

Polycyclic Aromatic Hydrocarbons in Materials of Burned Peatlands

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Abstract

Polycyclic aromatic hydrocarbons are common in small amounts in the environment as a natural constituent of organic-rich rocks. They are mostly formed under oxygen-depleted conditions during burning of materials containing organic carbon. The samples, collected from peatlands which had been partially burned were analyzed for 17 unsubstituted PAHs. The profiles sampled encompassed: peat layer, burned peat layer and surficial newly formed turf-root layer. The average contents of determined PAHs in the burned peat layer is 0.114 ± 0.048 ppm, and is similar to that in the underlying peats (0.101 ± 0.039 ppm). The newly formed surficial root layer reveals concentrations nearly three times higher, i.e. 0.313 ± 0.144 ppm. The PAH spectrum of both peat types practically includes only acenaphthene, fluorene, phenanthrene and fluoranthene. The presence of hydrocarbons with higher molecular weight, i.e. pyrene and chrysene, was noted only in some samples of burned peats; perylene was recorded only in moss peats. The PAH spectrum of newly-formed turf-root layer is different, and is characterized by the presence of all determined 4-ring and partly 5-ring [benzo(b)fluoranthene and benzo(e)pyrene] hydrocarbons. The relatively poor spectrum of PAHs in the burned peat layer, and the presence of larger amounts and greater diversity of these compounds in the newly-formed surficial layer, may indicate that most of these hydrocarbons must have originated from airborne PAH deposition.

Introduction

Due to their carcinogenic and mutagenic impact on animals, unsubstituted polycyclic aromatic hydrocarbons, such as benzo(a)pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(ghi)perylene, are included in the group of compounds regarded as Persistent Organic Pollutants (POP) (Gałuszko 2002). The polycyclic aromatic hydrocarbons (PAHs) are widespread in small amounts in the environment, making up natural constituents of organic-rich rocks, i.e. crude oils, hard and brown coals, and bituminous shales. PAHs are mostly formed during incomplete burning of organic matter in natural and

anthropogenic processes. The rapid development of industry and road transport has brought about a considerable increase of PAH emissions to the environment. Nowadays, the anthropogenic emissions have exceeded many times the natural emissions (Howsam & Jones 1998). The principal source of polycyclic aromatic hydrocarbons to the environment is processing of organic-rich materials, including coals, bituminous shales, crude oils, and burning of petrol and wood [17,10,14]. PAHs released to the atmosphere are mostly adsorbed on particulates less than $1 \mu\text{m}$ in diameter, and can stay in the air for tens of days travelling long distances [18]. One of the most important processes of PAH removal from atmosphere is their deposition on land surface. During the last 100-150 years the content of PAHs has increased several times in arable soils [12]. Also, the recent studies of glacier caps in Greenland have indicated

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a substantial increase in PAH concentration during the last 100 years [9]. This fact correlates well with an increase of exploitation and use of crude oils and coals. The studies of PAHs in recent soils by means of ^{13}C and ^{14}C isotope markers have indicated that these compounds are scarcely formed from contemporary plants or soil biomass; they are primarily of exogenic origin and are linked to atmospheric deposits derived from the burning of fossil fuel [15]. The studies of PAHs in combustion gases formed as a result of burning of various organic-rich materials have revealed a diverse share of compounds in a PAH mixture – a possible indicator of their origin [14].

Even though unsubstituted PAHs are often examined in air, waters, and present water sediments and soils, especially in urban and industrialized areas, the data are relatively scarce as for the presence in peat. The recent organic-rich deposits (soils and water sediments) are characterized by higher contents of PAHs than those depleted in organic matter [1]. Peats – the least altered organic sedimentary rocks – despite a very high concentration of organic carbon, reveal lower (in order of magnitude) contents of unsubstituted PAHs ranging from tens to several hundreds ppb as compared to their contents in hard and brown coals [2,3,4,16]. In peat the occurrence of relatively high contents of fluorene, phenanthrene, fluoranthene and pyrene is observed. PAH concentration seems to depend on genus of the peat; moss and rush peat are characterized by lower PAH contents than Sphagnum peat [4].

