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Sediment Fluxes of Polycyclic Aromatic Hydrocarbons in European High Altitude Mountain Lakes

PILAR FERNÁNDEZ,*
ROSA M. VILANOVA, AND
JOAN O. GRIMALT

Environmental Chemistry Department, Institute of Chemical and Environmental Research, (C.S.I.C.). Jordi Girona, 18-26.08034 Barcelona, Catalonia, Spain

Polycyclic aromatic hydrocarbons (PAH) were measured in superficial sediments from several high altitude mountain lakes for assessment of contemporary background PAH pollution levels in Europe. The sediments were obtained by gravity coring, and the upper 0–1 cm were analyzed by gas chromatography coupled to mass spectrometry. The parent PAH mixtures are very uniform irrespective of lake location, lake characteristics, and PAH load, corresponding to airborne combustion mixtures refractory to photooxidation and chemical degradation. The sedimentary fluxes are lowest in lake Arresjøen (Arctic area), $6.9 \mu\text{g}/\text{m}^2\text{yr}$, between 44 and $150 \mu\text{g}/\text{m}^2\text{yr}$ in west and central Europe and very high, $960\text{--}1700 \mu\text{g}/\text{m}^2\text{yr}$, in east Europe. Normalization of these values to TOC reflects a uniform pattern in correspondence with continental influence and east–west distribution. This pattern parallels the annual average atmospheric deposition fluxes of sulfate, pointing to combustion particles as the main way of PAH transport into these high altitude lakes. The lowest PAH/TOC ratios are found in the sites more distant from the continent ($4.6\text{--}4.9 \mu\text{g}/\text{g}$), the westernmost locations constitute another group (Iberian Peninsula, $7.2\text{--}7.8 \mu\text{g}/\text{g}$), higher values are found in the Alps and Pyrenees ($13\text{--}17 \mu\text{g}/\text{g}$), and the most polluted lakes are found in the Tatra mountains ($130 \mu\text{g}/\text{g}$).

Introduction

The impact of persistent organic pollutants (POPs) in the environment is deserving increasing attention. These compounds are characterized as environmentally stable, bioaccumulable, and toxic which are related to properties such as high chemical stability, hydrophobicity, and metabolic disruption potential. These features result in a high capacity of distribution throughout the planet being identified in the most remote areas such as the Arctic and Antarctica (1).

The widespread distribution of these compounds is also related to common volatility properties, pointing to atmospheric transport as the main distribution pathway in the environment (2–5). However, despite these relatively uniform chemical and environmental features, many aspects on origin, transport, accumulation, and toxic effects of these compounds on a global scale are still to be elucidated.

To this end, remote ecosystems other than polar regions need to be considered. High mountain lakes are interesting

study sites since their accumulated allochthonous materials are transported atmospherically. These lakes are selected as those situated above the regional timberline, hydrology-dependence from atmospheric fallout, and preservation from human disturbance both in lake and catchment. They may therefore be used as sentinel ecosystems for modelization of the atmospheric distribution and accumulation of POPs in remote areas, including flux quantitation and budget.

Many polycyclic aromatic hydrocarbons (PAH) can be included in the POP group. Several of them have been described as mutagenic, carcinogenic, and teratogenic (6) being included in the U.S. EPA and the EU priority pollutants lists. Their widespread occurrence is essentially due to formation and release during the incomplete combustion of organic matter (7–9).

Depending on their physicochemical properties, atmospheric PAH are distributed between the gas and particulate phases, mainly in association with small particles ($<1 \mu\text{m}$) (10–12). They can therefore be transported through the atmosphere over long distances entering into the aquatic environment by wet and dry deposition and/or gas–water interchange (13, 14). Once in the aquatic systems, most PAH are associated to the particulate phase due to their hydrophobic properties giving rise to accumulation in the sediments (15, 16). Sediments are therefore good environmental compartments for the record of the long-range distribution patterns of these compounds.

In this respect, previously reported data have shown relatively high levels of sedimentary PAH in rural and remote regions, in some cases not being significantly different from those reported in locations close to centers of human activity (13, 16, 17). These results prompt for a better understanding of the long-range distribution patterns of these compounds upon atmospheric transport. This goal is undertaken in the present study.

Sedimentary samples from high mountain lakes are analyzed for assessment of the contemporary background PAH pollution levels in Europe. The discussion is focused on PAH sediment fluxes. However, for purposes of comparison, concentration data are also given. The relative importance of pollution levels in these lakes is also evaluated by comparison to sediment data of other aquatic environments.

