

# Polycyclic aromatic hydrocarbons in peat cores from southern Poland: distribution in stratigraphic profiles as an indicator of PAH sources

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## SUMMARY

Polycyclic aromatic hydrocarbon (PAH) concentrations were measured in 44 peat samples taken from different stratigraphical layers of 12 mires located in four regions of southern Poland (the Sudeten and Tatra Mountains, Silesian Lowland and Orawa Basin). Relationships between PAH concentrations and botanical composition (genus) of the peat and its geochemical properties (contents of ash, nitrogen, organic carbon, humic acid, fulvic acid and exchangeable cations, as well as pH) were explored. The total concentration of 15 USEPA PAHs and benzo[e]pyrene was between 39 and 384 ng g<sup>-1</sup> in all samples except those from Lasówka, a fen in the Sudeten Mountains, where an extremely high PAH concentration (3746 ng g<sup>-1</sup>) was recorded. The concentrations of PAHs apart from perylene were influenced by the location and type of mire, indicating that most of these compounds were of anthropic origin. In some samples the perylene concentration greatly exceeded the total concentration of the other 16 PAHs measured. The high concentrations of perylene in deeper peat layers may have arisen through sorption from water during peat formation, or through biogenic processes.

**KEY WORDS:** atmospheric pollution, Black Triangle, mire geochemistry, peatland, polyarenes.

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), also known as polyarenes, are common in the environment and have been much studied since it was discovered that some of them are carcinogenic and mutagenic. PAHs are derived from both natural and anthropic sources (e.g. Coleman *et al.* 1997; Ollivon *et al.* 1995; Badley *et al.* 1994). Small amounts of PAHs have also been found in geological formations such as hard coal, brown coal, crude oil and bituminous shales (e.g. Simoneit & Fetzer 1996; Pu *et al.* 1990; Bence *et al.* 1996; Bojakowska & Sokołowska 2001a, 2001b, 2001c; Lavric & Spangenberg 2002). The concentration of anthropogenic PAHs in the environment is typically many times higher than that of PAHs of natural origin. The main anthropic sources are processes involving the combustion of organic matter with restricted oxygen supply (Howsam & Jones 1998).

Under natural conditions, polyarenes are formed as a result of the pyrolysis of organic materials at high temperatures during forest, steppe and peatland fires, and during volcanic eruptions (Cappacioni *et al.* 1995). The amounts and types of PAHs produced during the combustion of plant material depend upon the quantity of material, the character and

intensity of burning, and the plant species involved (McDonald *et al.* 2000; Oros & Simoneit 2001). Some natural PAHs are produced by vital metabolic processes and during crude oil formation. They can also be produced during decay processes leading to biotransformation of organic matter (Niederer *et al.* 1995; Dorn & Metz 1996; Jones *et al.* 1997) and by biochemical transformations of precursors of aromatic substances during the early diagenesis of sedimentary rocks. Amongst the most important natural precursors of polyarenes are isoprenoids, especially triterpenes and sterols (Neilson & Hynning 1998).

About 90% of the PAHs present in the environment can be stored in soils and sediments (Wild & Jones 1995), which are thus the best environmental "sink" for these compounds. However, the half-life of PAHs is longer in soil than in the atmosphere or in plants.

As locations for the biogenic accumulation of peat, which may be regarded as the youngest and least transformed sedimentary rock, mires provide records of the changing fluxes of organic compounds from both natural and anthropic sources (Berset *et al.* 2001). The peat is made up of layers that differ in their degree of decomposition, botanical composition and age; and different types

of peat show different microbial activity, acidity, degree of anaerobiosis and content of humic substances. The accessibility of these properties, especially botanical composition, makes it possible to investigate the natural processes of PAH formation from precursors of aromatic compounds, which are as yet poorly understood. In recent years, the PAH content of peat has been analysed across the stratigraphic profile (Wiłkomirski *et al.* 2002; Malawska *et al.* 2002a, 2002b).

The objectives of the study reported here were to determine the levels of polyarene pollution at selected mires in southern and western Poland; to study the variation in PAH content along depth gradients; to attempt to identify the sources of different PAHs in the peat; and to explore the relationships between PAH content and the physico-chemical properties of the peat.

## SITES AND METHODS

Peat samples were collected between June and October 2001 from four areas in southern and south-western Poland; namely the Sudeten Mountains (peatlands D1–D3), the Silesian Lowland (peatlands E1, E2), the Orawa Basin (peatlands F1, F2) and the Tatra Mountains (peatlands G1–G5). Details of the sites are given by Malawska *et al.* (2006). These areas encompass a wider variety of site conditions than the rest of Poland. Peatland F2 was a transition mire, peatlands D3, E1, E2 and G1 were fens, and the remainder were raised bogs.

The locations at which peat coring was carried out were selected on the basis of specialist geological documentation. At each site, a peat sample was collected from each horizon of the stratigraphic profile using a Russian sampler with chamber length 0.5 m. Horizons were determined according to their subfossil communities and allocated to a peat species according to Polish Standard PN-85/G-02500 (1985).

The peat samples were stored at  $-20^{\circ}\text{C}$  until analysis. They were then thawed and dried at  $5^{\circ}\text{C}$ , sieved through a 2 mm mesh to remove large particles and undecomposed plant debris, and subsequently kept at  $5^{\circ}\text{C}$ . Extraction was performed using dichloromethane in a Sottec apparatus and further purification was carried out by column chromatography on Florisil. Quantitative analysis employed the external standard method with the certified (Ultra Scientific Ltd.) standard. PAH concentrations were determined using a gas chromatograph (5890 II) equipped with a mass selective detector (GC/MSD Hewlett Packard) and a non-polar capillary HP-5 column (length 24 m,

diameter 0.2 mm, film thickness  $0.33\ \mu\text{m}$  diphenyl-95% dimethylpolysiloxane). The temperature programming applied was:  $70^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  at  $10^{\circ}\text{C min}^{-1}$ , then to  $300^{\circ}\text{C}$  at  $2.5^{\circ}\text{C min}^{-1}$  (7 min). The detector temperature was  $280^{\circ}\text{C}$  and the detection limit was *ca.*  $0.1\ \text{ng g}^{-1}$  dry weight, assuming 10 g of sample used. The PAHs determined were perylene and benzo[e]pyrene, together with 15 of the 16 listed as priority pollutants by the United States Environmental Protection Agency (USEPA), namely:

acenaphthene,  
acenaphthylene,  
anthracene,  
benzo[a]anthracene,  
benzo[a]pyrene,  
benzo[b]fluoranthene,  
benzo[ghi]perylene,  
benzo[k]fluoranthene,  
chrysene,  
dibenzo[ah]anthracene,  
fluoranthene,  
fluorene,  
indeno[123cd]pyrene,  
phenanthrene and  
pyrene.

