



## PAHs SPECTRUM IN THE SOILS OF THE INDUSTRIAL AREAS

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**Abstract.** Concentrations of seventeen unsubstituted polycyclic aromatic hydrocarbons and total organic carbon (TOC) were determined in soil samples collected in industrial areas where the raw organic-rich materials — hard coals, lignite, and oils were processed. The conducted studies have shown diversification of PAHs spectrum in soils in the vicinity of different pollution sources. In the PAHs spectrum in soils around power plant area, the predominating unsubstituted polyarenes are fluoranthene and pyrene; however, in soil of the brown coal-fired power plant area, a relative increase of perylene in comparison to other hydrocarbons is observed.

The PAHs spectrum of the soils taken in the vicinity of hard coal-fired power plant is characterised by a great share of benzo(b)fluoranthene, chrysene and benzo(a)pyrene. PAHs soil spectrum in the vicinity of hard coal-fired power plant, and PAHs soil spectrum in gasworks area and coking plant sites, point out to a certain similarity to PAHs spectrum of hard coal. In the copper smelter area, an increase of phenanthrene and chrysene (prevailing PAHs compounds in copper-bearing shales) is visible. A considerable share of fluorine and phenantrene in soils collected near the rectifying column in refinery is undoubtedly connected with the dominating share that hydrocarbons have in the composition of unsubstituted PAHs in crude oils.

Among the studied sites, only the PAHs/TOC ratio of the soils from the vicinity of the brown coal-fired power plant was relatively low ( $0.20 \times 10^{-4}$ ). In the remaining sites, PAHs/TOC ratio was higher, usually above  $1 \times 10^{-4}$ .

**Key words:** polycyclic aromatic hydrocarbons, power plant, gasworks, coking plant, refinery, copper smelter, Poland.

**Abstrakt.** Oznaczono zawartość węgla organicznego oraz siedemnastu wielopierścieniowych węglowodorów aromatycznych w próbkach gleb pobranych na terenach przemysłowych, gdzie w przeszłości przetwarzano surowce bogate w materię organiczną. Zaobserwowano zróżnicowanie spektrum WWA w glebach z obszarów będących w sąsiedztwie różnych źródeł zanieczyszczenia. W glebach w pobliżu elektrowni przeważającymi związkami są fluoranten i piren, przy czym w strefie elektrowni opalanej węglem brunatnym znaczący udział ma również perylen, a w sąsiedztwie elektrowni opalanych węglem kamiennym — benzo(b)fluoranten, benzo(a)piren i chryzen. Odnotowano, że spektra WWA w glebach w sąsiedztwie gazowni, koksowni i elektrowni opalanych węglem kamiennym wykazują podobieństwo do spektrum WWA w węglu kamiennym. Ponadto w spektrum WWA w glebach na terenie huty miedzi obserwowana jest podwyższona zawartość fenentrenu i chryzenu (przeważających składników WWA w łupkach miedzionośnych), zaś w glebach w sąsiedztwie kolumny rektyfikacyjnej na terenie rafinerii widoczny jest znaczący udział fluorenu i fenantrenu, co jest niewątpliwie związane z dużym udziałem tych WWA w ropie naftowej. W zbadanych glebach stosunek WWA/TOC jedynie w sąsiedztwie elektrowni opalanych węglem brunatnym jest względnie niski ( $0,20 \times 10^{-4}$ ), podczas gdy w pozostałych lokalizacjach był on znacznie wyższy i przekraczał najczęściej  $1 \times 10^{-4}$ .

**Słowa kluczowe:** wielopierścieniowe węglowodory aromatyczne, elektrownie, gazownie, koksownie, rafineria, huta miedzi.

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## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a numerous (several hundred substances) and very diversified group of compounds commonly found in small amounts in all environmental systems. Unsubstituted high molecular weight compounds, especially five- and higher ring (e.g. benzo(a)pyrene, benzo(b)fluoranthene, benzo(ghi)perylene) are the most hazardous to the environment quality because of their adverse biological effects, of their slow degradation and durability in the environment, and accumulation in soils and water sediments. Low molecular weight compounds (e.g. naphthalene, fluorene, phenanthrene) pose also a serious threat to the environment because of their strong toxicity for the aquatic organisms.

Low contents of PAHs are present in hard coals and brown coals, bituminous shales and crude oils (Pu *et al.*, 1990; Bence *et al.*, 1996; Simoneit, Fetzer, 1996; Bojakowska *et al.*, 2000; Bojakowska, Sokołowska, 2001a, b, c; Lavric, Spangenberg, 2002). Their occurrence have been confirmed in all the elements of environment: i.e. in carbonaceous chondrites and interplanetary dust, atmosphere, water, sediments and soils; they were also detected in food, cigarette smoke and vehicle exhaust gases, and in many other products, such as tars, asphalts, wood tars and creosotes (Bradley *et al.*, 1994; McGroddy, Farrington, 1995; Ollivon *et al.*, 1995; Harvey, 1998; Howsam, Jones, 1998; Maliszewska-Kordybach, 2000; Mimura *et al.*, 2002; Naraoka *et al.*, 2002).

