



Polycyclic aromatic hydrocarbons in hard coals from Poland

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Concentrations of seventeen unsubstituted polycyclic aromatic hydrocarbons (PAHs) have been determined in hard coal samples from the Carboniferous Upper Silesian, Lower Silesian and Lublin Coal Basins. Among the investigated coals the highest average content of PAHs was determined for the Lower Silesian coals — 6.619 ppm, whereas the means for the Upper Silesian and Lublin coals were 4.11 and 4.319 ppm respectively. Hard coals from the Lublin Coal Basin have relatively high contents of the 5- and 6-cyclic hydrocarbons and lower contents of the 3-cyclic hydrocarbons (0.180 ppm) than coals from the Lower Silesian and Upper Silesian Coal Basins, which contain 2.542 and 1.437 ppm respectively. Within the Upper Silesian Coal Basin there are differences in the PAH “profiles”: the coals from the eastern part of the basin have higher contents of the 5- and 6-cyclic aromatic hydrocarbons and lower contents of the 3-cyclic hydrocarbons than those from the western part of the basin.

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) together with polychlorinated biphenyls (PCBs) and chlororganic pesticides such as DDT or hexachlorobenzene, harmful to animals and persistent in the environment and so are included in the group of compounds termed persistent organic pollutants (POPs). The PAHs are present in small quantities in all subaqueous sediments, both recent and fossil. These compounds may be synthesised by plants and adsorbed by plant organisms from the atmosphere, or they may be products of microbial metabolism during decomposition of vegetable and animal matter. Moreover, they form during petroleum generation, during the diagenesis of coal and they are introduced to the environment during forest and peat fires, and during volcanic eruptions (Evans *et al.*, 1990; Maliszewska-Kordybach, 1993; Capaccioni *et al.*, 1995; Harvey, 1998; Howsam and Jones, 1998; Koziński and Saade, 1998; Neilson and Hynning, 1998). Presently combustion of coals, processing of mineral fuels in the coke plants and oil refineries, combustion of liquid fuels in car and plane engines, exploitation, transport and storage of liquid fuels are

the main sources of PAHs in the environment (Behymer and Hites, 1988; Harvey, 1998; Howsam and Jones, 1998).

In the natural environment the PAHs occur as a mixture of various unsubstituted and substituted aromatic compounds, consisting of two or more carbon rings. Contents of individual hydrocarbons and quantitative ratios between them are very variable in different rocks and substances. For this reason PAH “profiles” have been tentatively used in the determination of sedimentary environments. Higher contents of phenanthrenes were observed in marine deposits and in petroleum than in fresh-water deposits. On the other hand, relatively high amounts of fluorene and dibenzofurane are believed to be typical of fresh-water deposits (Pu *et al.*, 1990; Bojakowska and Sokołowska, 1999). Differences in PAH composition were also found in combustion gases emitted during the burning of various substances rich in organic matter (Beak *et al.*, 1991; Miguel *et al.*, 1998). Probably some of the unsubstituted PAHs present in sediments formed by combustion, e.g. pyrene, fluoranthene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, benzo(ghi)perylene and coronene; others might have come from biological precursors of the PAHs, e.g. perylene, which could form during diagenesis from abietic acid, a common

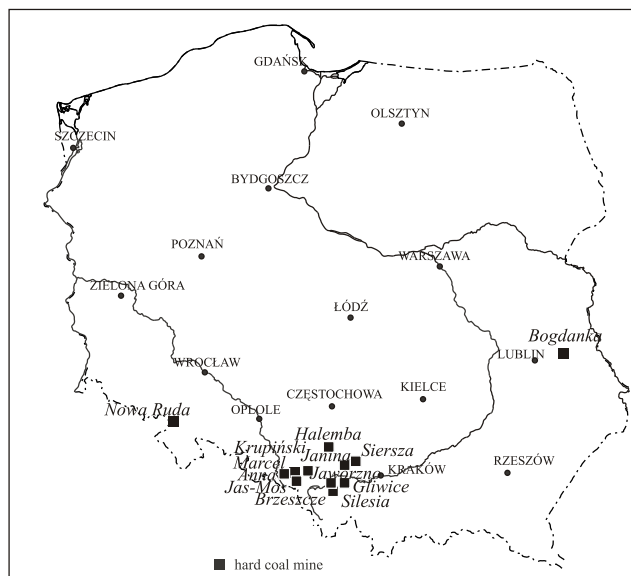


Fig. 1. Localisation of hard coal mines

diterpenoid of conifer resins. There are also compounds such as phenanthrene and chrysene, that might have formed from both combustion and diagenetic alteration of terpenoids (Jiang *et al.*, 1998).