The analysis procedures were checked for recovery rate and reproducibility according to quality assurance and quality control (QA/QC) standards for PAH determination. The extraction efficiency was investigated by spiking peat samples with four standards. For all of these compounds, recovery was in the range 79–94%. Reproducibility for individual PAHs was calculated from the results of replicate analyses, which indicated an error between 3.1 and 8.4%. Ten percent of the samples were extracted and analysed in duplicate. After analysis of every 10 samples, standard samples with known PAH contents were analysed. A solvent blank was analysed after every 20 samples as a check on the response of the gas chromatograph.

## RESULTS

Forty-four peat samples were taken from individual stratigraphic horizons of the 12 mires, classified on the basis of botanical origin, and assigned to one of three major genetic types:

- fen peat (14 samples) belonging to genera *Alnioni*, *Bryalo-Parvocaricioni* and *Magnocaricioni*;
- transition mire peat (4 samples) belonging to genera *Betulioni* and *Minero-Sphagnioni*; and
- raised bog peat (23 samples) belonging to genera *Ombro-Sphagnioni* and *Ledo-Pinioni*.

The remaining three samples consisted of gytja.

Tables 1a and 1b show the concentrations of the 17 unsubstituted PAHs in the peat samples. The levels of the 15 USEPA PAHs and benzo[e]pyrene were generally lower than those in the surface layers of mineral soils in unpolluted areas, with a mean value for all samples of  $84 \text{ ng g}^{-1}$ . For 11 of the mires, total concentrations of these 16 PAHs were between  $39$  and  $384 \text{ ng g}^{-1}$ ,  $>100 \text{ ng g}^{-1}$  in most samples, and  $<50 \text{ ng g}^{-1}$  in only two samples (from mires E1 and F2). At mire D3 (Lasówka), a very high concentration of  $3746 \text{ ng g}^{-1}$  was recorded.

The concentrations of pyrene and chrysene tended to be higher in fens than in transition mires and raised bogs. Five-ring PAHs, except for benzo[b]fluoranthene, occurred only in the Sudeten mires (D1–3). Indeno[123cd]pyrene was present only in the surface layers of mires D1–3, and in small amounts in the surface layer of mire G5 (Tatras). Benzo[ghi]perylene occurred in large amounts in mire D3, in the surface layers of mire D2, and in the middle layers of the raised bogs (F1, D1 and the Tatra raised bogs G2–5). Fluorene, phenanthrene and fluoranthene were present in all the mires; phenanthrene concentrations were almost identical in all samples except those from mire D3.

The concentration of perylene was in the range  $0$ – $2567 \text{ ng g}^{-1}$  and it increased with depth at all sites except the fens E1, E2, and G1. In fens, the concentration of perylene usually exceeded that of USEPA PAHs and benzo[e]pyrene, whereas in the majority of raised bogs (except D2) it accounted for only a small fraction of the total PAHs. In the most polluted mire (D3), the concentration of perylene was only  $1/50$  of the sum of USEPA PAHs and benzo[e]pyrene. Fluorene, phenanthrene, fluoranthene, pyrene and perylene dominated in all the peat types.

Figure 1 shows the concentrations of USEPA PAHs with different numbers of rings in their structures in each of the peat layers in the Sudeten mires (D1–D3) and the Silesian mires (E1, E2). Raised bogs D1 and D2 contained 3, 4, 5 and 6-ring PAHs, with the highest contents in the surface layers (not exceeding  $300 \text{ ng g}^{-1}$  in mire D1 and  $400 \text{ ng g}^{-1}$  in mire D2). In mire D1, 6-ring PAHs were present in the surface layers and in one deeper layer. The surface layers of mire D2 contained the highest concentrations of 5-ring PAHs as well as 6-ring PAHs that were absent from the deeper layers. In mire D3, there were 3, 4, 5 and 6-ring PAHs, reaching a concentration of almost  $4000 \text{ ng g}^{-1}$ . Here, PAHs with 4 rings were dominant, the concentrations of heavy 5 and 6-ring PAHs were higher than in the other mires, and 3-ring PAHs were least abundant.

Figure 2 shows the concentrations of USEPA PAHs with different numbers of rings in their structures in each of the peat layers of the Orawa mires (F1, F2) and the Tatra mires (G1–G5). In raised bog F1, 3, 4 and 6-ring PAHs were present in low concentrations, 3-ring PAHs were dominant and PAHs with 6 rings occurred throughout the stratigraphic profile. The wood peats of mires F2 and G1 were similar in that they had the lowest concentrations of USEPA PAHs found in any of the mires, with only 3 and 4-ring PAHs at concentrations not exceeding  $100 \text{ ng g}^{-1}$ . The Tatra raised bogs were characterised by small concentrations of 5-ring PAHs, which were present also in deeper peat layers, and 6-ring PAHs occurring in the deeper layers of raised bogs G2–G4. In mire G5, 6-ring PAHs were found only in the two shallowest peat layers.

Tables 2 and 3 summarise the geochemical properties of the peat genera and their PAH concentrations. The lowest concentrations of USEPA PAHs and benzo[e]pyrene were in alder (*Alnioni*) and birch (*Betulioni*) peats. The PAHs in *Sphagnum* transition mire (*Minero-Sphagnioni*) peat were mainly light (3 and 4-ring), 5-ring PAHs were absent and the only 6-ring PAH was benzo[ghi]perylene. The highest concentrations of 3-ring PAHs occurred in sedge fen (*Magnocaricioni*) and *Sphagnum* raised bog (*Ombro-Sphagnioni*) peat. USEPA PAHs and benzo[e]pyrene were also most abundant in sedge peat (e.g.  $3746 \text{ ng g}^{-1}$  in mire D3) and in *Sphagnum* raised bog peat, where the total concentration ranged from  $57$  to  $384 \text{ ng g}^{-1}$  and that of perylene from  $0$  to  $632 \text{ ng g}^{-1}$ . *Sphagnum* raised bog peat is typically located in the surface layers of mires, where it can accumulate pollutants from the atmosphere. Botanical composition can also influence the level of contamination by PAHs, which are lipophilic (Simonich & Hites 1994) so that plants that are rich in lipids may tend to absorb more PAHs.