Methodology

Sample Collection and Handling. Samples were obtained by sediment coring in the deepest point of the lake. At lake shore, the cores were then divided in sections of 0.25 or 0.5 cm, wrapped with prerinsed aluminum foil, and stored frozen at -20°C until analysis in the laboratory.

Wet surficial sediments (0.1–0.5 g, 0–1 cm) were extracted by sonication with methanol ($1 \times 20 \text{ mL}$; 20 min) and subsequently with dichloromethane–methanol (2:1; $3 \times 20 \text{ mL}$; 20 min). The combined extracts were spiked with perdeuterated PAH (anthracene- d_{10} , pyrene- d_{10} , and benzo[ghi]perylene- d_{12}) as analyte surrogates. Then, they were vacuum evaporated to 10 mL and hydrolyzed overnight with 20 mL of 6% KOH in methanol. The neutral fractions were recovered with *n*-hexane ($3 \times 10 \text{ mL}$), vacuum evaporated until dryness, and transferred to a glass column (35 cm \times 0.9 id) packed with 2 g of activated aluminum oxide (120°C overnight). Two fractions were collected: 5 mL of *n*-hexane–dichloromethane (95:5; aliphatic hydrocarbons and organochlorine compounds) and 10 mL of *n*-hexane–dichloromethane (1:2; PAH). All fractions were vacuum and nitrogen concentrated to almost dryness and redissolved in isooctane prior to instrumental analysis. Perylene- d_{10} was added as

* Corresponding author phone: 34 93 400 61 00; fax: 34 93 204 59 04; e-mail: pfrqam@cid.csic.es.

TABLE 1. General Features of the High Mountain Lakes Included in This Study

lake	mountain range (country)	latitude	longitude	altitude (m asl)	lake area (ha)	catchment area (km ²)	max. water depth (m)	surficial sed accum rate (g/m ² yr)	surficial TOC (%)
1. Escura	Serra Estrela (Portugal)	40°21'17"N	7°38'06"W	1680	0.22	0.051	12.5	160	11
2. Cimera	Sierra Gredos (Spain)	40°16'N	4°36'50"W	2140	4.5	0.85	9.4	325	2.8
3. La Caldera	Sierra Nevada (Spain)	37°03'N	3°20'W	3050	2.3	0.18	11.3	250	2.3
4. Redó	Pyrenees (Spain)	42°38'34"N	0°46'13"E	2240	24	1.55	73	125	4.1
5. Noir	Alps (France)	45°25'N	7°07'E	2750	1.2	0.59	11	110	3.5
6. Schwarsee ob Sölden	Alps (Austria)	46°57'57"N	10°56'46"E	2799	4.3	0.14	18	65	4.5
7. Gossenköllesee	Alps (Austria)	47°13'49"N	11°00'51"E	2417	1.7	0.16	9.9	78	9.0
8. Dlugi	Tatra (Poland)	49°13'36"N	20°00'39"E	1783	1.6	0.66	10.6	72	10
9. Starolesnianske	Tatra (Slovakia)	49°10'N	20°10'E	2000	0.75	0.027	4.1	96	14
10. Maam	Donegal (Ireland)	54°59'19"N	8°07'00"W	436	5	na ^a	8.5	140	23
11. Øvre Neadalsvatn	Caledonian (Norway)	62°46'30"N	9°00'E	728	50	16	18	102	6.4
12. Arresjøen	Danskoya ^b (Norway)	79°40'N	10°48'E	20	35	3	32	23	6.1

^a Not available, na. ^b Spitsbergen Island.

internal standard for the injection process. Procedural blanks were performed with each set of eight samples.

Total organic carbon was determined with a CHN analyzer after acidification for carbonate removal.