Data on the occurrence of unsubstituted PAHs in coals, important for environment protection, are scarce and wholly lacking for Polish coals. Most publication on the occurrence of PAHs in geologic environments has discussed the presence of the substituted PAHs in petroleum and parent rocks, their role as biomarkers, factors determining the maturity of petroleum and their source substance (Ramanampisoa and Radke, 1995; Smith *et al.*, 1995; Requejo *et al.*, 1996). Combustion of hard coal is one of the most important sources of emission of the unsubstituted PAHs to the environment. This emission probably includes compounds newly formed during combustion and those which “survived” the burning process (Howsam and Jones, 1998). The mass combustion of hard coal means that, the primary content of these harmful compounds in this fuel is likely to be important. Data on the occurrence of selected unsubstituted PAHs in hard coals from various Polish deposits are given here.

EXTENT AND METHODS OF INVESTIGATION

Samples of hard coals from several mines from the Carboniferous Upper Silesian, Lower Silesian and Lublin Coal Basins were selected (Fig. 1). The determinations of the PAHs in hard coals were made in four samples from the Bogdanka mine,

three samples from the Nowa Ruda mine and fifteen samples from Upper Silesian coal mines, thus jointly in 22 samples.

The Late Carboniferous productive rocks of the Upper Silesian Coal Basin (USCB) include four lithostratigraphic series: the Paralic Series, the Upper Silesian Sandstone Series, the Mudstone Series and the Kraków Sandstone Series. Stratigraphically, the Paralic Series to the Namurian A, the Upper Silesian Sandstone Series to the Namurian B and C, the Mudstone Series to the Westphalian A and B and the Kraków Sandstone Series to Westphalian B, C and D (Kotas, 1995). The samples were collected from the Libi Beds (Janina mine) and the Łaziska Beds (Siersza mine) of the limnic Kraków Sandstone Series, from the Orzesze Beds of the Mudstone Series (Brzeszcze and Krupiski mines), from the Ruda and the Saddle Beds of the Upper Silesian Sandstone Series (Halemba and Jas-Mos mines), as well as the Poruba Beds (Anna mine), the Jaklovec Beds (Marcel, Jas-Mos and Anna mines) and the Hrušov Beds (Gliwice mine) of the Paralic Series. There are different varieties of hard coal in the basin. The Upper Silesian coals represent a large spectrum from weakly carbonised power coals, through coking coals to anthracites. The carbonification grade of these coals from vitrinite reflectance (R_o) ranges from 0.5–0.75% in the eastern part of the basin to 0.7–1.9% in its western part (Jurczak-Drabek, 1996). The Upper Silesian coals are mainly humic and mostly used for electric power plants, less for coke production. Sapropelic coals occur rarely (Kruszewska and Dybova-Jachowicz, 1997). Carbonate rocks are absent from this basin.

Samples of coals of the Lower Silesian Coal Basin (LSCB) were collected in the eastern part of the Intra-Sudetic Depression from the coal-bearing sediments of the Żacle Formation (Westphalian) in the Nowa Ruda mine. The Lower Silesian Coal Basin is an intermontane basin, where coal-forming plants grew on flood plains (Bossowski *et al.*, 1995). Coals of the Nowa Ruda area are of medium carbonification grades yielding mean reflectance (R_o) varying from 1.13 to 1.59%, sporadically reaching 2% (Bossowski, 1995).

Samples from the Lublin Coal Basin (LCB) were collected from siltstone of the Lublin Formation (Westphalian B). The coal-bearing rocks comprise a marine-paralic, paralic-fluvial association. The Lublin Formation is dominated by siltstones and claystones with many seams of hard coal, and numerous fossilised plants and sideritic concretions. These are typical sediments of lake, flood water, swamp and river bed environments. The boundary between the paralic sediments and those formed in the limnic-fluvial environment is in their lower part (Porzycki, 1987). Carbonate rocks typically occur in this basin. The coals occurring in the basin are mainly of the flame and gas-flame type (Porzycki and Zdanowski, 1995). The reflectance (R_o) of these coals ranges from 0.6–0.9% typically.