The lowest and highest mean perylene concentrations were found in fen peats, with  $71.8 \text{ ng g}^{-1}$  in *Bryalo-Parvocaricion* and  $1574.5 \text{ ng g}^{-1}$  in *Alnioni* peat. Intermediate concentrations were found in transition mire (*Minero-Sphagnioni*,  $333.7 \text{ ng g}^{-1}$ ) and raised bog (*Ombro-Sphagnioni*,  $128.4 \text{ ng g}^{-1}$ ) peat. Sedge (*Magnocaricioni*) peat had a high mean perylene concentration ( $514.6 \text{ ng g}^{-1}$ ) as well as the highest concentration of USEPA PAHs due to the heavy pollution of mire D3.

The concentration of perylene was highly correlated with pH ( $r^2 = 0.6$ ), degree of peat decomposition ( $r^2 = 0.6$ ) and total nitrogen content ( $r^2 = 0.6$ ), suggesting that this compound is produced in large amounts in fen peat. Fens are less

Table 1. Peat stratigraphy and content of 17 unsubstituted PAHs (ng g<sup>-1</sup>) in peat samples from the Sudeten Mountains and Silesian Lowland mires. Peat species: *alb*: *Alno-Betuleti*; *aln*: *Alneti*; *bet*: *Betuleti*; *bry*: *Bryaleti*; *cab*: *Carici-Bryaleti*; *cap*: *Carici-Phragmiteti*; *car*: *Cariceti*; *cus*: *Cuspidato-Sphagneti*; *ers*: *Eriophoro-Sphagneti*; *eus*: *Eusphagneti*; *pin*: *Pineti*; *pis*: *Pino-Sphagneti*; *spc*: *Sphagno-Cariceti* (Polish Standard PN-85/G-02500, 1985).

study area	site code	site name	sample depth (cm)	peat species	acenaphthylene	acenaphthene	fluorene	phenanthrene	anthracene	fluoranthene	pyrene	benzo[a]anthracene	chrysene	benzo[b]fluoranthene	benzo[k]fluoranthene	benzo[e]pyrene	benzo[a]pyrene	dibenzo[ah]anthracene	indeno[123cd]pyrene	benzo[ghi]perylene	sum of 15 US EPA PAHs and benzo[e]pyrene	perylene
SUDETEN MOUNTAINS	D1	Zieleniec – Czarne Bagno	60-225	<i>ers</i>	4	7	16	60	0	28	19	9	40	43	21	16	0	0	32	0	295	0
			225-450	<i>eus</i>	4	7	18	67	0	20	13	0	12	0	0	0	0	0	0	0	141	0
			450-575	<i>ers</i>	8	8	24	72	6	21	15	0	13	16	0	0	0	0	0	29	212	0
			575-725	<i>ers</i>	0	10	19	83	5	41	22	0	17	13	0	0	0	0	0	0	210	425
			725-810	<i>cus</i>	0	0	6	31	0	13	7	0	0	0	0	0	0	0	0	0	57	38
	D2	Zieleniec – Topielisko	100-175	<i>ers</i>	0	5	14	70	4	39	25	11	39	44	19	18	15	0	45	36	384	0
			175-325	<i>ers</i>	0	9	17	65	4	52	32	10	42	56	13	26	13	0	39	0	378	516
			325-400	<i>eus</i>	11	15	35	95	5	25	17	0	10	12	0	0	0	0	0	0	225	591
			400-455	<i>spc</i>	0	6	12	41	0	17	10	0	0	0	0	0	0	47	0	0	133	903
			455-530	<i>car</i>	0	10	14	47	0	11	7	0	0	0	0	0	0	53	0	0	142	1203
			530-600	<i>car</i>	0	13	17	58	0	12	7	0	0	0	0	0	0	0	0	0	107	437
	D3	Lasówka	15-40	<i>car</i>	4	29	30	298	47	596	425	297	405	352	158	207	316	38	290	254	3746	81
SILESIA LOWLAND	E1	Chocianów I	60-70	<i>cab</i>	0	4	7	22	0	6	0	0	0	0	0	0	0	0	0	0	39	248
			70-115	<i>car</i>	0	6	14	53	0	14	8	0	0	0	0	0	0	0	0	0	95	273
			115-200	<i>cap</i>	6	12	21	56	0	29	15	0	11	0	0	0	0	0	0	0	150	966
			200-310	<i>cab</i>	6	8	21	61	4	22	15	0	8	0	0	0	0	0	0	0	145	39
			310-365	<i>gyttja with organic remains</i>	5	8	28	67	5	30	17	0	0	0	0	0	0	0	0	0	160	76
			365-420	<i>algal gyttja</i>	0	5	12	34	0	14	9	0	0	0	0	0	0	0	0	0	74	299
	E2	Chocianów III	30-73	<i>alb</i>	0	4	11	46	0	20	12	0	8	0	0	0	0	0	0	0	101	97
			73-130	<i>cap</i>	4	11	22	82	6	31	22	0	9	0	0	0	0	0	0	0	187	50

Table 1b. Peat stratigraphy and content of 17 unsubstituted PAHs (ng g<sup>-1</sup>) in peat samples from the Orawa Basin and Tatra Mountains mires. See legend to Table 1a for key to peat species.