GC-MS Analysis. The aromatic fractions were analyzed by GC (Carlo Erba GC8000 Series) coupled to a mass spectrometer (Fisons MD800). A 30 m HP-5MS column (0.25 mm i.d. × 0.25 μm film thickness) was used. The oven temperature program started at 90 °C (held for 1 min) to 120 °C at 15 °C/min and then to 300 °C at 4 °C/min and held for 10 min. Injector, transfer line, and ion source temperatures were 280, 300, and 200 °C, respectively. Helium was the carrier gas (1.1 mL/min), and the injector operated in the splitless mode (48 s). Data were acquired in the electron impact mode (EI, 70 eV ionization energy). PAH were determined in selected ion recording mode (SIR). The following diagnostic ions were selected: *m/z* 166, 184, 178, 192, 198, 202, 206, 216, 219, 226, 228, 234, 252, 276, 278, 300, and 302 (dwell time 40 ms per single ion, ion windows according to retention times of standards). PAH identification was performed by peak matching to retention time to reference standards and comparison to literature Lee retention indices (18, 19). Quantitative data were obtained by the external standard method (EPA mix 16, Dr. Ehrenstorfer). Compounds lacking reference standard were quantified using the response factor of the standard exhibiting the closest retention time. Recoveries for the overall procedure based on surrogate data were typically anthracene-*d*₁₀ 62 ± 18%, pyrene-*d*₁₀ 70 ± 18%, and benzo[ghi]perylene-*d*₁₂ 72 ± 12% (*n* = 27). Reported values were corrected by surrogate recoveries as follows: anthracene-*d*₁₀ for compounds having signals at ions *m/z* 166, 178, 184, 192; pyrene-*d*₁₀ for compounds at *m/z* 198, 202, 206, 216, 219, 226, 228; and benzo[ghi]perylene-*d*₁₂ for compounds at *m/z* 234, 252, 276, 278, 300, 302.

The whole analytical procedure was successfully calibrated with a standard reference material with certified PAH values (marine sediment HS-4, Institute for Marine Biosciences, Canadian National Research Council (20)). Fluxes were calculated by multiplication of the concentrations in the top cores (0.25–0.5 cm) with the sedimentation rates of the same upper core sections obtained from the ²¹⁰Pb deposition data.

Results and Discussion

Sampling Sites. A total of 12 lakes distributed throughout Europe were selected for study (Table 1). All but one fulfilled the above-mentioned conditions for high altitude mountain lakes. Lake Arresjøen in the Arctic (20 m asl) was selected as an example of one of the most remote European lakes.

Except Redó and Arresjøen (70 and 30 m water depth, respectively), all lakes have shallow water columns (4–18 m) with small catchment areas (0.027–16 km²) constituted

essentially by bare rock with few mosses and alpine meadows. All of them are covered annually with ice for at least several months.

All lakes are oligotrophic and have low total organic carbon in the waters: 0.23 mg/L (Dlugi) to 4.2 mg/L (Starolesnianske), averaging 1.4 mg/L. Conversely, the sedimentary total organic carbon is high: 23 mg/g dw (La Caldera) to 228 mg/g dw (Maam), averaging 84 mg/g dw. These high sedimentary organic carbon values likely reflect good organic matter preservation.

Distributions. The average PAH surface sediment distribution is represented in Figure 1. It is dominated by parent compounds, from phenanthrene to coronene, with a predominance of high molecular weight compounds of cata-condensed structures (21).

Despite the variability of PAH sources to the atmosphere, the PAH distributions in these high mountain lakes are remarkably similar (relative standard deviation values in the range of 26–40% for most compounds). Even the distribution of lakes with a very different PAH sedimentation flux are alike (e.g., Schwarsee ob Sölden and Starolesnianske, Figure 1). Only phenanthrene, retene, and perylene show more variability (relative standard deviation 95, 170, and 230%, respectively). These compounds may originate from biogenic sources besides combustion processes. Their higher variability probably reflects different biogenic/pyrolytic source ratios among lakes. In this respect, the PAH distributions more differentiated from average are found in Lakes Arresjøen and La Caldera, the main difference consisting of a dominance by phenanthrene (Figure 1). These two lakes are those with lower PAH concentrations of pyrolytic compounds, 180 and 260 ng/g, respectively. Thus, the higher relative proportion of phenanthrene is maybe related to a biogenic origin for this compound. However, in the case of lake Arresjøen it could also be due to the lower ambient temperatures which may enhance the condensation of this compound on the falling out particles. Apart from this feature, the relative abundance of the other parent PAH is very similar to the average even in these lakes.