Scope and Methods of Investigation

There are about 50,000 mires with a total area of about 12,000 km² in Poland [11]. Most of them are located in northeastern Poland, far from towns and industrial areas.

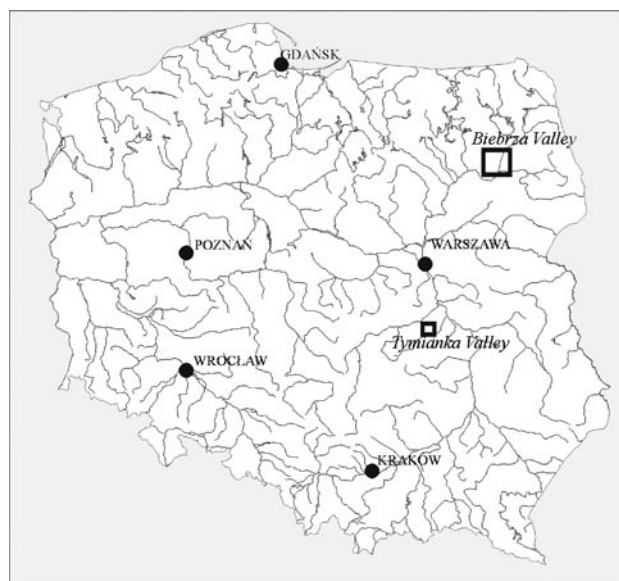


Fig. 1. Locations of studied burnt peatbogs.

The most numerous are fens which cover 92% of peatland area; raised and transition bogs account for 4.7% and 3.2%, respectively [19]. Fen areas are diverse; the number of the largest (more than 1,000 ha) does not exceed 230 [6]. The majority of mire areas is transformed in meadows, grasslands and forests. Natural and half-natural peatlands are scarce, including 109 peatland preserves for a total area of 7,400 ha [5].

The aim of the study was to determine the concentrations of unsubstituted PAHs in deposits derived from burned peatlands.

The samples were collected in 12 localities from mires in the Biebrza Valley and the Tymianka Valley (Fig. 1):

- (1) Wólka Piaseczna peatland (Biebrza Valley), burned to a depth of 25 cm (the fire was not completely extinguished during sampling); two points, i.e. mowed sedge-grass meadow with osier-bed and sedge rush with osier-bed, were sampled;
- (2) Brzeziny Kapickie peatland (Biebrza Valley), burned to a depth of 25-30 cm (fire was extinguished in 2000); two points from birch forest with Sphagnum and reed grass were sampled;
- (3) "Biebrza Triangle" peatland located in the Jegrzno and the Stary Elk Rivers and the Woźnawiejski Canal forks (fire was extinguished in 1993); the following samples were collected: 1 – rush-sedge peat with hair grass and a single birch burned to a depth of 45 cm (currently grown with reed, osier-bed and mosses), 2 – hair grass community and herbs with birch where peat was burned to a depth of 65 cm (currently grown with reed with mosses), 3 – grass-sedge meadow with birch, where peat was burned to a depth of 50 cm (currently grown with reed grass with young birch and osier-bed), 4 – grass meadow with herbs, birch and aspen, where peat was burned to a depth of 45 cm, 5 – at a site covered with sedge rush with birch and herbs from a peatbog burned to a depth of 40 cm (currently grown thickly by reed);
- (4) Siekluki peatland (Tymianka Valley), where fire was extinguished in 1992; the samples were collected from three localities: 1 – sedge rush burned to a depth of 60 cm (currently grown by osier hope), 2 – sedge rush burned to a depth of 50 cm (currently with prevailing osier hope), 3 – sedge rush burned to a depth of 35 cm (currently grown by young willow and aspen).

A total of 32 samples, including 12 from the burned peat layer, 12 from the underlying layer, 1 from the burned turf-root layer and 7 from the surficial layer deposited on the burned peat, were collected. Based on the botanical composition, the type and species of peat was determined (Table 1).

In samples derived from peat layers, burned peat layers and surficial layers 17 PAHs, i.e. acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)-

Table 1. List of collected samples.