In natural conditions, the formation of polycyclic aromatic hydrocarbons is the consequence of high temperature pyrolysis of organic substances during forest and mires fires (it is assumed that such fires are the biggest natural-source of PAHs). Moreover, PAHs are created during diagenesis of deposited materials (especially as a result of petroleum origin or alteration of organic matter in coal), and they may be formed during volcano eruptions or be synthesised by plants and by microorganisms during the decomposition of organic remnants (Ramanampisoa, Radke, 1995; Smith *et al.*, 1995; Requejo *et al.*, 1996; Sun, Xu, 2002). Polycyclic aromatic hydrocarbons

occur in the environment as a mixture of various unsubstituted and substituted compounds bearing two or more aromatic rings. The presence of the individual PAHs and their quantitative ratios vary greatly in different fossil fuels. For example, in lignite the unsubstituted PAH found in the largest amount is perylene, and its content is several tens time higher in comparison with other unsubstituted determined polyarenes, while PAHs spectrum of hard coals is characterised by the occurrence of four- and five-ring compounds of similar concentrations. On the other hand, in oils PAHs are composed mainly of three-ring hydrocarbons (Bojakowska, Sokołowska, 2001a, b, c).

It is assumed that polycyclic aromatic hydrocarbons are released to the environment mainly during an incomplete combustion of organic matter in natural and anthropogenic processes. Nowadays, PAHs emissions to environment from anthropogenic sources exceed many times emission from natural sources (Howsam, Jones, 1998). The biggest PAHs amounts are released to environment during the combustion of fossil fuel and biomass used for house heating, burning of petrol by vehicles, and as a result of heavy industry activity connected with coal and oil processing, mainly coking and gas plants, oil refineries, steel industry, aluminium and copper smelters.

The investigation of PAHs in recent soils by means of  $^{13}\text{C}$  and  $^{14}\text{C}$  isotope markers has indicated that these present in soil compounds are primarily of exogenic origin and they are probably linked to atmospheric dust deposition from burning of fossil fuel (Lichtfouse *et al.*, 1997). The studies of polyarenes in peat pointed out that peat formed in the pre-industrial period is characterised by a relatively poor unsubstituted PAHs spectrum, and the presence of mainly three-ring hydrocarbons: acenaphthene, fluorene and phenanthrene, and four-ring fluoranthene, while study of the recently formed peat reveals that PAHs concentrations are three times higher, and that that PAHs spectrum is similar to PAHs profile observed in recent river and lake sediments (Bojakowska, Sokołowska, 2003).

## MATERIAL AND METHODS

Concentrations of seventeen unsubstituted polycyclic aromatic hydrocarbons and total organic carbon (TOC) were determined in samples of soils collected in plant and factory areas and their protective zones where raw organic-rich materials: hard coals, lignite, oils, and bituminous shales are combusted or processed. Soil samples were taken at a depth of 0–20 cm in the following localities (Fig. 1):

- the power plant “Ostrołęka” in Ostrołęka (Mazowieckie Voivodship), hard coal-fired power plant where coals from Upper Silesian Coal Basin and Lublin Coal Basin are burnt,
- power plant “Bełchatów” in Rogowiec (Łódzkie Voivodship), the largest brown coal-fired power plant in Poland and Europe,
- coking plant “Przyjaźń” in Dąbrowa Górnicza (Śląskie Voivodship) with annual average production of coke of about 2.5 mln t,

- old gasworks in Mogilno (Kujawsko-Pomorskie Voivodship), where above 0.10 mln m<sup>3</sup> of gas was produced annually,

- refinery “Glimar” in Gorlice (Małopolskie Voivodship), the oldest refinery in Poland (set to work in 1883), producing special kind of kerosene, engine oils, industry oils, extra oils, and waxes; and still processing in average about 0.16–0.17 mln tons annually,

- copper smelter “Legnica” in Legnica, smelting copper from organic-rich Zechstein copper-bearing bituminous shales.

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)anthracene, and benzo(ghi)perylene, listed in the environmental studies by the US EPA (Kabata-Pendias *et al.*, 1995),