The uniform sedimentary PAH profile found in all lakes exhibits a high parallelism with the PAH composition in the atmospheric aerosols collected at these high altitude sites (22). This profile is quite ubiquitous and has been reported in sediments from remote/rural areas (23, 24) or in sites where organic pollutant inputs are mainly related to atmospheric transport and deposition (17, 25). To this end, the relative proportion of the compounds more labile to photooxidation is low. Thus, the ratio of benzo[a]pyrene/(benzo[a]pyrene + benzo[e]pyrene) and benz[a]anthracene/(benz[a]anthracene + chrysene + triphenylene) range between 0.16 and 0.41

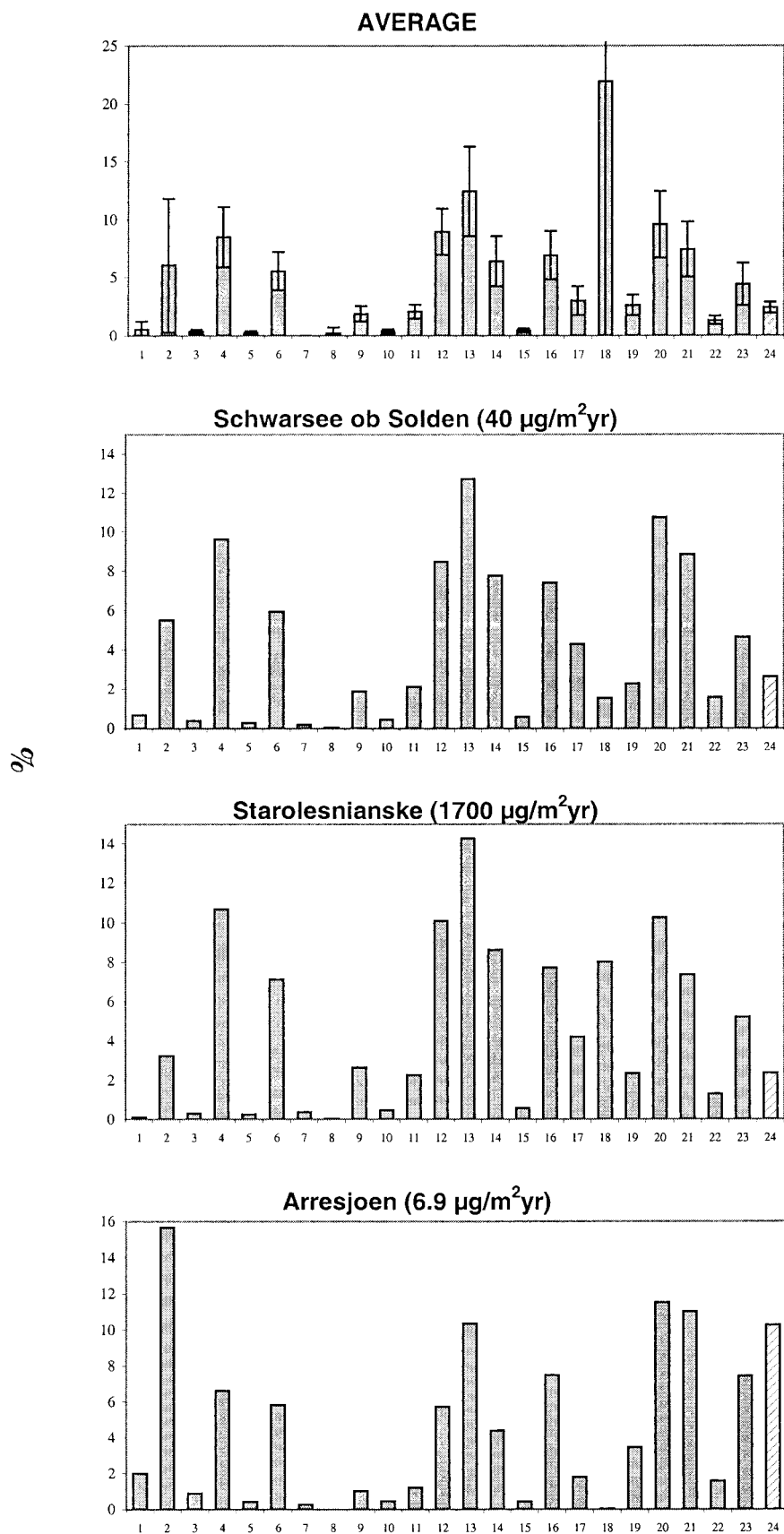


FIGURE 1. PAH distributions in sediments from high altitude mountain lakes. A, average composition of all lakes except Lake Arresjøen. See Table 2 for compound identification.

and 0.13–0.26, respectively, like in the remote sites of the North Pacific (3), Corsica (11), and the western Mediterranean Sea (25, 26).