No.	Peatland	Peat genera	Sample	Depth (cm)	Description
1	Wólka Piaseczna	Sedge-reed	WI/2	10-25	Burned peat (fire layer)
2			WI/3	40-50	Peat
3		Reed with sedges	WII/2	10-35	Burned peat (fire layer)
4			WII/3	10-48	Peat
5	Brzeziny Kapickie	Moss	BrI/2	0-25	Burned peat (fire layer)
6			BrI/3	30-40	Peat
7		Moss with sedges and bog-bean	BrII/2	0-30	Burned peat (fire layer)
8			BrII/3	35-45	Peat
9	"Biebrza Trójkąt"	Reed	BbI/1	0 – 5	Moss root layer
10			BbI/2	8-15	Burned peat (fire layer)
11			BbI/3	20-30	Peat
12		Reed	BbII/1	0-5	Moss root layer
13			BbII/2	8-13	Burned peat (fire layer)
14			BbII/3	20-28	Peat
15		Reed	BbIII/2	2-8	Burned peat (fire layer)
16			BbIII/3	15-25	Peat
17		Reed	BbIV/1	0-5	Organic surficial layer
18			BbIV/2	7-12	Burned peat (fire layer)
19			BbIV/3	20-30	Peat
20		Reed	BbV/1	0-5	Organic surficial layer
21			BbV/2	7-13	Burned peat (fire layer)
22			BbV/3	18-25	Peat
23	Siekluki	Sedge-moss with bog-bean	SI/1	1-5	Willow and aspen root layer
24			SI/2	7-12	Burned peat (fire layer)
25			SI/3	18-25	Peat
26		Sedge-moss	SII/1	0-5	Gray willow root layer
27			SII/2	6-10	Burned peat (fire layer)
28			SII/3	15-20	Peat
29		Sedge-moss overdried	SIII/1	0-4	Willow root layer
30			SIII/2	6-12	Burned peat (fire layer)
31			SIII/3	20-25	Peat

anthracene and benzo(ghi)perylene listed by the US EPA [13], and benzo(e)pyrene and perylene were determined. The fraction of aromatic hydrocarbons was obtained by a liquid-solid extraction method using SOXTEC apparatus; the solvent applied included dichloromethane. After desulfurizing using metallic copper, the extracts were concentrated in a TurboVap apparatus. The samples were tested using gas chromatograph with a mass spectrom-

eter detector (Hewlett-Packard GC/MSD, model 5890II) with a mass spectrometer detector (MSD 5971). A HP-1 nonpolar capillary column (length: 25 m, diameter: 0.2 mm, film: 0.33 μm (5%)-diphenyl-(95%)-dimethylpolysiloxane). The temperature was set from 70 to 200°C with a rate of 10°C/min and from 200-300°C with a rate of 2.5°C/min. The analyses were performed using an external standard method; the following standards were

Table 4. PAH concentrations in samples of turf-root layer (ppm).

Hydrocarbon	BbI/1	BbII/1	BbIV/1	BbV/1	SI/1	SII/1	SIII/1
Acenaphthylene (Ace)	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	0.002
Acenaphthene (Acf)	0.009	0.008	0.004	0.005	0.006	0.007	0.010
Fluorene (Fl)	0.016	0.018	0.007	0.009	0.009	0.012	0.017
Phenanthrene (Fen)	0.057	0.078	0.047	0.054	0.052	0.061	0.075
Anthracene (Ant)	< d.l.	< d.l.	0.003	0.003	0.004	0.003	0.003
Fluoranthene (Flu)	0.015	0.031	0.022	0.031	0.078	0.064	0.062
Pyrene (Pir)	0.008	0.018	0.013	0.018	0.059	0.044	0.041
Benzo[a]anthracene (BaA)	0.005	0.006	0.004	0.006	0.025	0.016	0.014
Chrysene (Ch)	0.016	0.013	0.011	0.014	0.061	0.04	0.035
Benzo[b]fluoranthene (BbF)	0.016	0.014	0.009	0.014	0.063	0.043	0.037
Benzo[k]fluoranthene (BkF)	0.008	0.01	< d.l.	0.009	0.037	0.024	0.018
Benzo[e]pyrene (BeP)	0.011	0.01	0.007	0.01	0.04	0.03	0.024
Benzo[a]pyrene (BaP)	0.008	0.008	< d.l.	0.008	0.034	0.024	0.019
Perylene (Per)	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	0.033	0.038
Indeno[1,2,3-cd]pyrene (IndP)	0.011	0.011	< d.l.	0.011	< d.l.	0.033	0.024
Dibenzo[ah]anthracene (DahA)	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
Benzo[ghi]perylene (Bper)	0.012	< d.l.	< d.l.	< d.l.	< d.l.	0.023	0.018