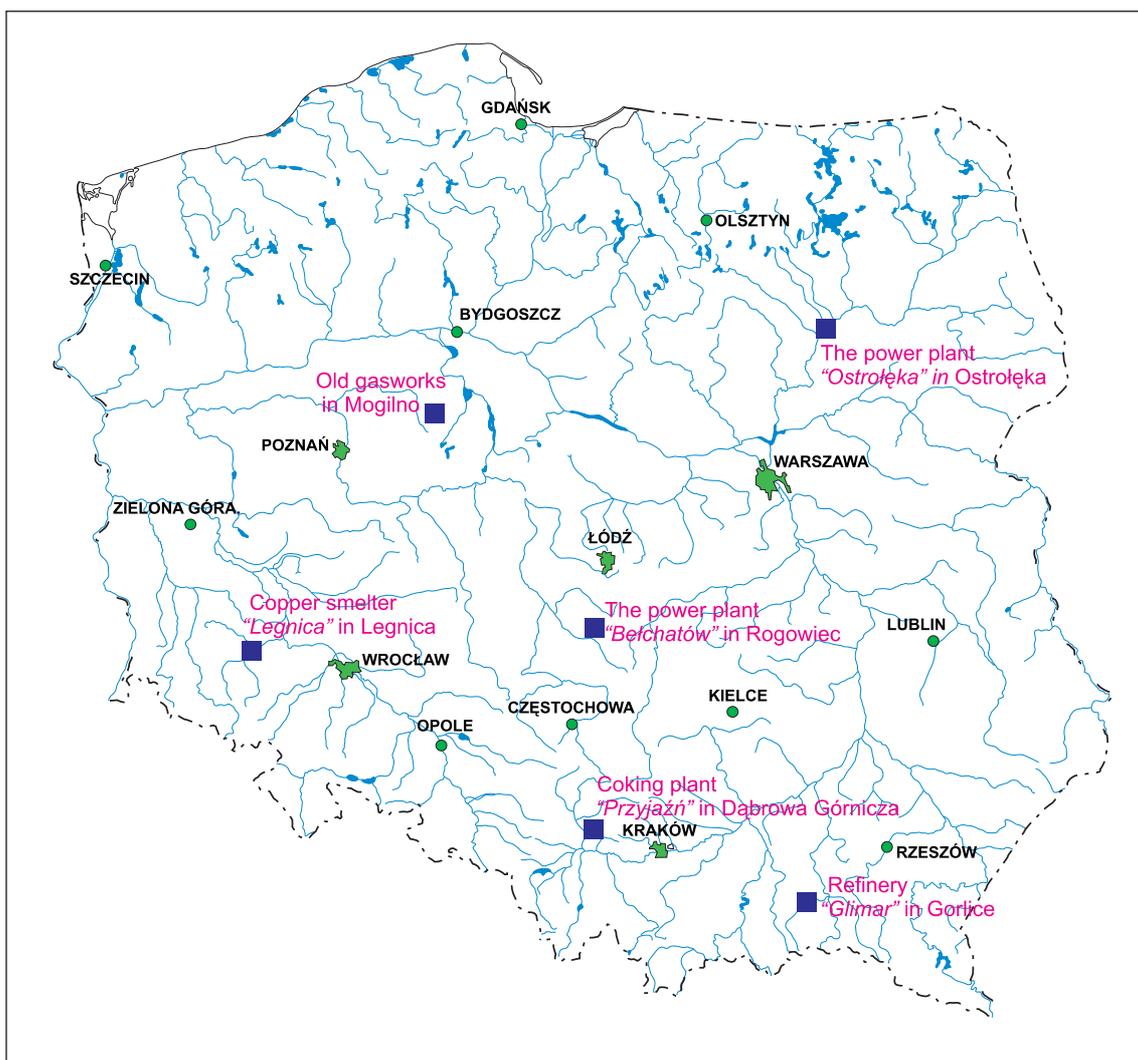


Fig. 1. Localization of sampling sites

and benzo(e)pyrene and perylene were determined in the soil samples. Fraction of aromatic hydrocarbons was obtained by a liquid-solid extraction method with the use of SOXTEC apparatus; the solvent applied included dichloromethane. After desulphurisation with the use of metallic copper, the extracts were concentrated in TurboVap apparatus. The samples were tested with the use of a gas chromatograph, with a mass spectrometer detector (Hewlett-Packard GC/MSD, model 5890II), and with a mass spectrometer detector (MSD 5971). A HP-1 nonpolar capillary

column (length: 25 m, diameter: 0.2 mm, film: 0.33  $\mu\text{m}$  (5%)-diphenyl-(95%)-dimethylpolysiloxane). The temperature was set on 70°C 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 with the use of an external standard method. The following standards were applied: PM-612 from Ultra Scientific and certified perylene and benzo(a)pyrene from Prochem. Total organic carbon (TOC) contents were determined with a coulometric titration method with the use of COULOMAT 702 CS/LI.

## RESULTS AND DISCUSSION

The production of electric and thermal energy by combustion of hard and brown coals is accompanied with PAHs emission. In soil samples collected in "Bełchatów" power plant area (brown coal-fired), polycyclic aromatic hydrocarbons occur in relatively small amounts, in spite of burning large quantities of brown coals in this power plant. Nevertheless, in nearly all studied soil samples, PAHs contents were higher than those observed

in unpolluted soil samples. PAHs concentration was within the range of 0.12 to 0.81 ppm (Table 1), and total organic contents in soils were within the range of 0.49% to 6.09%. PAHs/TOC ratios were within the range of  $0.08 \times 10^{-4}$ – $0.60 \times 10^{-4}$  (mean —  $0.20 \times 10^{-4}$ ). Fluoranthene and phenanthrene > pyrene > benzo(b)fluoranthene occurring in smaller concentrations were the prevailing hydrocarbons in PAHs profile (Fig. 2). The higher