study area	site code	site name	sample depth (cm)	peat species	acenaphthylene	acenaphthene	fluorene	phenanthrene	anthracene	fluoranthene	pyrene	benzo[a]anthracene	chrysene	benzo[b]fluoranthene	benzo[k]fluoranthene	benzo[e]pyrene	benzo[a]pyrene	dibenzo[ah]anthracene	indeno[123cd]pyrene	benzo[ghi]perylene	sum of 15 US EPA PAHs and benzo[e]pyrene	perylene
ORAWA BASIN	F1	Bór nad Czerwonym	50-160	<i>cus</i>	0	6	16	63	0	21	15	0	0	0	0	0	0	0	0	28	149	0
			160-240	<i>ers</i>	0	6	11	35	0	6	0	0	0	0	0	0	0	0	0	49	107	0
			240-295	<i>spc</i>	0	6	11	39	0	8	4	0	0	0	0	0	0	0	0	60	128	0
			295-350	<i>pis</i>	0	10	15	60	0	19	12	0	0	0	0	0	0	0	0	0	116	632
			350-395	<i>pis</i>	0	6	10	41	0	10	0	0	0	0	0	0	0	0	0	32	99	533
			395-430	<i>pin</i>	0	6	9	30	0	13	0	0	0	0	0	0	0	0	0	25	83	0
TATRA MOUNTAINS	G2	Puścizna Rękowiańska	20-50	<i>bet</i>	0	4	8	25	0	6	0	0	0	0	0	0	0	0	0	0	43	170
			50-80	<i>aln</i>	0	6	10	34	0	7	0	0	0	0	0	0	0	0	0	0	57	1945
	G1	Pardałówka	20-55	<i>aln</i>	0	5	8	28	0	9	7	0	0	0	0	0	0	0	0	0	57	2567
			55-110	<i>aln</i>	0	5	9	31	0	7	4	0	0	0	0	0	0	0	0	0	56	1689
	G2	Smreczyński Staw	15-35	<i>pin</i>	0	5	9	36	0	17	11	0	20	14	0	0	0	0	0	0	112	20
			35-80	<i>ers</i>	0	7	14	70	4	17	9	0	0	0	0	0	0	0	0	57	178	0
	G3	Ornak	60-125	<i>eus</i>	5	10	20	71	0	21	13	0	10	13	0	0	0	0	0	0	163	0
			125-180	<i>ers</i>	0	7	13	43	0	10	5	0	0	0	0	0	0	0	0	24	102	0
			180-210	<i>ers</i>	0	7	20	82	5	33	18	0	13	17	0	0	0	0	0	90	285	0
			243-280	<i>pis</i>	0	5	10	35	0	11	7	0	10	0	0	0	0	0	0	0	78	17
	G4	Toporowe Stawy	125-200	<i>ers</i>	0	7	13	45	0	9	4	0	0	0	0	0	0	0	0	0	78	0
			200-270	<i>eus</i>	0	6	14	53	0	17	9	0	10	13	0	0	0	0	0	27	149	0
			270-325	<i>spc</i>	0	10	18	44	0	22	13	0	11	13	0	0	0	0	0	0	131	98
			325-390	<i>gyttja with wood</i>	0	7	11	28	0	8	0	14	0	0	0	0	0	0	0	0	68	826
	G5	Pańszczyc Wielka	20-110	<i>eus</i>	0	8	14	54	0	15	11	0	9	0	0	0	0	0	20	0	131	0
			110-205	<i>ers</i>	0	6	14	57	0	13	7	0	0	0	0	0	0	0	0	33	130	0
			205-355	<i>bry</i>	0	6	13	49	0	11	6	0	0	0	0	0	0	0	0	0	85	0
			355-420	<i>bry</i>	0	6	14	66	4	20	12	0	0	0	0	0	0	0	0	0	122	0

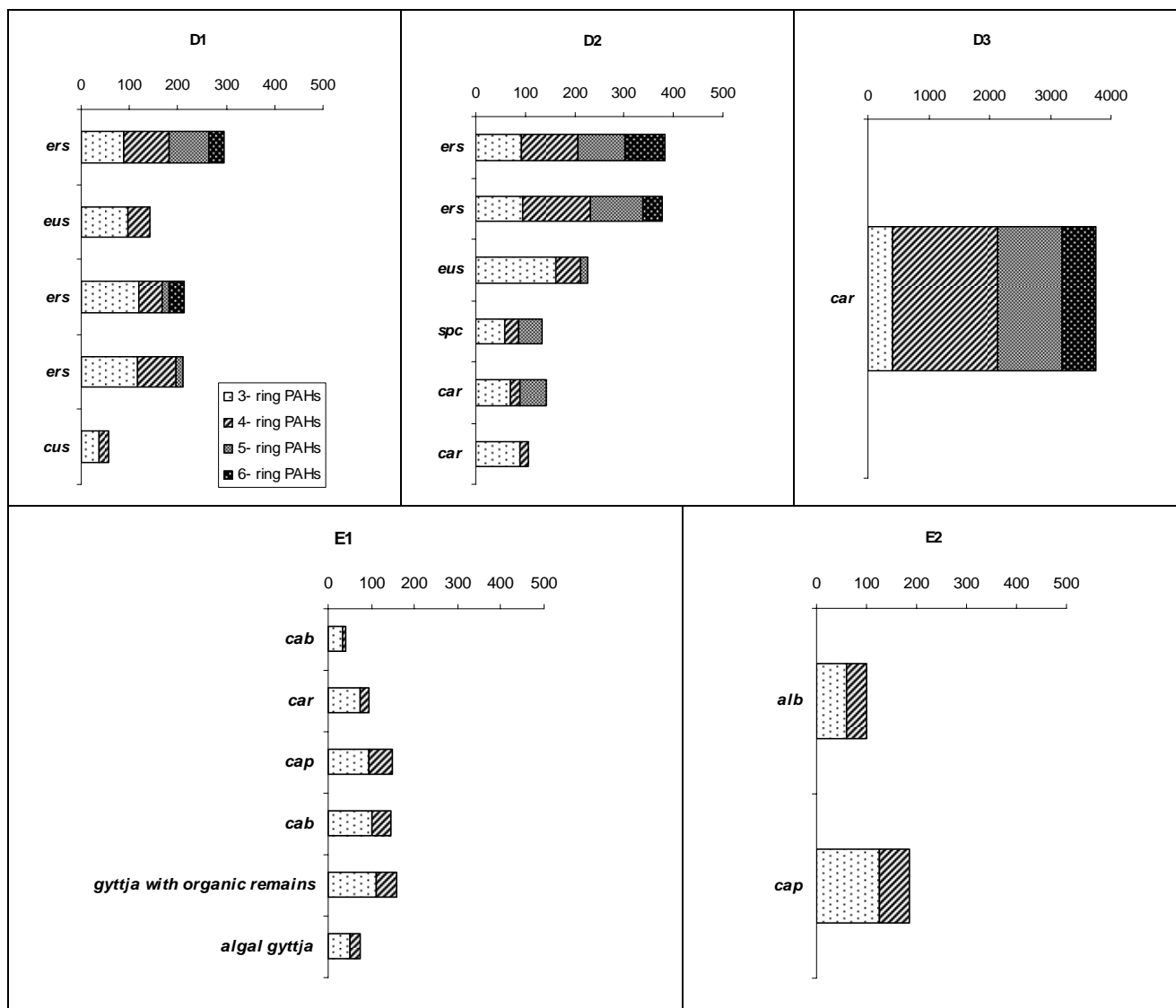


Figure 1. PAH contents ( $\text{ng g}^{-1}$ ) of peat samples from the study sites in the Sudeten Mountains (D1–D3) and the Silesian Lowland (E1, E2), arranged in order of depth from the mire surface. Each bar is divided to indicate the content of PAHs with different numbers of rings in their chemical structures.

acidic and more fertile than raised bogs and microbial activity is enhanced at higher pH; this may also explain the high concentration of perylene in gyttja, which is 100% decomposed. A significant negative correlation ( $r^2 = -0.5$ ) was found between the concentrations of benzo[ghi]perylene and total nitrogen, suggesting that benzo[ghi]perylene is produced by natural biochemical transformation of the perylene precursors in nitrogen-poor raised bogs. The concentration of phenanthrene, which is also likely to be produced in mires through biochemical transformation of precursors of aromatic compounds (Simoneit 1998), was independent of geochemical factors. Presumably,

different processes can lead to phenanthrene production; thus, they may occur under a large variety of geochemical conditions. It is possible that phenanthrene precursors are common in peat, independent of the conditions.

