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Polycyclic aromatic hydrocarbons in brown coals from Poland

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Concentrations of seventeen unsubstituted polycyclic aromatic hydrocarbons (PAHs) have been determined in brown coal samples from several deposits in Poland. Content of the total determined PAHs ranges from 0.247 to 4.894 ppm, with an average value of 1.542 ppm. Unsubstituted PAHs concentrations in brown coals from tectonic depression deposits are several times higher than in brown coals from lensoid deposits. Among the investigated PAHs, perylene is the most abundant, exceeding other determined PAHs more than tenfold. Samples taken from coal lensoid deposits contain more chrysene and benzo(a)anthracene than samples from tectonic depressions, which have more acenaphthylene, fluoranthene and pyrene.

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INTRODUCTION

Brown coals formed by alteration of accumulated plant material, when PAHs also orginated. Their precursors were mainly terpenoids; for example, diterpenoids may change to pimanthene or retene, while triterpenoids may change to dimethylchrysene or trimethylpicene. However, hopanoids and steroids may be the precursors of PAHs as well (Smith *et al.*, 1995; Neilson and Hynning, 1998; Simoneit, 1998). Substituted PAHs, via dehydrogenation and dealkylation during diagenesis, change to unsubstituted compounds. Unsubstituted PAHs are included among permanent organic pollutants (POPs) together with polychlorinated biphenyls (PCBs) and chlororganic pesticides such as DDT or hexachlorobenzene.

PAHs occur in the environment as a mixture of various compounds bearing two or more aromatic rings. There is much variability in the occurrence of individual PAHs and of their quantitative properties. Among the unsubstituted PAHs occurring in peat, only fluorene, phenanthrene, fluoranthene, pyrene and perylene are present in appreciable amounts, perylene being the main component of this group (average content 1.22 ppm), whereas in hard coal the composition of the PAHs mixture is more variable and the perylene content is low, usually *ca.* 0.03 ppm (Bojakowska and Sokołowska, 1999). Studies of PAHs in Tertiary brown coals from Australian deposits showed that substituted hydrocarbons with five rings prevailed, whereas in brown coal from the Baise Basin in southern China the unsubstituted PAHs were fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(a)pyrene and benzo(e)pyrene (Chaffee and Johns, 1983; Wang and Simoneit, 1991).

Burning of coals is a source of emission of the unsubstituted PAHs to the environment, whose synthesis takes place during combustion. However, some PAHs compounds present in coal survive combustion (Howsam and Jones, 1998), making the original concentration of these harmful compounds in raw coal important. Coal with high contents of unsubstituted PAHs may be also rich in their precursor, which during combustion may alter into harmful unsubstituted PAHs.

The aim of the present study was to make the first investigation of the occurrence of selected PAHs in brown coal samples from the most important Polish deposits.

EXTENT AND METHODS OF THE INVESTIGATIONS

Among the Polish Tertiary brown coal deposits, the Miocene brown coals exploited around Konin-Turek (Adamów, Koźmin, Kazimierz, Lubstów), Bełchatów and Turów (Fig.1) are the most important, with large resources at shallow depth enabling open pit exploitation. The deposits of Adamów,

