Chan, C.H., Shackleton, M., Bidleman, T.F., Brice, K.A., Burniston, D.A., Cussion, S., Gatz, D.F., Harlin, K., Schroeder, W.H., 1996. Atmospheric deposition of toxic chemicals to the Great Lakes: a review of data through 1994. *Atmos. Environ.* 30, 3505–3527.
- International Agency for Research on Cancer. IARC, 1991. *Monographs on the Evaluation of Carcinogenic Risks to Humans*. Vol. 43–53, Lyon.
- Junge, C.E., 1977. In: Suffet, I.H. (Ed.), *Fate of Pollutants in the Air and Water Environments*. Part 1. Wiley, New York, pp. 7–26.
- Keith, L.H., Telliard, W.A., 1979. Priority pollutants I. A perspective view. *Environ. Sci. Technol.* 13, 416–423.
- Leister, D.L., Baker, J.E., 1994. Atmospheric deposition of organic contaminants to the Chesapeake bay. *Atmos. Environ.* 28, 1499–1520.
- Levsen, K., Behnert, S., Winkeler, H.D., 1991. Organic compounds in precipitation. *Fresenius' J. Anal. Chem.* 340, 665–671.
- Ligocki, M.P., Leuenberger, C., Pankow, J.B., 1985a. Trace organic compounds in rain-II. Gas scavenging of neutral organic compounds. *Atmos. Environ.* 19, 1069–1617.
- Ligocki, M.P., Leuenberger, C., Pankow, J.B., 1985b. Trace organic compounds in rain. – III. Particle scavenging of

- neutral organic compounds. *Atmos. Environ.* 19, 1619–1626.
- Lintelmann, J., Gunther, W.J., Rose, E., Kettrup, A., 1993. Behaviour of polycyclic aromatic hydrocarbons (PAHs) and triazine herbicides in water and aquifer material of a drinking water recharge plant. I. The area of investigation and the determination methods for PAHs and triazine herbicides in the aqueous matrix. *Fresenius' J. Anal. Chem.* 346, 988–994.
- Manoli, E., Samara, C., 1996. Polycyclic aromatic hydrocarbons in waste waters and sewage sludge: extraction and clean-up for HPLC analysis with fluorescence detection. *Chromatographia* 43 (3&4), 135–142.
- Manoli, E., Samara, C., 1999a. Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. *Trends Anal. Chem.* 18, 417–428.
- Manoli, E., Samara, C., 1999b. Occurrence and mass balance of polycyclic aromatic hydrocarbons in the Thessaloniki sewage treatment plant. *J. Environ. Qual.* 28, 176–186.
- McVeety, B.D., Hites, R.A., 1988. Atmospheric deposition of polycyclic aromatic hydrocarbons to water surfaces: a mass balance approach. *Atmos. Environ.* 22, 511–536.
- Moore, S.W., Ramamoorthy, S., 1984. *Organic Chemicals in Natural Waters. Applied Monitoring and Impact Assessment.* Springer, New York.
- Nikolaou, K., Masplet, P., Mouvier, G., 1984. Source and chemical reactivity of polynuclear aromatic hydrocarbons in the atmosphere – a critical review. *Sci. Total Environ.* 32, 103–132.
- Papageorgopoulou, A., Manoli, E., Touloumi, E., Samara, C., 1999. Polycyclic aromatic hydrocarbons in the ambient air of Greek towns in relation to other atmospheric pollutants. *Chemosphere* 39, 2183–2199.
- Pirrone, N., Keeller, G.J., Holsen, T.M., 1995. Dry deposition of semivolatile organic compounds to lake Michigan. *Environ. Sci. Technol.* 29, 2123–2132.
- Poster, D.L., Baker, J.E., 1996. Influence of submicron particles on hydrophobic organic contaminants in precipitation. 2. Scavenging of polycyclic aromatic hydrocarbons by rain. *Environ. Sci. Technol.* 30, 349–354.
- Ramsar Convention, 1971. International Agreement for the Protection of Wetlands. Ramsar, Iran, 2 February.
- Triantafyllou, A.G., 1994. Experimental and theoretical study of the diffusion and dispersion conditions of atmospheric pollutants in the area: Amydeo, Ptolemaida, Kozani, Servia. Ph.D. Thesis, University of Athens, Greece (in Greek).
- US EPA, 1992. In: Clansky, K.B., Bathesda, M.D. (Eds.), *Suspect Chemical Sourcebook, Source list 10.* EPA Human Health Assessment Group Substances 1992, second ed. Roytech Publications Inc.
- Voutsas, D., Manoli, E., Samara, C., Sofoniou, M., Stratis, I., 1999. A study of surface water quality in Macedonia, Greece: Speciation of nitrogen and phosphorus. *Wat. Air Soil Pollut.*, accepted for publication.