Figure 3a shows the result of a cluster analysis that explored the similarity of peat genera on the basis of their PAH contents. The fen peat genera *Alnioni*, *Magnocaricioni* and *Bryalo-Parvocaricioni* were most similar, and were grouped at the next level with *Betulioni* (transition mire) peat. The second similarity group contained the raised bog peat genera *Ombro-Sphagnioni*, *Minero Sphagnioni* and *Ledo-Pinioni*.

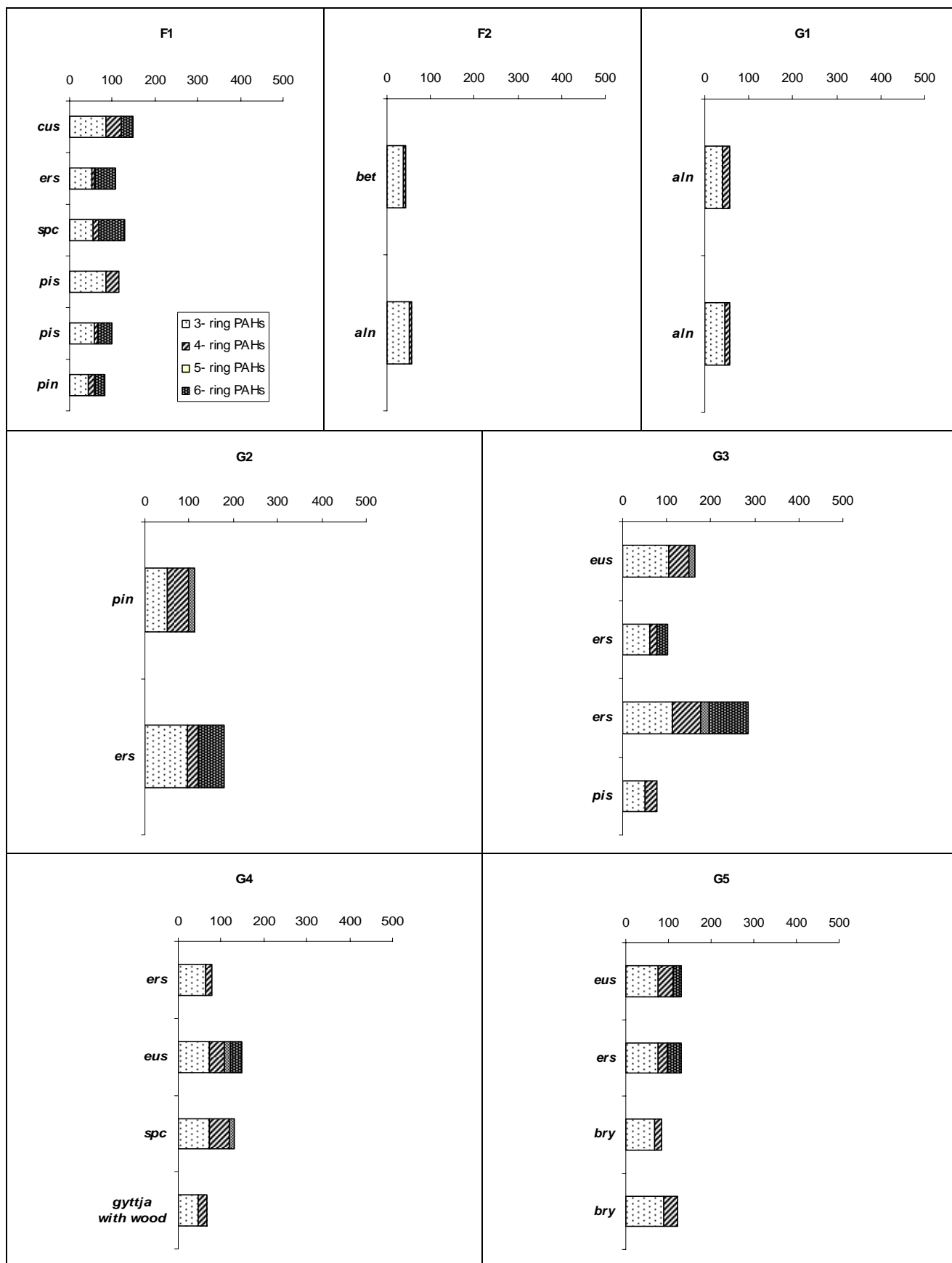


Figure 2. PAH contents ( $\text{ng g}^{-1}$ ) of peat samples from the study sites in the Orawa Basin (F1, F2) and the Tatra Mountains (G1–G5), arranged in order of depth from the mire surface. Each bar is divided to indicate the content of PAHs with different numbers of rings in their chemical structures.

Table 2. The variation of peat chemical properties according to peat type (see legend to Table 1a for key to peat species). Mean, range and standard deviation (SD) are shown for each chemical property. After Malawska *et al.* (2006).