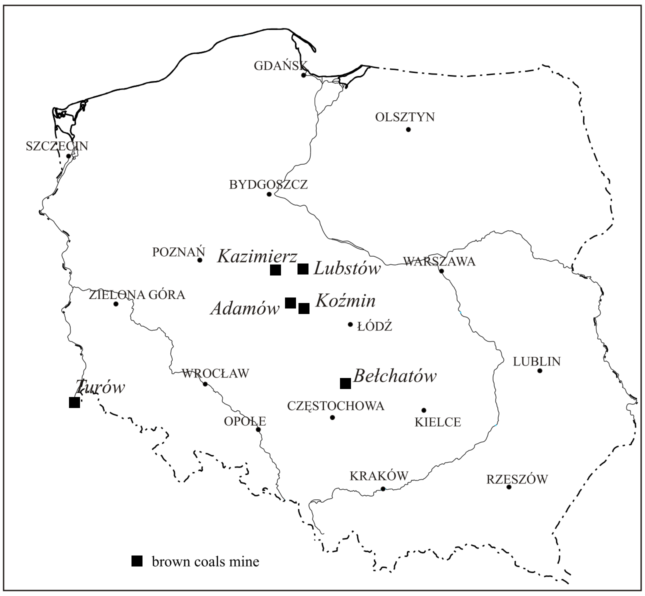

Fig. 1. Localisation of sampling brown coals deposits

Koźmin and Kazimierz are believed to represent lensoid deposits, with sedimentation of the plant material limited to restricted to morphological basins such as lakes, river channels and oxbows (Ciuk, 1987). However, the Turów, Bełchatów and Lubstów deposits were formed in tectonic rifts active in Tertiary times (Ciuk, 1987). Polish brown coals are soft. Brown coals of the Central Polish area have a higher ash content (20–24%) than the coals from the south-west region, whose ash content is 8–20% (Ciuk, 1987).

The Miocene lignite-bearing sediments of the Polish Lowlands and adjacent areas are divided into four lithostratigraphical units: the I Middle Polish Group of Seams (Middle Miocene) and the II Lusatia Group of Seams , the III Ścinawa Group of Seams and the IV Dąbrowa Group of Seams of Early Miocene age (Piwocki and Ziembińska-Tworzydło, 1997).

Determinations of PAH concentrations were performed on 20 samples of brown coal from Turów, Bełchatów, Adamów, Lubstów, Kazimierz and Koźmin. Coal samples representing the I Middle Polish Group of Seams, were collected from Kazimierz (2 samples), Adamów (3 samples) and in the upper seam at Lubstów (1 sample). Coals of the II Lusatia Group of Seams were taken from the lower seam at Lubstów (2 samples), from Turów, which occurs between Turoszów and Bogatynia and is one of the largest brown coal deposits in Poland (3 samples), and from Bełchatów (4 samples). Moreover, three samples were investigated which came from the lower brown coal seam at Turów, of the III Ścinawa Group of Seams.

17 PAHs were determined: acenaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, benzo(a)anthracene, fluoranthene, pyrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, perylene, indeno(1, 2, 3-cd)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene, fifteen of which are on the list of PAHs selected for environmental studies by the US Environmental Protection Agency. Analyses were performed in the Central Chemical Laboratory of the Polish Geological Institute using a *Hewlett Packard* gas chromatograph *type 5890 II* with a mass spectrometer *GS-MSD 5981* detector. The non-polar column HP-1 of 25 m long and 0.2 mm diameter was applied. Analyses were made using an internal standard. Detection limits of the compounds were as follows: acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene — 0.001 ppm; benzo(a)anthracene, chrysene — 0.002 ppm, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, perylene — 0.003 ppm, indeno(1, 2, 3-cd)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene — 0.005 ppm.

RESULTS AND DISCUSSION

The total contents of determined PAHs in the brown coals ranged between 0.247 and 4.894 ppm with a mean of 1.54 ppm. This is several times higher than their content in peat, where it reaches 0.27 ppm (Bojakowska *et al*., 2000). This higher content of PAHs in brown coals results firstly from a relative enrichment, caused by diagenetic alterations (compaction, decrease of porosity, dehydratation), resulting in carbon content increase, and a decrease in volatiles and water. Secondly, it is caused by alteration of some substituted PAH to unsubstituted PAH.

The highest contents of 3-cyclic aromatic hydrocarbons were found in brown coals from Turów; they range from 0.022 to 0.524 ppm (Tab. 1). The average contents in brown coals from the tectonic depressions at Turów and Bełchatów, were 0.087 and 0.159 ppm respectively and these are several times higher than in brown coal lensoid deposits at Adamów-Konin (Fig. 2), were they averaged 0.025 ppm, concentrations similar to those in peat (Bojakowska *et al.*, 2000).

The highest average contents of 4-cyclic aromatic hydrocarbons was also observed in coals from Turów. All coals possessed relatively high contents of chrysene. The highest concentrations of fluoranthene and pyrene were also seen in the samples from Turów (Fig. 2).

The 5- and 6-cyclic aromatic hydrocarbons are represented in brown coals mainly by perylene, whose content is several tens times higher than those of other investigated hydrocarbons (Fig. 2). Its average content in the coals from the Adamów-Konin lensoid deposits is lower (0.436 ppm) than those in coals in the tectonic depressions, which were 1.752 ppm at Turów and 2.356 ppm at Bełchatów.