Likewise, the content of methylphenanthrenes and dimethylphenanthrenes relative to phenanthrene is very low, 0.14–0.57 and 0.1–0.49, respectively, in consistency with

TABLE 2. PAH Surface Sediment Concentrations (ng/g dry wt)

compound	Escura	Cimera	La Caldera	Redó	Noir	Schwarsee ob Sölden	Gossen-kölle	Diugi	Staroles-nianske	Maam	Øvre Neådalsvatn	Arresjøen
1. fluorene	8.7	1.1	4.3	3.0	2.1	6.2	2.8	29	16	3.1	2.1	3.8
2. phenanthrene	50	10	42	45	23	48	46	470	590	49	22	28
3. anthracene	2.0	0.59	0.82	3.6	1.1	3.5	4.4	33	54	3.1	2.7	1.7
4. fluoranthene	77	22	18	86	52	85	71	1400	1950	78	45	16
5. acephen-anthrylene	3.0	0.78	0.81	2.6	0.93	2.4	1.8	48	45	2.0	1.8	1.3
6. pyrene	49	15	13	50	34	52	49	810	1300	40	37	12
7. benzo[a]fluorene	7.4	nd ^e	0.38	0.85	1.4	1.8	1.5	49	69	8.1	nd ^e	0.70
8. retene	2.6	0.20	2.3	2.5	0.17	0.41	1.5	3.8	5.6	1.2	12	0.73
9. benzo[ghi]-fluoranthene	25	5.0	3.9	18	7.8	17	11	360	480	36	6.9	3.2
10. cyclopenta[cd]-pyrene	3.3	0.75	0.80	2.3	0.95	3.9	2.3	76	89	3.2	2.4	1.4
11. benz[a]-anthracene	14	4.8	4.3	20	14	19	21	340	420	22	19	3.5
12. chrysene + triphenylene	59	25	16	82	67	74	79	1500	1800	150	54	17
13. benzo[b+j]-fluoranthene ^a	93	29	13	130	72	110	71	1800	2600	190	160	31
14. benzo[k]-fluoranthene	64	17	9.2	23	34	68	70	950	1600	82	47	14
15. benzo[a]-fluoranthene	4.5	0.79	0.76	3.3	1.1	5.2	3.2	77	100	6.3	6.0	1.4
16. benzo[e]pyrene	58	16	8.1	50	37	65	43	1000	1400	110	100	22
17. benzo[a]pyrene	23	5.1	4.6	15	16	38	30	470	770	21	37	5.0
18. perylene	16	37	2.4	4.1	480	31	5.8	73	110	1800	90	1.1
19. indeno-[7,1,2,3-cdef]-chrysene	27	7.7	3.3	28	9.1	20	15	36	430	44	33	10
20. indeno[1,2,3-cd]-pyrene	89	23	14	56	42	94	98	1400	1900	85	84	34
21. benzo[ghi]-perylene	72	21	11	39	35	78	46	1200	1350	79	85	32
22. dibenz[ah]-anthracene	14	2.9	2.7	7.6	6.6	14	12	190	240	16	11	4.7
23. coronene	39	12	6.8	16	18	41	17	680	950	31	52	21
24. methyl-178	12	3.1	24	15	9.7	7.6	22	200	250	30	7.5	4.0
25. dimethyl-178	13	1.8	15	13	6.7	4.6	12	100	140	24	4.8	3.0
PAHtot ^b	800	260	180	690	960	880	700	13 000	18 000	2900	800	260
PAHpyr ^c	780	220	180	680	480	850	690	13 300	18 000	1100	700	260
PAH ^d	650	190	150	600	430	730	620	12 000	16 000	910	690	210
PAHpyr/TOC (ng/g OC)	7200	7800	7700	17 000	14 000	14 000	8700	130 000	130 000	46 000	14 000	4300

^a Sum of *b* and *j* isomers. ^b Sum of all parent compounds. ^c Sum of all parent compounds except perylene and retene. ^d Sum of phenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[ghi]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene for comparison. ^e Below detection limit, nd.

the preferential loss of petrogenic hydrocarbons observed in the atmospheric PAH distributions of remote areas (25). Therefore, the PAH distribution in high altitude lake sediments is consistent with the previously reported atmospheric PAH homogeneization process by which only the compounds stable to photooxidation and chemical degradation survive long-range transport (2, 24, 25).