Table 1

## Polycyclic aromatic hydrocarbons in soils (ppm)

Hydrocarbon	“Bełchatów” power plant (n = 10)	“Ostrołęka” power plant (n = 8)	“Przyjaźń” coking plant (n = 10)	Gasworks Mogilno (n = 4)	“Glimar” Refinery (n = 4)	“Legnica” copper smelter (n = 12)
Acenaphthylene (Ace)	<u>&lt;0.001–0.002</u> 0.001	<u>0.001–0.031</u> 0.007	<u>0.002–2.537</u> 0.767	<u>0.17–8.7</u> 2.655	<u>0.001–0.952</u> 0.242	<u>0.001–0.019</u> 0.010
Acenaphthene (Acf)	<u>0.001–0.015</u> 0.004	<u>0.003–0.012</u> 0.006	<u>0.002–0.556</u> 0.227	<u>0.07–1.3</u> 0.465	<u>0.003–0.122</u> 0.035	<u>0.002–0.022</u> 0.014
Fluorene (Fl)	<u>0.002–0.013</u> 0.005	<u>0.003–0.01</u> 0.007	<u>0.002–4.183</u> 0.762	<u>0.12–1.8</u> 0.885	<u>0.006–0.142</u> 0.053	<u>0.003–0.034</u> 0.022
Phenanthrene (Fen)	<u>0.017–0.092</u> 0.036	<u>0.031–0.125</u> 0.077	<u>0.002–41</u> 7.267	<u>3.16–41.8</u> 21.243	<u>0.035–0.328</u> 0.170	<u>0.044–0.506</u> 0.235
Anthracene (Ant)	<u>&lt;0.001–0.011</u> 0.004	<u>0.008–0.024</u> 0.014	<u>0.01–7.553</u> 1.576	<u>0.66–37.6</u> 11.310	<u>0.005–1.571</u> 0.415	<u>0.01–0.158</u> 0.046
Fluoranthene (Flu)	<u>0.016–0.119</u> 0.049	<u>0.025–0.533</u> 0.178	<u>0.067–45</u> 9.841	<u>14.35–418.8</u> 135.92	<u>0.035–0.237</u> 0.110	<u>0.054–1.115</u> 0.365
Pyrene (Pir)	<u>0.012–0.086</u> 0.036	<u>0.055–0.428</u> 0.151	<u>0.042–29</u> 6.908	<u>12.35–401.6</u> 125.02	<u>0.034–0.230</u> 0.112	<u>0.042–0.824</u> 0.276
Benzo(a)anthracene (BaA)	<u>0.005–0.045</u> 0.018	<u>0.032–0.291</u> 0.094	<u>0.027–22.211</u> 6.024	<u>8.75–492.3</u> 141.03	<u>0.018–0.184</u> 0.071	<u>0.028–0.573</u> 0.164
Chrysene (Ch)	<u>0.01–0.061</u> 0.029	<u>0.054–0.424</u> 0.178	<u>0.39–25.198</u> 6.692	<u>8.94–471</u> 140.52	<u>0.034–0.332</u> 0.154	<u>0.058–0.629</u> 0.269
Benzo(b)fluoranthene (BbF)	<u>0.011–0.075</u> 0.034	<u>0.048–0.513</u> 0.175	<u>0.039–51.049</u> 10.753	<u>9.5–415.9</u> 132.07	<u>0.039–0.288</u> 0.106	<u>0.036–0.481</u> 0.191
Benzo(k)fluoranthene (BkF)	<u>0.006–0.044</u> 0.020	<u>0.022–0.189</u> 0.073	<u>0.015–17.923</u> 3.685	<u>4.74–147.7</u> 48.81	<u>0.012–0.107</u> 0.042	<u>0.019–0.302</u> 0.106
Benzo(e)pyrene (BeP)	<u>0.009–0.055</u> 0.024	<u>0.034–0.328</u> 0.130	<u>0.02–35.061</u> 6.700	<u>7.51–324.6</u> 101.14	<u>0.036–0.490</u> 0.165	<u>0.033–0.349</u> 0.144
Benzo(a)pyrene (BaP)	<u>0.007–0.052</u> 0.022	<u>0.034–0.444</u> 0.152	<u>0.023–44.339</u> 8.976	<u>8.64–309.2</u> 90.92	<u>0.017–0.352</u> 0.109	<u>0.019–0.477</u> 0.138
Perylene (Per)	<u>&lt;0.003–0.085</u> 0.019	<u>0.007–0.106</u> 0.034	<u>0.004–13.415</u> 2.521	<u>2.81–87.5</u> 25.90	<u>0.002–0.048</u> 0.019	<u>0.005–0.123</u> 0.032
Dibenzo(ah)anthracene (DahA)	<u>&lt;0.005–0.009</u> 0.004	<u>0.006–0.071</u> 0.024	<u>0.05–5.216</u> 1.173	<u>1.32–61.1</u> 18.78	<u>0.008–0.324</u> 0.119	<u>0.005–0.07</u> 0.025
Indeno(1,2,3-cd)piren (IndP)	<u>0.009–0.057</u> 0.023	<u>0.036–0.442</u> 0.136	<u>0.026–31.149</u> 6.522	<u>8.17–274.4</u> 87.37	<u>0.018–1.516</u> 0.465	<u>0.02–0.336</u> 0.118
Benzo(ghi)perylene (Bper)	<u>0.008–0.053</u> 0.021	<u>0.034–0.416</u> 0.132	<u>0.023–26.772</u> 5.567	<u>7.68–227</u> 72.32	<u>0.024–2.809</u> 0.881	<u>0.022–0.297</u> 0.111
Σ PAHs	<u>0.119–0.813</u> 0.351	<u>0.367–3.652</u> 1.278	<u>0.049–57.921</u> 12.089	<u>98.94–3722.3</u> 1156.36	<u>0.372–8.108</u> 3.266	<u>0.401–6.081</u> 2.266
TOC (%)	<u>0.49–6.09</u> 2.33	<u>0.83–6.49</u> 2.49	<u>1.80–88.30</u> 25.77	<u>4.93–27.30</u> 15.88	<u>1.87–7.67</u> 4.53	<u>0.73–3.11</u> 1.73
Σ PAHs/TOC x 10 <sup>-4</sup>	<u>0.08–0.60</u> 0.20	<u>0.06–2.29</u> 0.80	<u>&lt;0.01–83.61</u> 11.62	<u>20.07–136.35</u> 55.88	<u>0.20–1.24</u> 0.56	<u>0.48–6.99</u> 1.53

minimum–maximum  
geometric mean

n — number of samples

perylene contents in comparison to hydrocarbon contents in other soils (which in general occur in very small concentrations) are noteworthy. In the burnt brown coals, the average PAHs content is 2.685 ppm, and the average perylene content — 2.356 ppm. The average concentration of the polyarenes is as follows: benzo(b)fluoranthene — 0.052 ppm and acenaphthene — 0.041 ppm (Bojakowska, Sokołowska, 2001c).