The contents of 17 PAHs: 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,

Table 1

PAHs in hard coals from different deposits (ppm)

Hydrocarbons	Lublin Coal Basin (n = 4)	Lower Silesian Coal Basin (n = 3)	Upper Silesian Coal Basin (n = 15)
Acenaphthylene (Ace)	$\frac{< 0.001 - 0.006}{0.003}$	$\frac{0.011 - 0.013}{0.012}$	$\frac{< 0.001 - 0.059}{0.017}$
Acenaphthene (Acf)	$\frac{0.005 - 0.03}{0.017}$	$\frac{0.023 - 0.035}{0.029}$	$\frac{0.002 - 0.107}{0.038}$
Fluorene (Fl)	$\frac{0.005 - 0.039}{0.018}$	$\frac{0.441 - 0.665}{0.562}$	$\frac{0.003 - 0.641}{0.238}$
Phenanthrene (Fen)	$\frac{0.024 - 0.205}{0.117}$	$\frac{1.595 - 2.204}{1.920}$	$\frac{0.006 - 2.328}{1.092}$
Anthracene (Ant)	$\frac{0.025 - 0.052}{0.038}$	$\frac{0.015 - 0.027}{0.020}$	$\frac{< 0.001 - 0.236}{0.052}$
Fluoranthene (Flu)	$\frac{0.153 - 0.456}{0.283}$	$\frac{0.066 - 0.139}{0.101}$	$\frac{0.006 - 0.447}{0.112}$
Pyrene (Pir)	$\frac{0.353 - 0.722}{0.577}$	$\frac{0.15 - 0.283}{0.219}$	$\frac{0.007 - 0.415}{0.186}$
Benzo(a)anthracene (BaA)	$\frac{0.323 - 0.871}{0.563}$	$\frac{0.252 - 0.516}{0.384}$	$\frac{0.008 - 0.614}{0.292}$
Chrysene (Ch)	$\frac{0.313 - 0.75}{0.471}$	$\frac{0.797 - 1.254}{1.079}$	$\frac{0.014 - 1.276}{0.600}$
Benzo(b)fluoranthene (BbF)	$\frac{0.305 - 1.001}{0.552}$	$\frac{0.28 - 0.628}{0.470}$	$\frac{0.143 - 0.859}{0.325}$
Benzo(k)fluoranthene (BkF)	$\frac{0.172 - 0.214}{0.202}$	$\frac{0.039 - 0.065}{0.053}$	$\frac{0.017 - 0.889}{0.151}$
Benzo(e)pyrene (BeP)	$\frac{0.298 - 0.849}{0.473}$	$\frac{0.593 - 1.346}{1.076}$	$\frac{0.076 - 1.38}{0.448}$
Benzo(a)pyrene (BaP)	$\frac{0.346 - 0.769}{0.513}$	$\frac{0.154 - 0.46}{0.302}$	$\frac{0.056 - 0.574}{0.233}$
Perylene (Per)	$\frac{0.019 - 0.05}{0.035}$	$\frac{< 0.003 - 0.007}{0.004}$	$\frac{< 0.003 - 0.157}{0.030}$
Indeno(1, 2, 3-cd)pyrene (IndP)	$\frac{0.061 - 0.21}{0.123}$	$\frac{0.025 - 0.07}{0.051}$	$\frac{< 0.005 - 0.908}{0.128}$
Dibenzo(ah)anthracene (DahA)	$\frac{0.024 - 0.061}{0.037}$	$\frac{0.066 - 0.135}{0.102}$	$\frac{0.017 - 0.128}{0.043}$
Benzo(ghi)perylene (Bper)	$\frac{0.092 - 0.405}{0.201}$	$\frac{0.104 - 0.341}{0.236}$	$\frac{0.044 - 0.364}{0.123}$
Total PAH _A	$\frac{0.060 - 0.332}{0.180}$	$\frac{2.085 - 2.943}{2.542}$	$\frac{0.013 - 2.902}{1.437}$
Total PAH _B	$\frac{1.321 - 2.777}{1.544}$	$\frac{1.265 - 2.192}{1.784}$	$\frac{0.038 - 2.425}{1.190}$
Total PAH _C	$\frac{1.354 - 3.556}{2.595}$	$\frac{1.263 - 3.052}{2.293}$	$\frac{0.81 - 3.657}{1.483}$
Total PAH ₁₇ = PAH _A + PAH _B + PAH _C	$\frac{2.735 - 6.665}{4.319}$	$\frac{4.613 - 8.187}{6.619}$	$\frac{1.184 - 8.303}{4.110}$