Furthermore, the occurrence of this distribution also indicates that the PAH mixtures are not significantly modified by water column processes during sedimentation. In these cold environments no relationship between water column depth and PAH composition changes during deposition is observed.

Concentrations. All sediments analyzed contained PAH at concentrations well over the quantitation limit (Table 2). The lakes with lower levels were those located at the periphery, being represented by Arresjøen, Cimera, and La Caldera (concentrations of parent compounds excluding perylene and retene 210, 190, and 150 ng/g, respectively). The lakes situated in more central sites, Pyrenees, Alps, Scandinavia, and also some of the periphery—Escura and Maam—, exhibit concentrations of these compounds in the 430–910 ng/g range. These levels are significantly lower than those in the Tatra mountains, 13 000–18 000 ng/g.

Table 2 concentrations can be compared with those reported in other aquatic systems, both freshwater and

marine. However, this is complicated by the different analytical methodologies (e.g., total vs specific compound determinations) and quantitation criteria (e.g., compounds included in the calculations) of other studies. Therefore, the PAH levels selected for comparison were chosen among those studies using similar analytical methods and compound grouping. As summarized in Table 3, the PAH concentrations detected in the central European lakes (excluding the Tatra mountains) are intermediate between contaminated sites near to urban/industrial centers (values of thousand ng/g) and remote marine or lacustrine areas (a few hundred ng/g). In contrast, the lakes from the Tatra mountains have PAH levels similar or exceeding the concentrations reported for sediments near to urban areas. The high concentrations found in the lakes of this mountain range are consistent with high fallout values of other atmospheric pollutants such as sulfate and nitrate (27). Irrespectively of quantitation or analytical methods, an obvious conclusion from Table 3 data is that atmospheric transport of PAH to these environments has been very significant, particularly in some European regions, despite their geographical remoteness from populated areas.

Fluxes. The PAH pollution load in these lakes can also be evaluated in terms of sedimentation fluxes. These have been calculated from Table 2 concentrations, sedimentation rates determined from ²¹⁰Pb and ¹³⁷Cs data, and sediment densities (28; Table 1). The lowest flux is found in Lake Arresjøen, 6.9

TABLE 3. PAH Sediment Concentrations and Fluxes

location	PAH (ng/g) ^a	PAH ($\mu\text{g}/\text{m}^2 \text{ yr}$)	ref
High Altitude Mountain Lakes			
West and Central Europe	180–1100 (150–910)	44–150 (38–130)	this study
East Europe	13000–18000 (11000–16000)	960–1700 (820–1500)	this study
Arresjøen (Arctic)	260 (210)	6.0 (4.9)	this study
Remote Lakes			
Lake Siskiwit (U.S.A.)		(100)	(2)
Lake Sagamore (Adirondack Park, NY)	2900		(33)
Lake Woods (Adirondack Park, NY)	11000		(33)
Larto Lake (rural LA, U.S.A)	100		(34)
lakes in Adirondacks region (U.S.A.)	(2500–4000)	(200–650)	(35)
lakes located at Northern Great Lakes (U.S.A.)	(300–1800)	(105–550)	(35)
lakes in Northern Florida (U.S.A.)	(750–1450)	(280–540)	(35)
lakes in Northern New England (U.S.A.)	(2000–2800)	(130–680)	(35)
Urban/Industrial Lakes			
Lake Michigan (U.S.A.)	1300–3500	90–1050	(17)
Lake Zürich (CH)	15000		(9)
Lake Lucerne(CH)	5000		(9)
Greifensee (CH)	6000		(9)
Washington (U.S.A.)	7000		(9)
Priest Pot (U.K.)	16000	6200	(36)
Windermere (U.K.)	12000	4700	(36)
Mediterranean Sea (Remote)			
Ligurian Sea off Monaco	(600–720)		(37)
Adriatic Sea	(12–170)		(38)
Island of Crete (100–1000 m)	15–160		(39)
Western deep basin	430–600	160–190	(23)
Eastern deep basin	150–570	10–100	(23)
Mediterranean Sea Coastal Areas			
Venice Lagoon		100	(30)
Gulf of Lions	420–760	290–680	(23)
coastal area near urban centers (Spain)	(1400–2300)		(40)
Rhone prodelta	1200–2400	4900–18000	(23)
Ebro prodelta	62–190	120–750	(23)
Catalan Coast	340–480	300	(23)
Black Sea			
near the mouth of Danube river	1500 (1100)		
in abyssal plain sediments	290–780 (210–640)	18–47 (13–38)	(31)
Coastal Areas (U.S.A.)			
Basin of Puget Sound, WA	(1100)	(3100)	(41)
Narragansett Bay, RI		400–3100	(42)

^a Otherwise noted, PAH values correspond to PAHpyr in Table 2, determined individually by GC-MS or GC-FID. In brackets, sum of phenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[fluoranthene], benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene.