PAHs contents were higher in the “Ostrołęka” power plant area and its impact zone than in the neighbouring “Bełchatów” power plant, and were within the range of 0.367 ppm to 3.652 ppm (Table 1). Coals from Lublin Coal Basin and Upper Silesian Coal Basin burnt in this plant contained PAHs in the average of 4.32 ppm and 4.11 ppm respectively (Bojakowska, Sokołowska, 2001b). Although the burnt hard

coals contained nearly two times more PAHs, the quantity of coal burnt in this power plant is considerably lower than in the “Bełchatów” power plant. Total organic carbon contents in soil were within the range of 0.83–6.49%, and PAHs/TOC ratios were  $0.06 \times 10^{-4}$  –  $2.29 \times 10^{-4}$ . Values higher than  $1 \times 10^{-4}$  were detected in soil samples containing above 1 ppm of PAHs.

In the “Ostrołęka” power plant area soils, PAHs “fingerprints” are characterised by a great share of 5- and 4-ring hydrocarbons in comparison to “Bełchatów” power plant area soils. Fluoranthene, chrysene and benzo(b)fluoranthene were predominating in PAHs spectrum in soils sampled near the “Ostrołęka” power plant. A significant share of benzo-(a)pyrene in determined hydrocarbons (Fig. 3) is visible. This PAHs profile is similar to PAHs profile of hard coal of Bogdanka mine (Lublin Coal Basin), characterised by a relatively great share of the unsubstituted PAHs (Bojakowska, Sokołowska, 2001b). Soils PAHs spectrum differs from the

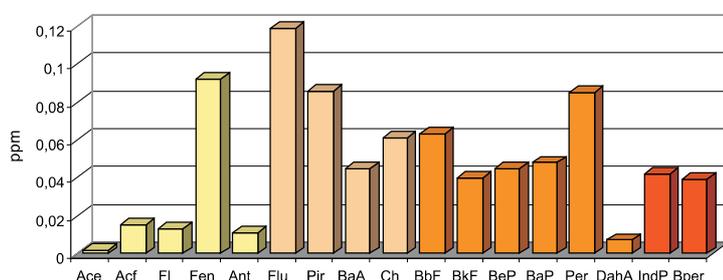


Fig. 2. Polycyclic aromatic hydrocarbons in soil from “Bełchatów” power plant area

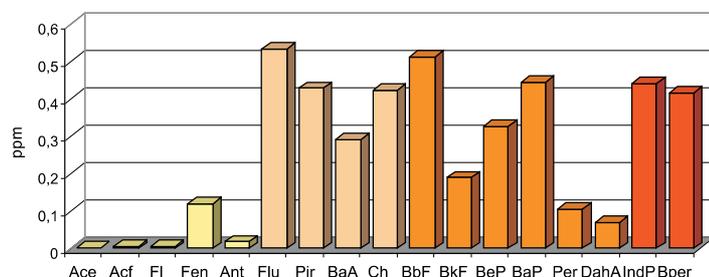


Fig. 3. Polycyclic aromatic hydrocarbons in soil from “Ostrołęka” power plant area

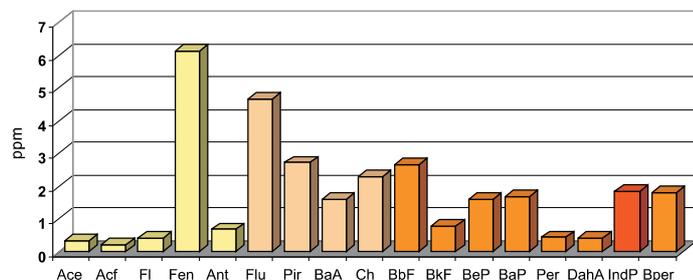


Fig. 4. Polycyclic aromatic hydrocarbons in soil from “Przyjaźń” coking plant area

hard coal PAHs spectrum by greater share of 5-ring compounds and phenanthrene.

Coke manufacturing based on high temperature degassing of coal without air access, creates perfect conditions for forming PAHs. For many years such production was one of the main sources of PAHs emission to environment because of lack of total isolation and air-tight sealing of coke oven batteries. In soil samples collected in a coking plant area, PAHs contents were within the range of 0.049–307.1 ppm. Concentration of PAHs exceeded many times 10 ppm. The highest content was observed in the sample taken near a tar tank.

The studied soil samples were characterised by organic carbon contents within the range of 1.80–88.30%, and the values of PAHs/TOC ratio were within the range of  $<0.01 \times 10^{-4}$  –  $83.61 \times 10^{-4}$ . In soils with high PAHs contents, the PAHs/TOC ratio was 100–1000 times higher in comparison to unpolluted soils. Fluoranthene, pyrene, and benzo-(b)fluoranthene were predominating compounds in PAHs spectrum in soil from the coking plant area in Dąbrowa Górnicza (Fig. 4). These PAHs profiles were characterised by a relatively large benzo(a)pyrene share in the composition of the determined hydrocarbons.

Ancient gasworks, similarly to most of chemical industry plants and works operating in the late XIXth and early XXth centuries, were particularly poisonous to the environment because of numerous leakages in most of the plant facilities, and inefficient operation of the too small purifying installations. Soils around old gasworks sites, which have not been reclaimed yet, are characterised by very high PAHs content. In soil samples taken near the gas tanks, tar tanks, and gas production oven, PAHs contents were within the range of 98.94–3722.3 (the average was 1156 ppm). The highest PAHs contents were detected in soil samples collected in the vicinity of tar tanks, and they were only a bit smaller nearby gas tanks. In general, the studied soils were characterised by high content of organic carbon. The average TOC content was 15.88%, and the average value of PAHs/TOC ratio —  $55.88 \times 10^{-4}$ .