Thus coals from Turów and Bełchatów contain more unsubstituted PAHs mostly perylene and acenaphthylene and pyrene, than the coals from Adamów-Konin (Tab. 2). The first two, deposited in tectonic depressions, are thicker, the rocks belonging to the II Lusatia Group of Seams and the III Ścinawa

Table 1

PAHs in brown coals from different deposits (ppm)

Hydrocarbons	Konin-Turek (*n* = 10)	Bełchatów (*n* = 4)	Turów (*n* = 15)
Acenaphthylene (Ace)	$\frac{<0.001-0.007}{0.003}$	$\frac{0.007-0.069}{0.029}$	$\frac{<0.001-0.163}{0.061}$
Acenaphthene (Acf)	$\frac{<0.001-0.034}{0.006}$	$\frac{0.006-0.129}{0.041}$	$\frac{<0.001-0.028}{0.009}$
Fluorene (Fl)	$\frac{0.001-0.004}{0.003}$	$\frac{<0.001-0.008}{0.004}$	$\frac{0.003-0.014}{0.006}$
Phenanthrene (Fen)	$\frac{0.003-0.021}{0.010}$	$\frac{0.005-0.025}{0.013}$	$\frac{0.011-0.344}{0.082}$
Anthracene (Ant)	$\frac{<0.001-0.007}{0.003}$	$\frac{<0.001-0.001}{0.001}$	$\frac{<0.001-0.006}{0.001}$
Fluoranthene (Flu)	$\frac{0.002-0.104}{0.022}$	$\frac{0.012-0.038}{0.023}$	$\frac{0.008-0.092}{0.051}$
Pyrene (Pir)	$\frac{0.001-0.029}{0.013}$	$\frac{0.013-0.04}{0.025}$	$\frac{0.011-0.123}{0.051}$
Benzo(a)anthracene (BaA)	$\frac{<0.002-0.053}{0.016}$	$\frac{<0.002-0.041}{0.019}$	$\frac{<0.002-0.023}{0.005}$
Chrysene (Ch)	$\frac{0.005-0.174}{0.042}$	$\frac{0.018-0.065}{0.039}$	$\frac{0.006-0.088}{0.049}$
Benzo(b)fluoranthene (BbF)	$\frac{<0.003-0.104}{0.044}$	$\frac{0.043-0.07}{0.052}$	$\frac{<0.003-0.089}{0.029}$
Benzo(k)fluoranthene (BkF)	$\frac{<0.003-0.033}{0.013}$	$\frac{0.014-0.027}{0.021}$	$\frac{<0.003-0.027}{0.010}$
Benzo(e)pyrene (BeP)	$\frac{<0.003-0.047}{0.018}$	$\frac{0.013-0.038}{0.024}$	$\frac{<0.003-0.068}{0.016}$
Benzo(a)pyrene (BaP)	$\frac{<0.003-0.036}{0.015}$	$\frac{0.01-0.047}{0.031}$	$\frac{<0.003-0.044}{0.017}$
Perylene (Per)	$\frac{<0.003-1.305}{0.436}$	$\frac{0.74-3.053}{2.356}$	$\frac{0.25-4.132}{1.752}$
Indeno(1, 2, 3-cd)pyrene (IndP)	$\frac{<0.005-0.105}{0.013}$	< 0.005	$\frac{<0.005-0.067}{0.019}$
Dibenzo(ah)anthracene (DahA)	< 0.005	< 0.005	$\frac{<0.005-0.036}{0.009}$
Benzo(ghi)perylene (Bper)	$\frac{<0.005-0.121}{0.033}$	< 0.005	$\frac{<0.005-0.079}{0.032}$
Total PAH_A	$\frac{0.009-0.058}{0.025}$	$\frac{0.023-0.185}{0.087}$	$\frac{0.022-0.524}{0.159}$
Total PAH_B	$\frac{0.009-0.261}{0.093}$	$\frac{0.081-0.131}{0.105}$	$\frac{0.026-0.284}{0.156}$
Total PAH_C	$\frac{0.091-1.354}{0.574}$	$\frac{0.838-3.213}{2.493}$	$\frac{0.346-4.485}{1.884}$
Total $PAH_{17} = PAH_A + PAH_B + PAH_C$	$\frac{2.247-1.456}{0.691}$	$\frac{1.008-3.404}{2.685}$	$\frac{0.695-4.894}{2.198}$