$\frac{\text{min. content} - \text{max. content}}{\text{mean value}}$; 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]

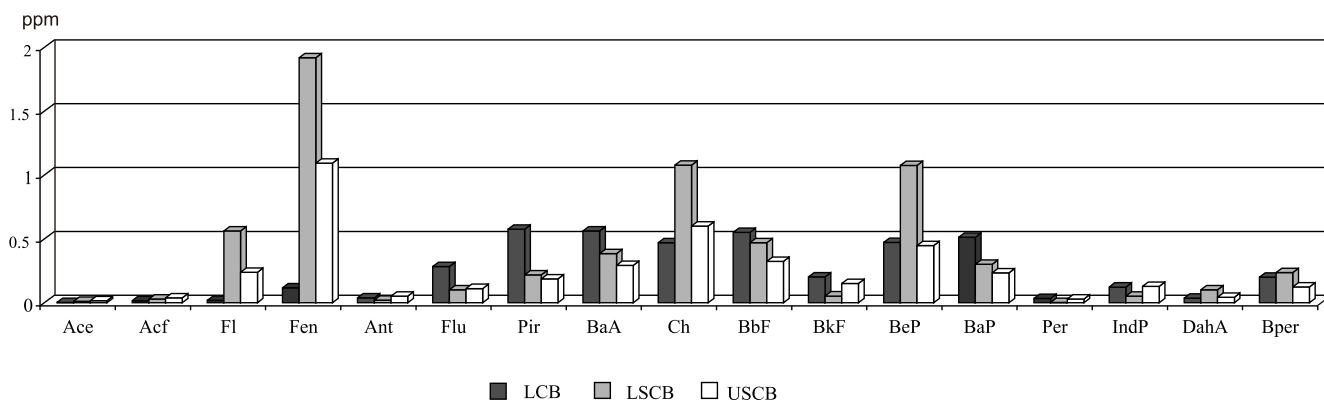


Fig. 2. PAHs in hard coals of the three regions studied

LCB — Lublin Coal Basin, LSCB — Lower Silesian Coal Basin, USCB — Upper Silesian Coal Basin; for other explanations see Table 1

benzo(ghi)perylene were determined. Fifteen of them 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 by 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 in diameter was applied. Analyses were made using an internal standard. Detection limits 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 highest mean PAH concentration was found in the Lower Silesian coals (6.619 ppm), the means for the Upper Silesian and Lublin coals being 4.110 ppm and 4.319 ppm respectively (Tab. 1, Fig.1). The mean content of the seventeen unsubstituted PAHs in these hard coals is significantly higher than their content in recent lacustrine sediments or peats (lacustrine sediments contain about 2 ppm, peats — 0.2–0.3 ppm) and it is also higher than the average contents of these compounds in brown coals (0.7–2.7 ppm) (Bojakowska and Sokołowska, 1999). Quantitative relations between individual hydrocarbons of this group are variable in these deposits.

The PAHs distribution in hard coals depends on several factors. The main ones are:

1. Type of the sediment (autochthonous or allochthonous), vegetation spectrum, sedimentary environment (boggy, limnic or brackish-marine), nutrient levels (eutrophic or oligotrophic),

physico-chemical conditions of the environment (pH, Eh, temperature).

2. The biochemical evolution (processes such as rotting, mouldering, alteration to peat and decay, depend on redox conditions).

3. The geochemical conditions during conversion into coal, as temperature and pressure increased. PAHs in coals developed from natural compounds, mainly terpenoids. The precursors of PAHs might be diterpenoids found in resins, then altered to substituted PAHs such as pimanthene or retene, or triterpenoids in plant tissue, altered into dimethylchrysene or trimethylpicene. Other PAH precursors might be hopanoids present in the bacteria remnants, tetraterpenoids found in green sulphur bacteria and steroids, which might alter into dimethylphenanthrene (Simoneit, 1998). Some substituted PAHs alter to unsubstituted compounds during diagenesis.