$\mu\text{g}/\text{m}^2 \text{ yr}$, constituting one of the lowest values reported in the literature (Table 3 and Figure 3). The lakes in west and central Europe have similar values ranging between 44 $\mu\text{g}/\text{m}^2 \text{ yr}$ (La Caldera) and 150 $\mu\text{g}/\text{m}^2 \text{ yr}$ (Lough Maam), with average and standard deviation fluxes of 79 and 36 $\mu\text{g}/\text{m}^2 \text{ yr}$, respectively. The east European lakes are those with highest fluxes, 960–1700 $\mu\text{g}/\text{m}^2 \text{ yr}$, consistently with the high concentrations found in these lakes.

The high fluxes in these lakes from the Tatra mountains are similar to those found in lakes situated near urban or industrial areas (90–1050, 4700, 6200 $\mu\text{g}/\text{m}^2 \text{ yr}$; Table 3). In contrast, the fluxes in west and central Europe are lower than those reported in sediments from northeast U.S.A. remote sites that have essentially received atmospherically transported inputs (100–680 $\mu\text{g}/\text{m}^2 \text{ yr}$; Table 3). The difference is even higher when considering that the reported U.S. flux values include a lower number of individual parent compounds.

Comparison to the fluxes reported for marine systems shows that the values in the central and west Europe are in the same range than those in the eastern (23) and western Mediterranean Sea deep basins (10–190 $\mu\text{g}/\text{m}^2 \text{ yr}$ (23, 29))

or in the Venice Lagoon (100 $\mu\text{g}/\text{m}^2 \text{ yr}$ (30)). In contrast, they are higher than those in open deep sediments from the Black Sea (18–47 $\mu\text{g}/\text{m}^2 \text{ yr}$ (31)) and lower than those measured in the Catalan Coast in the northwestern Mediterranean Sea (300 $\mu\text{g}/\text{m}^2 \text{ yr}$ (23)). In any case, the differences are not large suggesting that in the case of parent compounds, atmospheric PAH deposition is also a very significant source of these pollutants both in coastal and open sea environments.

Comparison of these lake sedimentary fluxes with atmospheric deposition fluxes in remote areas such as the central and western Mediterranean Sea (29–97 and 40–80 $\mu\text{g}/\text{m}^2 \text{ yr}$, (29, 32)) shows similar values to those found in the west and central Europe. These values are a bit lower than those reported for dry PAH deposition in Lake Siskiwit, Great Lakes (168 $\mu\text{g}/\text{m}^2 \text{ yr}$ (2)).

TOC Normalization. PAH standardization to TOC fluxes provides a simplified picture of the geographical distribution of these pollutants in the lakes considered for study. Whereas the two lakes from the Tatra Mts. exhibit deposition fluxes of 960 and 1700 $\mu\text{g}/\text{m}^2 \text{ yr}$, the PAH/TOC ratios are 130 $\mu\text{g}/\text{g}$ in both cases (Figure 2). Likewise, whereas lakes Escura, Cibera, and La Caldera in the Iberian Peninsula exhibit