applied: PAH mixture (PM-612) from Ultra Scientific and certified perylene and benzo(a)pyrene from Prochem. The determinations were done in the Central Chemical Laboratory of the Polish Geological Institute in Warsaw.

Results and Discussion

All the peat samples underlying the burned layer contain 3-ring hydrocarbons, i.e. acenaphthene, fluorene, phenanthrene, and one 4-ring hydrocarbon – fluoranthene (Table 2). Of the remaining determined hydrocarbons, the presence of pyrene and perylene was noted in moss and sedge-moss peat samples. Apart from perylene, no 5- and 6-ring hydrocarbons were found in the peat samples examined. The average concentration (mean) of total PAHs in these peats was 0.101 ± 0.039 ppm (Table 5). Moss and sedge-moss peats from Brzeziny Kapickie and Siekluki peatlands are distinguished not only for higher PAH content than reed peats from Biebrza Trójkąt and Wólka Piaseczyńska peatlands, but also for the presence of perylene and pyrene [4].

The content of examined PAHs in samples collected from the burned layer was not significantly different from that in the underlying layer (Table 3). A somewhat elevated concentration of anthracene was noted only in the burned peat samples from Brzeziny Kapickie peat-bog; traces of chrysene in some of them and the lack of perylene in deposits formed as a result of burning of moss peats were observed. The layer discussed does not show a considerable amount of 5- and 6-ring hydrocarbons, the origin of which seems to be connected with the burning process of materials enriched with organic matter. The average content of total PAHs in the burned peat layer was 0.114 ± 0.048 ppm and was not statistically different from that calculated for the unburned peat layer that occurs beneath the fire layer - Table 5.

The newly formed turf-root layer, covering burned peatbogs, is featured by a totally different PAH composition. In all the samples examined a higher concentration of fluoranthene and the presence of all 4- and 5-ring hydrocarbons including benzo(b)fluoranthene and benzo(e)pyrene was noted (Table 4). Most of the samples also contain benzo(a)pyrene and benzo(k)fluoranthene. The average contents of total PAHs in the newly formed surficial root layer is 0.313 ± 0.114 ppm, and is three times higher than that in the burned peat layer although statistically significant differences were observed only for the groups of 4- and 5-cyclic hydrocarbons (Table 5). The contents of different examined PAHs in this layer is particularly featured by a relatively high level of phenanthrene, chrysene, benzo(e)pyrene and benzo(b)fluoranthene. The shares of examined compounds in PAH composition are similar to that observed in Upper Silesian hard coals and air-borne dusts (Fig. 2) [1,2,3,8], in spite of considerable differences in concentrations of this compounds (4.11 ppm and 18.09 ppm, respectively). Compared to hard coals, the turf layer is highlighted only by high contents of fluoranthene.

Conclusions

1. The average content of total PAHs in the burned peat layer is 0.114 ± 0.048 ppm, and is similar to that in the underlying layer (0.101 ± 0.039 ppm); the newly-formed surficial root layer reveals three times higher concentrations of PAHs averaging 0.313 ± 0.144 ppm.
2. The spectrum of PAHs in both the burned peats and the underlying peats consists of acenaphthene, fluorene, phenanthrene and fluoranthene. The presence of hydrocarbons with a higher molecular mass, i.e. pyrene and chrysene, was noted only in some burned peat samples; perylene was recorded only in moss peats.

Table 5. Basic statistic of samples.