Among the studied polyarenes, 4-ring compounds fluoranthene and pyrene were predominating. 3-ring phenanthrene and 4-ring chrysene and benzo(a)anthracene had also a substantial share (Fig. 5). In hard coal, which was a raw material for gasification of PAHs spectrum, the prevailing compounds are chrysene and benzo(e)pyrene, besides phenanthrene (Bojakowska, Sokołowska, 2001b). Very high benzo(a)pyrene contents, often above permissible standards used for that compounds in industrial land, were detected in nearly all the samples. A diverse spectrum of PAHs at different gasworks was observed, but in all the cases fluoranthene and pyrene were the prevailing compounds in the PAHs profiles.

In the area of a refinery, a release of polycyclic aromatic hydrocarbons to the environment may have taken place from the delivery time, through storage, refinery operations, and dispatch, until the final products. In crude oils, a certain amount of unsubstituted PAHs is present. It can get to the environment during

transport, storage, and distillation. PAHs are also formed during thermal processing of crude oils, especially during cracking and reforming of crude oils, during the fuel production and other refinery products. High-boiling residues, e.g. asphalts are particularly enriched in PAHs. High contents of PAHs exceeded several ppm were identified in the vicinity of amanipulation tank, in a refinery site. They were higher there than near a rectifying column. Total organic content was within the range of 1.87–7.67%, and PAHs/TOC ratio was from  $0.20 \times 10^{-4}$  to  $1.4 \times 10^{-4}$ . PAHs profiles of soils taken near the manipulation tank and the rectifying column are various. In the soil samples collected near the manipulation tank, noteworthy is a great share of six-ring compounds and benzo(e)pyrene, not observed in other samples, while in soils near the rectifying column, phenanthrene and chrysene prevailed (Fig. 6). The considerable share of phenanthrene in soils is undoubtedly connected with a great share of that hydrocarbon in the composition of unsubstituted PAHs in crude oils (Bojakowska, Sokołowska, 2001a).

Copper smelting of the organic-rich Zechstein copper-bearing bituminous shales (containing in average 8.04% of TOC; Kucha, Mayer, 1996) generates polycyclic aromatic hydrocarbons emission to the environment. The studies of unsubstituted PAHs in the Legnica–Głogów Copper District soils have shown the increased level of these compounds in the smelter's vicinity. The detection of PAHs in copper-bearing shales have pointed out that the average content of 17 compounds was 6.94 ppm (from 2.63 ppm to 11.60 ppm), and that fenantrene, chrysene, benzo(b)fluoranthene, and benzo(e)pyrene were prevailing hydrocarbons in the PAHs composition (Bojakowska, Sokołowska, 2002).

Contents of the determined PAHs in the studied soils were from 0.401 ppm to 6.081 ppm, and were higher than those observed in unpolluted soils (<0.2 ppm). The soil samples collected in the protected zone have shown lesser variability of PAHs contents (from 1.26 ppm to 3.06 ppm; mean — 2.05 ppm) than soil samples taken in the smelter area (from 0.40 ppm to 6.08 ppm; mean — 2.42 ppm). Smelter area soils were characterised by TOC contents ranging from 1.54% to 3.11%, and PAHs/TOC ratio within the range of  $0.81 \times 10^{-4}$ – $1.09 \times 10^{-4}$ .

The protected zone soils contain total organic carbon within the range of 0.73–2.36%, and PAHs/TOC value of  $0.48 \times 10^{-4}$ – $6.99 \times 10^{-4}$ . Fluoranthene, pyrene, chrysene, and phenanthrene are predominating in PAHs spectrum of these soils (Fig. 7).

It was observed that the diversification of some hydrocarbons composition has determined PAHs. All soil samples collected in the smelter area were characterised by higher content of chrysene and smaller content of phenanthrene than in the soil samples taken in the impact zone. PAHs fingerprints of soils in the “Legnica” smelter area and its protected zone, are distinguished

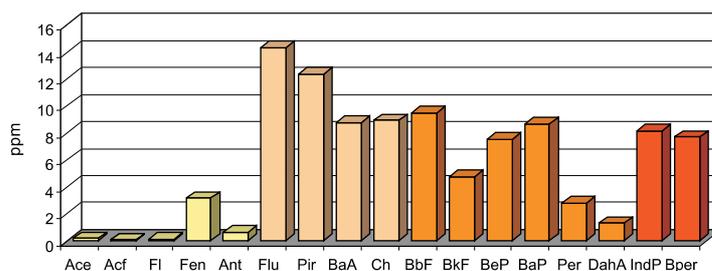


Fig. 5. Polycyclic aromatic hydrocarbons in soil from gasworks area in Mogilno

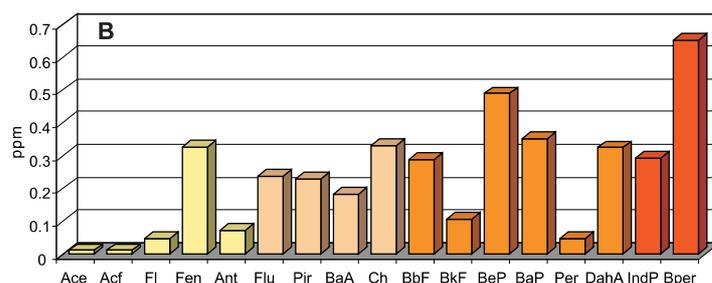
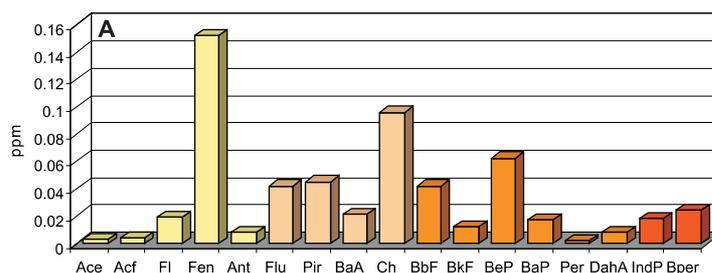