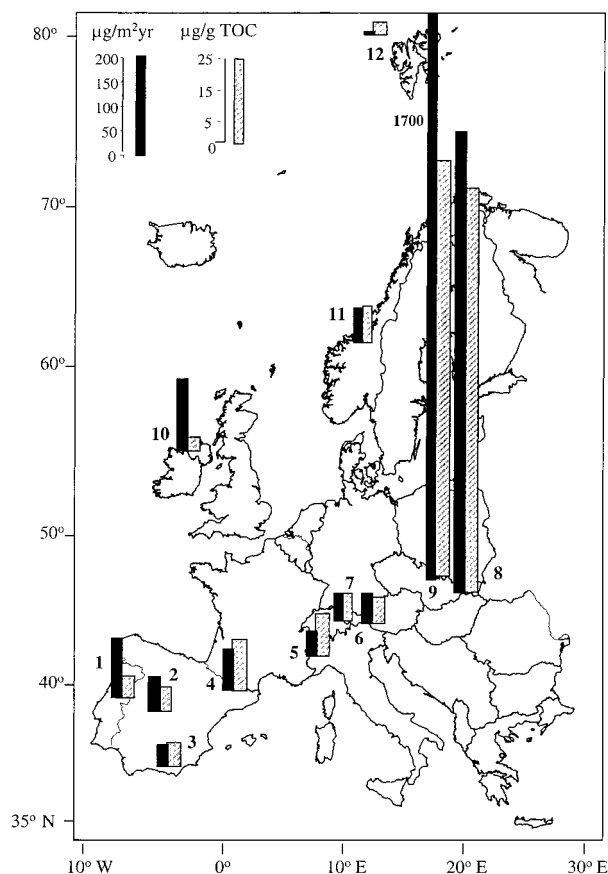


FIGURE 2. Sedimentary PAH fluxes ($\mu\text{g}/\text{m}^2 \text{ yr}$) and PAH values normalized to TOC ($\mu\text{g}/\text{g TOC}$) in sediments from high altitude mountain lakes. Lake identification as in Table 1.

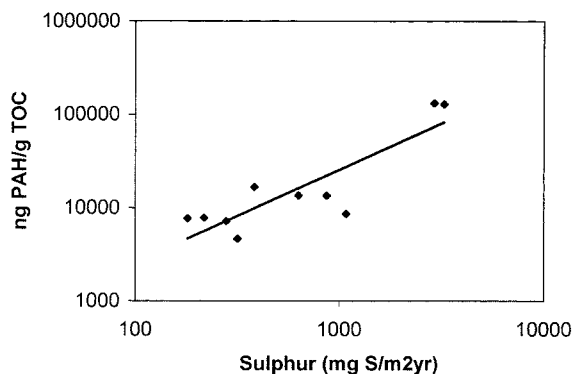


FIGURE 3. Log scale representation of the TOC normalized sedimentary PAH concentrations in the high altitude lakes vs annual average sulfate deposition in the lake areas.

sedimentation fluxes of 120, 70, and $44 \mu\text{g}/\text{m}^2 \text{ yr}$, respectively, the PAH/TOC ratios are 7.2, 7.8, and $7.7 \mu\text{g}/\text{g}$, respectively, showing a uniform value for this region. Those lakes situated at more distant sites from continental influence, Arresjøen and Maam, also show a significant uniformity for this ratio, 4.9 and $4.6 \mu\text{g}/\text{g}$, respectively, whereas the deposition fluxes were 6.0 and $140 \mu\text{g}/\text{m}^2 \text{ yr}$, respectively. Finally, these ratios show rather uniform values for the samples in the Alps and the Pyrenees ($13\text{--}17 \mu\text{g}/\text{g}$, with the exception of $7.7 \mu\text{g}/\text{g}$ for Gossenkölle Lake).

This homogenization of PAH concentration/fluxes when referring to TOC is unlikely to reflect changes in sedimentary preservation since all lakes have high TOC contents. Furthermore, as indicated above, the PAH mixtures arriving at these high altitude lakes have undergone intensive photo-

oxidation and chemical degradation during transport. Thus, the PAH mixtures accumulated in the sediments probably constitute one of the most refractory fractions. Conversely, the observed trend probably reflects normalization in terms of sedimentary focusing factor.

Thus, normalization to TOC shows a uniform pattern in terms of continental influence and east–west distribution. The lowest PAH/TOC values, $4.6\text{--}4.9 \mu\text{g}/\text{g}$, are found in the lakes situated at higher distance from continental inputs. Westernmost sites (Iberian Peninsula) constitute another group, $7.2\text{--}7.8 \mu\text{g}/\text{g}$. In central Europe the lakes in the Alps and the Pyrenees define another group ($13\text{--}17 \mu\text{g}/\text{g}$). Finally the highest values are found in the Tatra Mts. ($130 \mu\text{g}/\text{g}$).

This uniform pattern of TOC normalized PAH concentration/fluxes is consistent with the annual average atmospheric sulfate deposition fluxes. Log scale representation of the PAH/TOC ratios vs sulfate deposition in the lake regions (EMEP data) exhibits a linear concentration with a high regression coefficient ($r = 0.97$; Figure 3). This good correspondence points to association to combustion particles as the main PAH transport route into high altitude lakes.

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