Hydrocarbon	Peat (n=12)				burned peat (n=12)				turf-root layer (n=7)			
	Median	Mean	Geometric mean	Standard deviations	Median	Mean	Geometric mean	Standard deviations	Median	Mean	Geometric mean	Standard deviations
Acenaphthene (Acf)	0.005	0.005	0.005	0.002	0.003	0.003	0.003	0.002	0.007	0.007	0.007	0.002
Fluorene (Fl)	0.008	0.009	0.008	0.004	0.006	0.006	0.005	0.004	0.012	0.013	0.012	0.004
Phenanthrene (Fen)	0.024	0.031	0.028	0.017	0.037	0.045	0.037	0.029	0.057	0.061	0.060	0.012
Anthracene (Ant)	< d.l.	< d.l.	< d.l.		< d.l.	0.002	0.002	0.002	0.003	0.003	0.002	0.001
Fluoranthene (Flu)	0.007	0.009	0.007	0.005	0.011	0.010	0.009	0.005	0.031	0.043	0.037	0.024
Pyrene (Pir)	0.004	0.004	0.003	0.003	0.006	0.006	0.004	0.004	0.018	0.029	0.023	0.019
Benzo[a]anthracene (BaA)	< d.l.	< d.l.	< d.l.		< d.l.	< d.l.	< d.l.		0.006	0.011	0.009	0.008
Chrysene (Ch)	< d.l.	< d.l.	< d.l.		0.007	0.008	0.007	0.004	0.016	0.027	0.022	0.019
Benzo[b]fluoranthene (BbF)	< d.l.	< d.l.	< d.l.		< d.l.	< d.l.	< d.l.		0.016	0.028	0.022	0.020
Benzo[k]fluoranthene (BkF)	< d.l.	< d.l.	< d.l.		< d.l.	< d.l.	< d.l.		0.010	0.016	0.012	0.012
Benzo[e]pyrene (BeP)	< d.l.	< d.l.	< d.l.		< d.l.	0.004	< d.l.		0.011	0.019	0.016	0.013
Benzo[a]pyrene (BaP)	< d.l.	< d.l.	< d.l.		< d.l.	< d.l.	< d.l.		0.008	0.015	0.011	0.011
Pyrene (Per)	< d.l.	0.010	0.006	0.015	< d.l.	< d.l.	< d.l.		< d.l.	0.012	0.006	0.016
Dibenzo[ah]anthracene (DahA)	< d.l.	< d.l.	< d.l.		< d.l.	< d.l.	< d.l.		0.011	0.014	0.011	0.010
Sum A	0.039	0.047	0.043	0.024	0.048	0.057	0.048	0.035	0.084	0.084	0.082	0.017
Sum B	0.014	0.018	0.015	0.009	0.025	0.026	0.023	0.013	0.069	0.110	0.092	0.069
Sum C	< d.l.	< d.l.	< d.l.		< d.l.	< d.l.	< d.l.		0.051	0.095	0.076	0.063
Sum D	< d.l.	< d.l.	< d.l.		< d.l.	< d.l.	< d.l.		< d.l.	0.025	0.020	0.018
Sum	0.084	0.101	0.095	0.039	0.103	0.114	0.106	0.048	0.240	0.313	0.285	0.144

Sum A - total 3-cyclic PAHs (acenaphthene, fluorene, phenanthrene, anthracene), (detection limit – 0.008 ppm)

Sum B - total 4-cyclic PAHs (fluoranthene, pyrene, benzo(a)anthracene, chrysene), (detection limit – 0.012 ppm)

Sum C – total 5-cyclic PAHs (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene), (detection limit – 0.04 ppm)

Sum D – total 6-cyclic PAHs (indeno[1,2,3-cd]pyrene and benzo[ghi]perylene), (detection limit – 0.02 ppm)