Fig. 6. Polycyclic aromatic hydrocarbons in soil from “Glimar” refinery area. A — rectifying column, B — manipulation tank

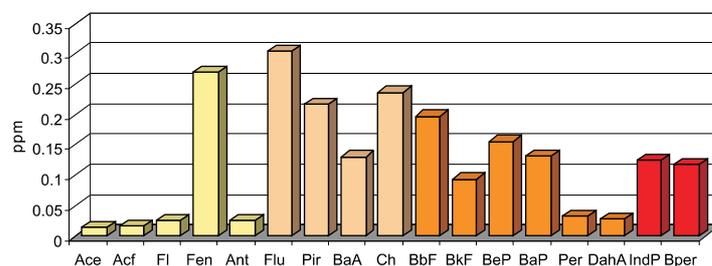


Fig. 7. Polycyclic aromatic hydrocarbons in soil of “Legnica” copper smelter area

from agricultural and forest areas soils by a relatively higher fluoranthene, pyrene, chrysene, and phenanthrene contents in the determined PAHs. The chrysene occurring in the processed bituminous shales may be the chrysene source in soils of the copper smelter area (Bojakowska, Sokołowska, 2003).

The PAHs contents in the studied soil samples, and the share of particular compounds as well, are a result of many processes: atmospheric deposition of PAHs originating from natural sources (forest, prairie, and bogs fires), PAHs of the anthropogenic origin (coal and petrol combustion), incorporation of PAHs, contained in decayed plant materials (fallen tree leaves, which earlier absorbed these compounds from the atmosphere or synthesised them) to

soil, PAHs formed during the microbiological degradation processes or photo degradation and volatilisation of the low molecular weight PAHs compounds, and PAHs synthesised by soil microorganisms.

In general, the natural contents of PAHs in soils do not exceed 0.2 ppm (Bojakowska *et al.*, 2000; Maliszewska-Kordybach, 2000). Areas which the soil samples were collected from are covered by the Quaternary postglacial deposits (fluvioglacial silts, sands, aeolian sands, boulder clays) or Holocene deposits (sands, silts, peat, gravels, clays). Generally, soils formed from these formations are characterised by low contents of PAHs. The occurrence of higher PAHs contents, especially above 0.5 ppm, points to the anthropogenic origin of the compounds in soils.

## CONCLUSIONS

Analyses of the obtained results allow to make an assumption that PAHs spectrum in soils, in the vicinity of industrial plant, depends to a certain degree on PAHs presence in the processed raw materials. The conducted studies have shown diversification of PAHs spectrum in soils in the vicinity of different sources of pollution, and their analyses may provide information on the origin of PAHs sources. In PAHs spectrum in the soils around power plant area, the predominating unsubstituted polyarenes are fluoranthene and pyrene.

However, in soils of the of brown coal-fired power plant area, a relative increase of perylene in comparison to other hydrocarbons is observed. On the other hand, PAHs spectrum of the soils taken in the vicinity of hard coal-fired power plant is characterised by a great share of benzo(b)fluoranthene, chrysene, and benzo(a)pyrene. Furthermore, PAHs soil spectrum in the vicinity of hard coal-fired power plant, and PAHs soil spectrum in gasworks area and coking plant sites, in spite of certain differences, point out to a certain similarity to PAHs spectrum of hard coal, which is distinguished by relatively high contents of fluoranthene, pyrene, and benzo(b)fluoranthene. Moreover, in the copper smelter area, an increase of phenanthrene and chry-

sene (prevailing PAHs compounds in copper-bearing shales) is visible in of PAHs spectrum, and a considerable share of phenanthrene in soils collected near the rectifying column is undoubtedly connected with the dominating share that hydrocarbon has in the composition of unsubstituted PAHs in crude oils.

The value of PAHs/TOC ratio may be a useful parameter in assessing the degree of soil pollution. Generally, organic carbon contents in the unpolluted soil are within the range of 1–3%, and PAHs contents do not exceed 0.2 ppm, hence PAHs/TOC ratio does not exceed  $0.1 \times 10^{-4}$ . Therefore, it may be assumed that the PAHs/TOC ratio higher than  $0.1 \times 10^{-4}$  points out to PAHs soil pollution. Among the studied sites, only the PAHs/TOC ratio of the soils in the vicinity of “Bełchatów” power plant was relatively low ( $0.20 \times 10^{-4}$ ). In the remaining sites, PAHs/TOC ratio was higher and was usually above  $1 \times 10^{-4}$ .

In all the studied sites, PAHs contents higher than natural, occurring in unpolluted soil, were detected. In some cases, PAHs contents were increased a slight degree only, e.g. in the vicinity of power plants; in other localisations PAHs contents were extremely high, exceeded by several tens or several hundred ppm, e.g. old gasworks areas or coking plant site.