	PEAT TYPE	FEN			TRANSITION MIRE	RAISED BOG
	PEAT GENERA	<i>Alnioni</i>	<i>Bryalo-Parvocaricioni</i>	<i>Magnocaricioni</i>	<i>Betulioni; Minero-Sphagnioni</i>	<i>Ombro-Sphagnioni; Ledo-Pinioni</i>
	PEAT SPECIES	<i>aln, alb</i>	<i>cab, bry</i>	<i>car, cap</i>	<i>bet; spc</i>	<i>cus, eus, ers, pis; pin</i>
PROPERTIES	NO. OF SAMPLES	4	4	6	4	23
degree of decomposition (%)	mean	52.5	32.5	44.0	35.0	38.6
	min - max	45 - 65	20 - 40	20 - 60	20 - 50	10 - 65
	SD	8.7	8.7	15.6	15.0	19.5
pH (KCl)	mean	5.1	4.9	4.8	5.1	4.8
	min - max	4.3 - 5.7	3.9 - 5.6	4.2 - 5.7	4.7 - 5.6	4.5 - 5.2
	SD	0.6	0.7	0.6	0.5	0.2
pH (water)	mean	4.8	3.4	4.0	3.8	3.3
	min - max	4.1 - 5.4	2.8 - 4.6	3.1 - 5.3	3.4 - 4.3	3.1 - 3.9
	SD	0.5	0.8	0.8	0.5	0.2
ash content (%)	mean	18.0	1.9	17.0	2.2	3.5
	min - max	6.4 - 25.7	0.9 - 3.5	1.7 - 69.3	1.2 - 3.5	0.8 - 25.5
	SD	8.9	1.2	29.4	1.1	4.9
nitrogen (%)	mean	1.9	1.4	1.6	1.4	1.2
	min - max	1.5 - 2.3	0.6 - 2.2	0.7 - 2.1	1 - 1.7	0.5 - 2.2
	SD	0.4	0.6	0.6	0.4	0.4
total organic carbon (C org) (%)	mean	11.0	5.6	6.7	5.0	5.7
	min - max	7.7 - 17.1	3.6 - 8.9	4.9 - 9.8	4.5 - 5.3	2.5
	SD	4.1	2.4	1.9	0.4	2.3
humic acid content (%)	mean	8.2	3.9	5.2	3.3	3.7
	min - max	3.7 - 13.3	2.7 - 6.4	1.5 - 9.2	2.3 - 4.6	0.9 - 6.2
	SD	3.9	1.7	2.7	1.2	1.6
fulvic acid content (%)	mean	2.8	1.6	1.5	1.8	2.0
	min - max	1.3 - 4.1	0.9 - 2.5	0.7 - 3.4	0.7 - 2.4	0.8 - 5.2
	SD	1.3	0.9	1.1	1.0	1.0
sodium (mmol kg <sup>-1</sup> )	mean	5.2	4.8	1.7	3.9	4.6
	min - max	3.9 - 6.1	2.2 - 7.8	0.9 - 4.3	1.3 - 7.0	0.9 - 10.0
	SD	0.9	3.0	1.3	3.0	3.0
potassium (mmol kg <sup>-1</sup> )	mean	1.3	1.4	1.3	1.3	1.5
	min - max	0.8 - 1.8	0.5 - 1.8	0.5 - 4.1	1.0 - 1.5	0.8 - 4.0
	SD	0.4	0.6	1.6	0.3	0.8
magnesium (mmol kg <sup>-1</sup> )	mean	205.0	117.5	7.9	107.5	75.0
	min - max	19.0 - 378.0	3.3 - 305.0	3.3 - 23.8	5.0 - 274.0	2.9 - 347.5
	SD	197.0	144.0	8.8	145.5	85.54
calcium (mmol kg <sup>-1</sup> )	mean	372.3	115.8	139.5	86.8	69.0
	min - max	263.0 - 518.0	43.5 - 207.8	22.8 - 422.5	22.5 - 123.8	14.5 - 708.0
	SD	109.1	78.9	169.0	55.8	134.9

The influence of peat type on the sorption of PAHs from the atmosphere was explored by conducting a cluster analysis in terms of the occurrence of individual PAHs in different peat genera (Figure 3b). This analysis distinguishes four

major groups. The first group consists of acenaphtylene, acenaphtene, anthracene, dibenzo [ah]anthracene, benzo[k]fluoranthene and benzo[e] pyrene and the second group pyrene, chrysene, benzo[b]fluoranthene, benzo[a]anthracene, benzo[a]



Table 3. Summary of PAH content (ng g<sup>-1</sup>) according to peat species. Mean, range and standard deviation (SD) are shown for each PAH compound; n.d. - not detected.

PAH COMPOUND		PEAT SPECIES				
		<i>aln, alb</i>	<i>cab, bry</i>	<i>car, cap</i>	<i>bet, spc</i>	<i>cus, eus, ers, pis, pin</i>
acenaphthylene	mean	n.d.	1.5	2.8	n.d.	1.3
	min - max	n.d.	0 - 6	0 - 6	n.d.	0 - 11
	SD	n.d.	3.0	2.7	n.d.	2.9
acenaphthene	mean	5.0	6.0	13.6	7.3	7.2
	min - max	4 - 6	4 - 8	6 - 19	6 - 10	0 - 15
	SD	0.8	1.6	8.9	2.3	2.9
fluorene	mean	9.5	13.8	20.2	13.7	15.3
	min - max	8 - 11	7 - 21	14 - 30	11 - 18	6 - 35
	SD	1.3	5.7	6.6	3.8	5.8
phenanthrene	mean	34.8	49.5	107.2	41.3	56.5
	min - max	28 - 46	22 - 66	47 - 298	39 - 44	30 - 95
	SD	7.9	19.7	107.5	2.5	17.8
anthracene	mean	n.d.	2.0	10.6	n.d.	1.3
	min - max	n.d.	0 - 4	0 - 47	n.d.	0 - 6
	SD	n.d.	2.3	20.5	n.d.	2.2
fluoranthene	mean	10.8	14.8	136.2	15.7	19.7
	min - max	7 - 20	6 - 22	11 - 596	8 - 22	6 - 52
	SD	6.2	7.5	257.2	7.1	11.3
pyrene	mean	5.8	8.3	95.4	9.0	11.4
	min - max	0 - 12.0	0 - 15.0	7.0 - 425.0	4.0 - 13.0	0 - 32.0
	SD	5.1	6.7	184.4	4.6	7.9
benzo[a]anthracene	mean	n.d.	n.d.	59.4	n.d.	1.2
	min - max	n.d.	n.d.	0 - 297	n.d.	0.0
	SD	n.d.	n.d.	132.8	n.d.	3.3
chrysene	mean	2.0	2.0	85.0	3.7	9.8
	min - max	0 - 8	0 - 8	0 - 405	0 - 11.0	0 - 46
	SD	4.0	4.0	179.0	6.4	13.1
benzo[b]fluoranthene	mean	n.d.	n.d.	70.4	4.3	9.6
	min - max	n.d.	n.d.	0 - 352	0 - 13	0 - 56
	SD	n.d.	n.d.	157.4	7.5	15.8
benzo[k]fluoranthene	mean	n.d.	n.d.	31.6	n.d.	2.1
	min - max	n.d.	n.d.	0 - 158	n.d.	0 - 21
	SD	n.d.	n.d.	70.7	n.d.	6.0
benzo[e]pyrene	mean	n.d.	n.d.	41.4	n.d.	2.4
	min - max	n.d.	n.d.	0 - 207	n.d.	0 - 26
	SD	n.d.	n.d.	92.6	n.d.	6.8
benzo[a]pyrene	mean	n.d.	n.d.	63.2	n.d.	1.1
	min - max	n.d.	n.d.	0 - 316	n.d.	0 - 15
	SD	n.d.	n.d.	141.1	n.d.	3.9
indeno[123cd]pyrene	mean	n.d.	n.d.	58.0	n.d.	5.4
	min - max	n.d.	n.d.	0 - 290	n.d.	0 - 45
	SD	n.d.	n.d.	129.7	n.d.	13.3
dibenzo[ah]anthracene	mean	n.d.	n.d.	18.2	15.7	n.d.
	min - max	n.d.	n.d.	0 - 53	0 - 47	n.d.
	SD	n.d.	n.d.	25.5	27.1	n.d.
benzo[ghi]perylene	mean	n.d.	n.d.	50.8	20.0	15.9
	min - max	n.d.	n.d.	0 - 254	0 - 60	0 - 90
	SD	n.d.	n.d.	113.6	34.6	23.6
sum of 15 USEPA PAHs and benzo[e]pyrene	mean	67.8	97.8	864.0	130.7	160.4
	min - max	56 - 101	39 - 145	95 - 3746	128 - 133	57 - 384
	SD	22.2	46.3	1611.4	2.5	92.0
perylene	mean	1574.5	71.8	514.6	333.7	128.4
	min - max	97 - 2567	0 - 248	50 - 1203	0 - 903	0 - 632
	SD	1051.7	118.9	533.8	495.5	229.2