Sum = Sum A + Sum B + Sum C + Sum D

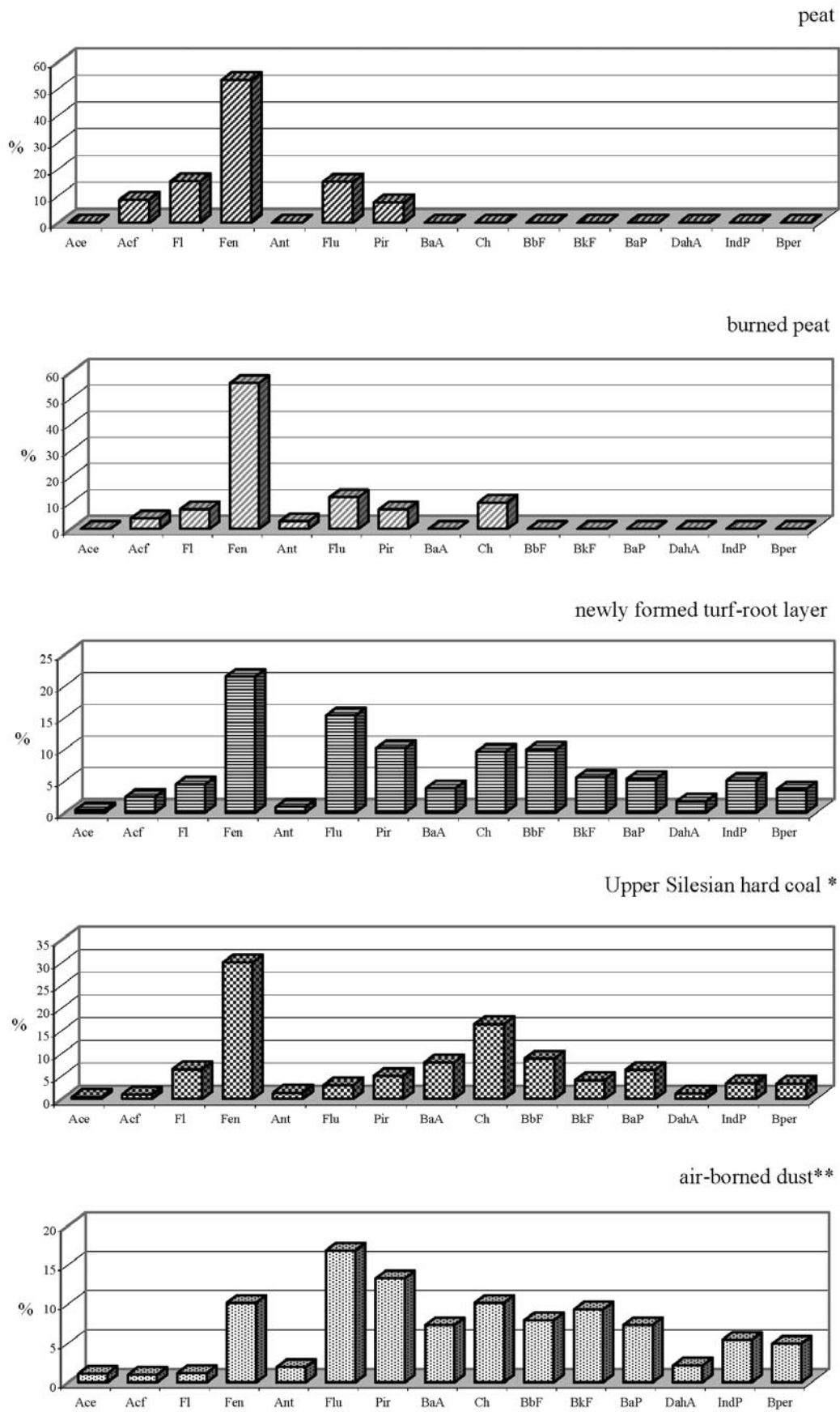


Fig. 2. Polycyclic aromatic hydrocarbons profiles (percentage by share).
 * - data of Bojakowska & Sokołowska [2], ** - data of Gardner et al. [8]

3. The concentration of PAHs in the newly-formed turf-root layer is different and is characterized by the presence of all determined 4-ring hydrocarbons, as well as some 5-ring ones, i.e. benzo(b)fluoranthene and benzo(e)pyrene.
4. The relatively poor PAH spectrum in the burned peat layer and the presence of distinctly larger numbers and diversity of these compounds in the newly-formed surficial layer as well as similarity of PAH profiles of turf-root layer samples and air-borne dusts may indicate that most of these hydrocarbons in turf-root layer could be derived from deposited airborne PAHs.

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