## REFERENCES

- BENCE A., KVENVOLDEN K., KENNICUTT M., 1996 — Organic geochemistry applied to environmental assessments of Prince William Sound Alaska, after the Exxon Valdez oil spill — a review. *Org. Geochem.*, **24**, 1: 7–42.
- BOJAKOWSKA I., SOKOŁOWSKA G., 2001a — Polycyclic hydrocarbons in crude oils from Poland. *Geol. Quart.*, **45**, 1: 81–86.
- BOJAKOWSKA I., SOKOŁOWSKA G., 2001b — Polycyclic hydrocarbons in hard coals from Poland. *Geol. Quart.*, **45**: 87–92.
- BOJAKOWSKA I., SOKOŁOWSKA G., 2001c — Polycyclic hydrocarbons in brown coals from Poland. *Geol. Quart.*, **45**: 93–98.
- BOJAKOWSKA I., SOKOŁOWSKA G., 2002 — Composition of polycyclic aromatic hydrocarbons in soils of the “Legnica” copper-works influence zone [Eng. summ.]. *Prz. Geol.*, **50**, 12: 1180–1184.
- BOJAKOWSKA I., SOKOŁOWSKA G., 2003 — Wielopierścieniowe węglowodory aromatyczne (WWA) w glebach zmienionych antropogenicznie. *Biul. Państw. Inst. Geol.*, **405**: 29–60.
- BOJAKOWSKA I., GLIWICZ T., SOKOŁOWSKA G., 2000 — Wyniki monitoringu geochemicznego osadów wodnych Polski w latach 1998–1999. Biblioteka Monitoringu Środowiska.
- BRADLEY L., MAGEE B., ALLEN S., 1994 — Background levels of polycyclic aromatic hydrocarbons (PAHs) and selected metals in New England urban soils. *J. Soil Contamination*, **4**, 3: 1–13.
- HARVEY R., 1998 — Environmental chemistry of PAHs and related compounds. Chemistry (ed. A. H. Neilson): 1–54. Springer-Verlag Berlin, Heidelberg.
- HOWSAM M., JONES K., 1998 — Sources of PAHs in the environment. *Ibidem*: 137–174.

- KUCHA H., MAYER W., 1996 — Geochemia. In: Monografia KGHM Polska Miedz S. A.: 237–250.
- LAVRIC J., SPANGENBERG J., 2002 — Aromatic hydrothermal petroleum from a mercury deposit (Idrija, Slovenia). *Geochimica et Cosmochimica Acta*, **66**, 15A: A435.
- LICHTFOUSE E., BUDZINSKI H., GARRIGUES P., EGLINTON T., 1997 — Ancient polycyclic aromatic hydrocarbons in modern soils:  $^{13}\text{C}$ ,  $^{14}\text{C}$  and biomarker evidence. *Org. Geochem.*, **26**: 353.
- MALISZEWSKA-KORDYBACH B., 2000 — Polycyclic aromatic hydrocarbons in agroecosystems — example of Poland. *Polycyclic Aromatic Compounds*, **21**: 287–295.
- McGRODDY S., FARRINGTON J., 1995 — Sediment porewater partitioning of polycyclic aromatic hydrocarbons in three cores from Boston Harbor, Massachusetts. *Environ. Sci. Technol.*, **29**, 6: 1542–1550.
- MIMURA K., ARAO T., SUGIURA M., SUGISAKI R., 2002 — Shock reaction of phenanthrene. *Geochimica et Cosmochimica Acta*, **66**, 15A: A513.
- NARAOKA H., MITA H., KOMIYA M., SHIMOYAMA A., 2002 —  $\delta$  of individual PAHs from the Murchinson and an Antarctic carbonaceous chondrite. *Ibidem*: A546.
- OLLIVON D., GARBON B., CHESTERIKOFF A., 1995 — Analysis of distribution of some polycyclic aromatic hydrocarbons in sediments and suspended matter in the river Seine (France). *Water, Air, and Soil Pollution*, **81**: 135–152.
- PU F., PHILP R., ZHENXI L., GUANGGUO Y., 1990 — Geochemical characteristics of aromatic hydrocarbons of crude oils and source rocks from different sedimentary environments. *Org. Geochem.*, **16**, 1/3: 427–435.
- RAMANAMPISOA L., RADKE M., 1995 — Extractable aromatic hydrocarbons in a short-term organic cycle of the Kimmeridge Clay formation, Vorkshire (U.K.): relationship to primary production and thermal maturity. *Org. Geochem.*, **23**, 9: 803–817.
- REQUEJO A., SASSEN R., MCDONALD T., DENOUX G., KENNICUTT M., BROOKS J., 1996 — Polynuclear aromatic hydrocarbons (PAHs) as indicators of the source and maturity of marine crude oils. *Org. Geochem.*, **24**, 10/11: 1017–1033.
- SIMONEIT B., FETZER J., 1996 — High molecular weight polycyclic aromatic hydrocarbons in hydrothermal petroleum from the Gulf of California and Northeast Pacific Ocean. *Org. Geochem.*, **24**, 10/11: 1065–1077.
- SMITH J., GEORGE S., BATTS B., 1995 — The geosynthesis of alkylaromatics. *Org. Geochem.*, **23**, 1: 71–80.
- SUN Y., XU S., 2002 — High molecular weight polynuclear aromatic hydrocarbons as indicators for high temperature alteration of reservoir oil. *Geochimica et Cosmochimica Acta*, **66**, 15A: A753.