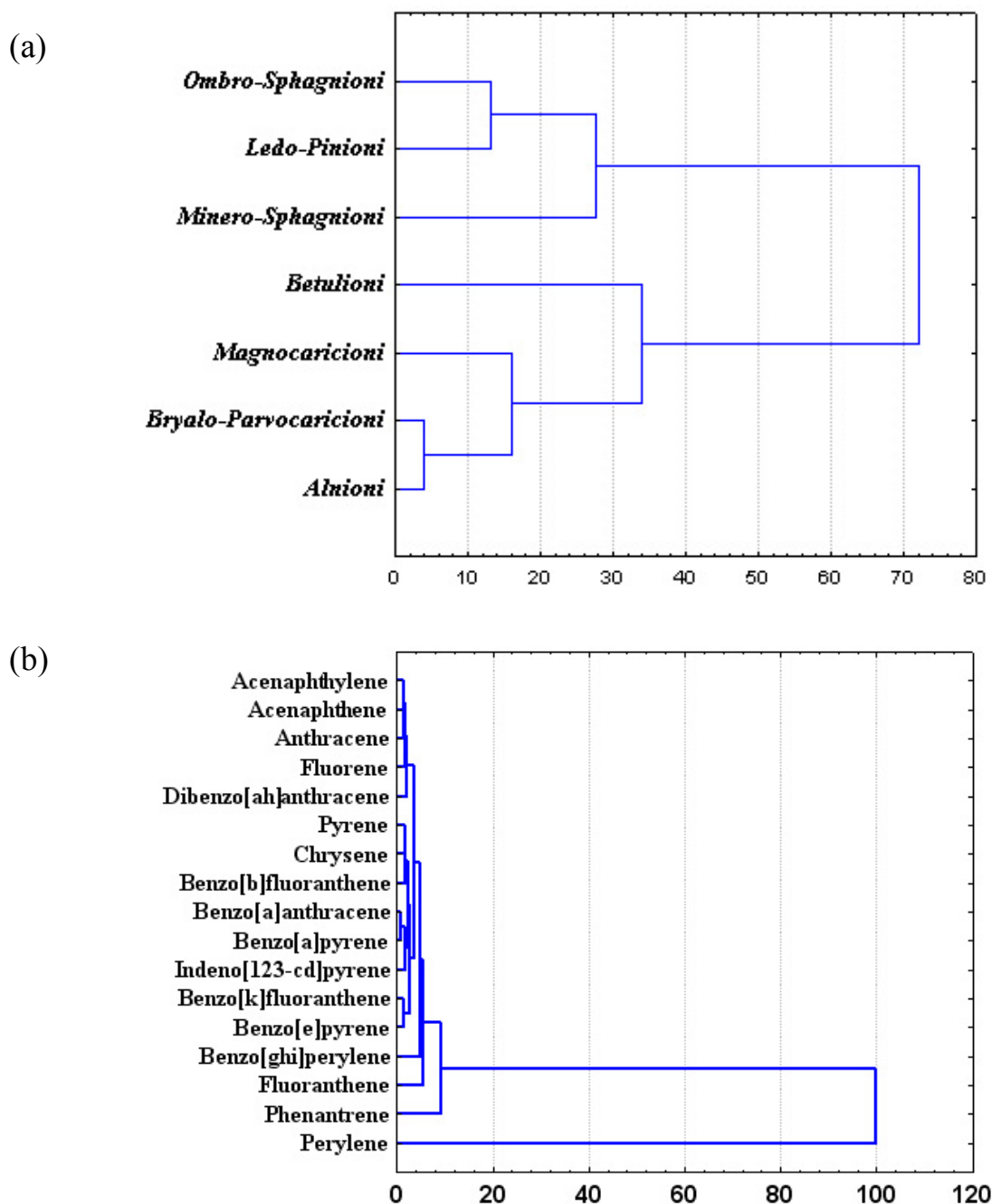


Figure 3. The results of cluster analyses showing (a) similarity between botanical peat types in terms of their percentage contents of 15 USEPA PAHs, benzo[e]pyrene and perylene; and (b) similarity between the 17 PAHs in terms of their association with peat genus using average linkage between groups. Ordinates: city-block (Manhattan) distances.

pyrene, indeno[123cd]pyrene and benzo[ghi]perylene. The third group contains phenanthrene and fluoranthene and is most similar to perylene, which is the only member of the fourth group. Thus, the analysis of similarity of peat types in terms of PAH content showed that the concentrations of USEPA PAHs, benzo[e]pyrene and perylene differentiate peat types at the generic level.

## DISCUSSION

Evidence from peat samples indicates that there is continuous and widespread diffuse PAH contamination throughout Poland, with enhanced inputs affecting some areas. The values recorded in the present study were elevated in only 18% of the peat samples, and a concentration higher than 600

ng g<sup>-1</sup>, which is considered to be indicative of soil pollution, was found only in mire D3 (3746 ng g<sup>-1</sup>). According to Danish standards, the PAH concentration of unpolluted mineral soils is 20–50 ng g<sup>-1</sup> (van Brummelen *et al.* 1996) and a total concentration of 200 ng g<sup>-1</sup> is regarded as the upper limit of natural PAH occurrence (Kabata-Pendias *et al.* 1995). The Danish government has adopted an intervention value of 4000 ng g<sup>-1</sup>, although such levels typically occur in urban and industrial soils (van Brummelen *et al.* 1996). Many environmental standards are stated in terms of the admissible concentration of benzo[a]pyrene only, as an index of PAH pollution which may be used to estimate the total PAH concentration (i.e. the sum of the 16 EPA PAHs, Wilcke *et al.* 1997). Benzo[a]pyrene occurred only in the Sudeten mires (mire D3 and the surface layers of mire D2), which are located in one of the most polluted regions of Poland.