$\frac{\text{min. content} - \text{max. content}}{\text{mean value}}$; total PAH_A — total of 3-cyclic aromatic hydrocarbons [acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene]; total PAH_B — total of 4-cyclic aromatic hydrocarbons [fluoranthene, pyrene, benzo(a)anthracene, chrysene]; total PAH_C — total of 5- and 6-cyclic aromatic hydrocarbons [benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1, 2, 3-cd)pyrene, dibenzo(ah)anthracene, benzo(ghi)perylene]

Table 2

PAHs in brown coals from different lithostratigraphical units (ppm)

Hydrocarbons	Mean			Mediana		
	I	II	III	I	II	III
Acenaphthylene (Ace)	0.004	0.035	0.055	0.003	0.021	0.002
Acenaphthene (Acf)	0.007	0.024	0.004	0.003	0.010	0.005
Fluorene (Fl)	0.003	0.004	0.007	0.003	0.005	0.003
Phenanthrene (Fen)	0.010	0.051	0.035	0.008	0.017	0.044
Anthracene (Ant)	0.003	0.002	0.002	0.003	< 0.001	< 0.001
Fluoranthene (Flu)	0.027	0.029	0.049	0.009	0.022	0.066
Pyrene (Pir)	0.013	0.026	0.064	0.014	0.027	0.057
Benzo(a)anthracene (BaA)	0.019	0.009	0.008	0.016	< 0.002	< 0.002
Chrysene (Ch)	0.050	0.037	0.045	0.036	0.019	0.041
Benzo(b)fluoranthene (BbF)	0.043	0.042	0.034	0.023	0.043	0.011
Benzo(k)fluoranthene (BkF)	0.012	0.016	0.011	0.008	0.014	0.004
Benzo(e)pyrene (BeP)	0.017	0.017	0.027	0.012	0.013	0.011
Benzo(a)pyrene (BaP)	0.013	0.024	0.016	0.007	0.022	0.002
Perylene (Per)	0.485	1.648	1.860	0.368	1.380	1.198
Indeno(1, 2, 3-cd)pyrene (IndP)	0.016	0.004	0.031	0.003	0.003	0.024
Dibenzo(ah)anthracene (DahA)	< 0.005	0.007	< 0.005	< 0.005	< 0.005	< 0.005
Benzo(ghi)perylene (Bper)	0.037	0.014	0.036	0.032	0.003	0.041
Total PAH_A	0.078	0.116	0.103	0.021	0.060	0.065
Total PAH_B	0.114	0.101	0.166	0.087	0.099	0.187
Total PAH_C	1.351	1.773	2.018	0.485	1.397	1.224
Total $PAH_{17} = PAH_A + PAH_B + PAH_C$	1.542	1.990	2.287	0.552	1.605	1.272

I — the I Middle Polish Group of Seams (n = 8); II — the II Lusatia Group of Seams (n = 9); III — the III Ścinawa Group of Seams (n = 3)

Group of Seams. Coals from the smaller lensoid deposits: Adamów, Koźmin and Kazimierz are included in I Middle Polish Group of Seams. In the tectonically bounded deposit at Lubstów the PAH characteristics of the coals collected in the upper measures at the mine (I Middle Polish Group of Seams) is similar to the characteristics of the lensoid deposits coals. It is not yet known whether the PAH content of brown coals and the quantitative relations between the studied PAH compounds depend on the age of the coals or on depositional conditions.

A dominance of perylene among the unsubstituted PAHs is a common feature of peats and brown coals, this compound being several tens of times more abundant than other unsubstituted PAHs. Carboniferous hard coal are completely different in this respect: phenanthrene, chrysene and benzo(e)pyrene are the main components and the average content of perylene (0.03 ppm) is very low (Bojakowska and Sokołowska, 1999). The differences in the amounts and composition of the PAHs in Palaeozoic and younger coals probably resulted not only from the intensity of diagenesis, but also from the composition of the accumulated vegetable material. In the Tertiary, conifers, angiosperm trees and perennial herbs with subordinate ferns, mosses and water plants represent the primary material. Recent coal-forming environments are dominated by angiosperm herbs and sphagnum mosses with subordinate trees. In the Carboniferous, the lycopods, horsetails, ferns and cordaites, together with mosses and herb lycopods, ferns and primitive conifers were the main coal-producing plants.