The observed variability of the unsubstituted PAHs in the various hard coals is controlled therefore by a number of factors.

Hard coals from the Lublin Coal Basin have relatively high contents of the hydrocarbons such as: fluoranthene, pyrene, benzo(a)anthracene and benzo(a)pyrene, and lower contents of the 3-cyclic hydrocarbons (0.180 ppm) than the coals from the Lower Silesian and Upper Silesian Coal Basins, equaling 2.542 and 1.437 ppm, respectively. Lower Silesian hard coals are distinguished by the highest content of fluorene, phenanthrene, chrysene, benzo(e)pyrene, dibenzo(ah)anthracene and benzo(ghi)perylene when compared to the coals of the other two basins.

The PAH “profile” varies within the Upper Silesian Basin: the coals collected in the mines in the western part of the basin are characterised by higher concentrations (45%) of the 3-cyclic hydrocarbons — phenanthrene and fluorene — in comparison to the coals in the eastern part of the basin (21%). Coals from the western part of the Upper Silesian Basin are poorer in 5- and 6-cyclic aromatic hydrocarbons (ca. 26% of

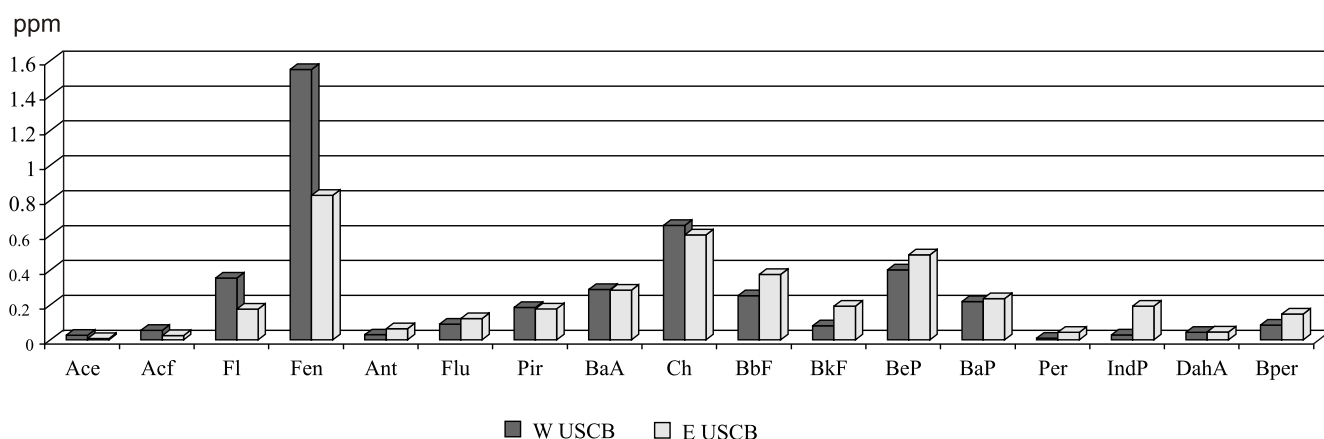


Fig. 3. Differentiation of PAHs in Upper Silesian hard coals

W USCB — west Upper Silesian Coal Basin, E USCB — east Upper Silesian Coal Basin; for other explanations see [Table 1](#)

the total determined PAHs) than the coals from the eastern part of the basin (*ca.* 51%). The coals collected in the western part of the basin have lower concentrations of benzo(b)fluoranthene, benzo(k)fluoranthene, perylene, indeno(1, 2, 3-cd)pyrene and benzo(ghi)perylene (Fig. 3). The higher contents of the 5- and 6-cyclic aromatic hydrocarbons and lower amounts of the 3-cyclic aromatic hydrocarbons in the eastern part of the basin probably reflect the sedimentary environment. In the western part of the basin the coals were sampled from seams of paralic origin, and in the eastern part

from seams of limnic origin. Nevertheless, the observed differences in the PAH “profile” were probably caused by the alteration of the lower molecular weight PAHs into high molecular weight compounds due to hydrothermal processes, in the eastern part of the basin.

The coals investigated from the Lower Silesian Coal Basin and the western part of the Upper Silesian Coal Basin have higher contents of phenanthrene, fluorene and chrysene. Coals from these deposits have a higher carbonification grade.

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