Punt *et al.* (1999) found phenanthrene, fluoranthene and pyrene in bottom sediments. Bojakowska & Sokołowska (2001d) also recorded PAHs in sediments, at concentrations that were similar to the concentrations found in the south-west Polish peatlands; the perylene concentration (45 ng g<sup>-1</sup>, 0.045 ppm) was considerably lower, however. A problem in relating the PAH concentration in sediments to atmospheric deposition is that sedimentary PAH concentrations reflect not only atmospheric deposition but also sources such as biochemical transformations of naturally occurring aromatic precursor compounds. For peatlands, especially ombrotrophic bogs, the principal PAH source is atmospheric deposition, and transport of hydrophobic compounds is limited. This makes them ideal archives for the historic deposition of organic pollutants (Sanders *et al.* 1995).

In the most polluted sites, e.g. F1 and the Sudeten mires, the highest concentrations of USEPA PAHs occurred in the surface layers, which were formed during the industrial era. Similarly Sanders *et al.* (1995), studying PAH migration from the atmosphere to an ombrotrophic mire in north-western England, found the highest concentrations of USEPA PAHs in the shallowest peat layers; whilst Wickstrom & Tolonen (1987), Cranwell & Koul (1989) and Simcik *et al.* (1996) found that PAH concentrations in sediments increased during the second half of the 19th century. In other south-west Polish mires, the highest concentrations of USEPA PAHs were found in the middle layers of peat, where benzo[ghi]perylene and phenanthrene dominated. Deeper (96–102 cm) peat layers of mires in Switzerland, formed in Roman times, contained 125 ng g<sup>-1</sup> of PAHs, and this can be

related to forest fires and volcanic eruptions (Berset *et al.* 2001). According to Jiang *et al.* (2000), ancient forest fires can explain the presence of many unsubstituted PAHs in the environment, including fluoranthene, pyrene, benzo[a]anthracene, benzo-fluoranthenes, benzopyrenes, indeno[123,-cd]pyrene, and probably phenanthrene and chrysene. It is more difficult to determine the sources of PAHs in surface peat layers because smoke from forest fires contains the same PAHs as those emitted from anthropic sources (Simoneit 1998). However, the majority of PAHs in the modern setting originate from high-temperature anthropic processes such as the combustion of organic matter (power and heat generating plants, power stations, domestic fires) and traffic pollution, and the waste can be transported over long distances. Thus PAH concentrations in sediments reflect the history of fossil fuel combustion (Silliman *et al.* 2001).

The Sudeten sites are the most polluted of the study mires because they are affected by the air masses of the so-called "Black Triangle", the area of ecological disaster caused by the dense concentration of coal-fired power stations at the junction of the state boundaries of Poland, Germany and the Czech Republic. However, the pollution of the Zielenieckie mires with PAHs is one-tenth that of the nearby Lasówka fen. This may be because the Zielenieckie mires are tightly surrounded by spruce forest, whereas the Lasówka fen lies on an open, grassy hillslope. Coniferous trees may be capable of absorbing large amounts of PAHs, and many authors have used pine needles to examine the level of air pollution by PAHs (Tremolada *et al.* 1996; Holoubek *et al.* 2000; Lang *et al.* 2000). PAH concentration decreases with increasing distance from roads (Butler *et al.* 1984, Yang *et al.* 1991, Pathirana *et al.* 1994). Both the Sudeten mires and the mires of the Orawsko-Nowotarska Basin are close to busy highways or frontier crossings and so receive airborne PAHs from exhaust gases generated by motor vehicles.

The 12 mires investigated are located in four mountainous regions of southern Poland. They were formed during the Holocene glaciation so that their peat deposits have been forming for about 10,000 years. Hence, the occurrence of each of the 17 unsubstituted PAHs in the deeper peat layers reflects the combination of source (natural or anthropic) and mobility for each PAH. Some authors report that translocation of PAHs in both mineral and peat soils depends on the physical and chemical properties of the soil (Martens *et al.* 1997, Aamot *et al.* 1995, Sanders 1995) and the ease of translocation can be associated with, for instance, lipid concentration and

thus with the botanical composition of the peat. It has also been shown that 3-ring PAHs can be translocated downwards in gaseous form, whereas 5 and 6-ring PAHs are practically immobile. Thus the presence of 3-ring USEPA PAHs throughout the stratigraphic profiles reflects their mobility. On the other hand the presence in deeper peat layers of perylene, a 5-ring PAH that cannot be effectively translocated, leads to the conclusion that this PAH can be formed from natural precursors.

Perylene has been found widely in both marine and freshwater sediments but is either absent, or present only in small concentrations, in typical surface sediments (Jiang *et al.* 2000). However, there is no agreement yet as to whether perylene precursors are of terrestrial or aquatic origin. Silliman *et al.* (1998) show that there are no strong correlations between perylene and land or aquatic sources of organic matter. In this paper we report high concentrations of perylene in some genera of wood peat (*Alnioni* and *Ledo-Pinioni*) in the deeper layers of the study mires.

The highest concentrations of perylene occurred in woody peat, which is classified as fen peat with total nitrogen content 14–20% (<5% for bog peat). This explains the positive correlation between perylene concentration and N concentration. The concentration of possible chemical precursors of perylene is high in woody peat because such peat was formed mostly from higher plant residues containing greater quantities of isoprenoids than are found in moss residues. On the other hand, benzo[ghi]perylene was found only in the upper layers of moss peat (bog) deposits, suggesting an anthropic source.

The cluster analysis exploring the interrelationships between the different PAHs suggests that the individual PAHs in the different peat genera originated from different sources. Perylene is derived from its natural precursors *via* post-deposition transformation during early diagenesis, and much smaller amounts of perylene than of other PAHs are produced during combustion processes (Yunker *et al.* 2002). Thus the abundance of perylene in some peats may reflect biochemical transformations from plant precursors. The results of some studies suggest that land-derived organic matter may provide the principal precursor material for perylene (Jiang *et al.* 2000, Silliman *et al.* 2001).

The PAHs present in the peat layers formed during the industrial era are derived from anthropic sources, mainly from motor vehicles but also from the combustion of fuels and biomass for heating. In many cases, these compounds reach mires by long-distance transport in the atmosphere, which may

carry them across state boundaries. The same PAHs are formed during natural peatland and forest fires, so that it is difficult to identify the sources of PAHs detected in the uppermost *ca.* 1 m of peat. PAHs in deeper peat layers may originate from natural biomass fires and some, such as perylene and possibly phenanthrene and benzo[ghi]perylene, may be the products of biochemical transformations of aromatic compounds.

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