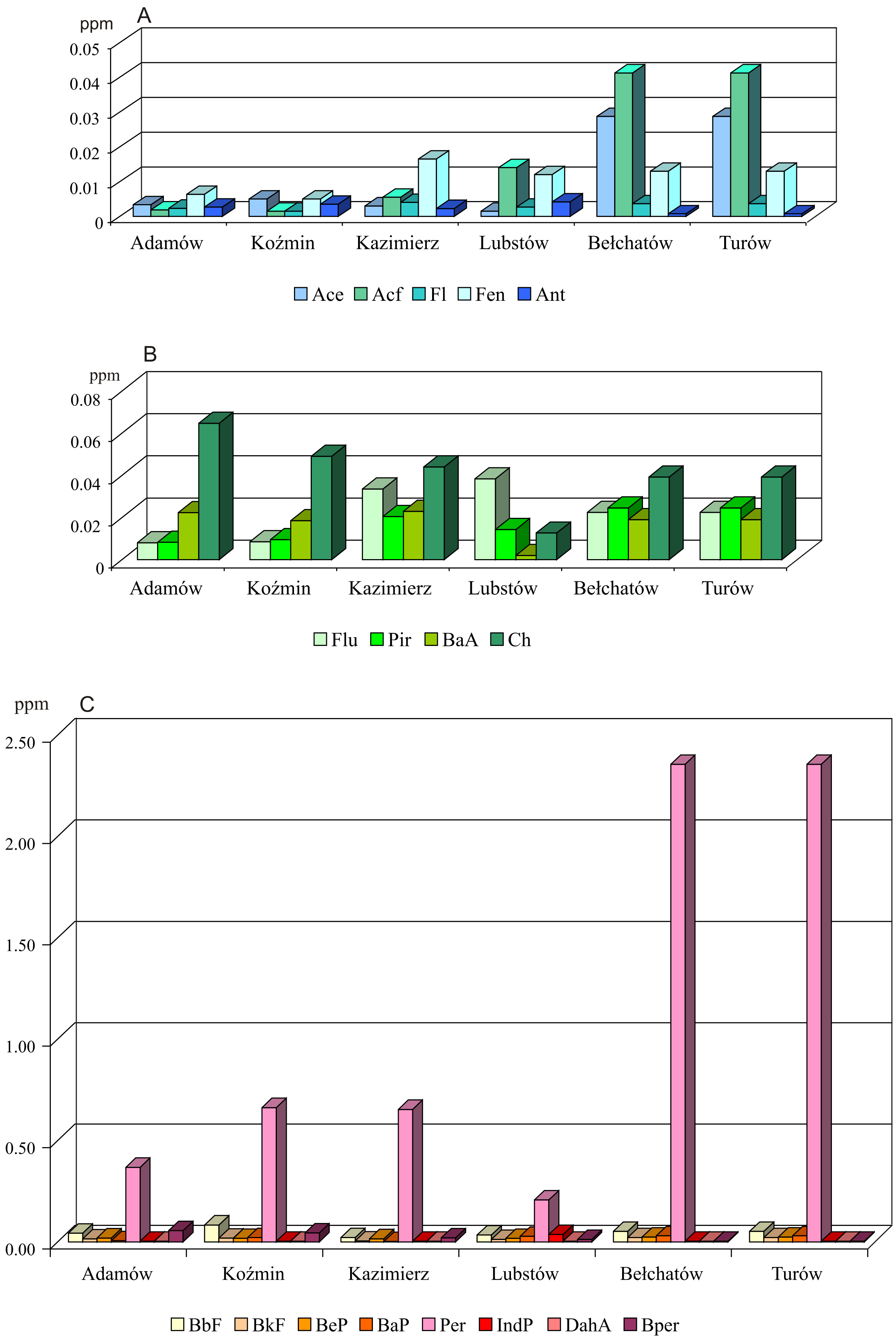

Fig. 2. PAHs in brown coal: **A** — 3-cyclic, **B** — 4-cyclic, **C** — 5-cyclic

For explanations see Table 1

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