

## Composition and source of polycyclic aromatic compounds in deposited dust from selected sites around the Upper Silesia, Poland

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About 300 polycyclic aromatic compounds were identified using the GC-MS method in deposited dust collected in sites located outside the industrial belt of the Upper Silesia agglomeration. Concentrations of selected polycyclic aromatic hydrocarbons (PAH) range from 6.8 µg/g dust for anthracene to 142 µg/g dust for fluoranthene. Concentrations of highly carcinogenic PAH e.g. benzo(a)pyrene, benzo(a)fluoranthene and benzo(a)anthracene range from 49 to 145.5 µg/g of dust. Significant concentrations (up to 35 µg/g of dust) of carcinogenic C<sub>22</sub>H<sub>14</sub> PAHs (*m/z* 278) and C<sub>24</sub>H<sub>14</sub> PAHs (*m/z* 302) were determined in all samples. Aromatic ketones and quinones as well as aromatic nitrogen and sulphur compounds with concentrations ranging from 2 to 45 µg/g of dust, were found in the polar NSO fraction. Molecular composition of hydrocarbons in the deposited dust is characteristic of the terrestrial organic matter, as suggested by the presence of long chain *n*-alkanes with odd carbon skeleton predominance. However, relatively high concentrations of steranes and distribution of homohopanes different from terrestrial organic matter suggest that part of extractable organic matter may be from diesel engine exhausts and/or paved road dust. The origin of the organic compounds adsorbed on the deposited dust is related to not complete coal combustion and possibly to other sources, such as automobile exhaust. The occurrence of phenyl-polyaromatic hydrocarbons and polyphenyls such as terphenyls, phenylnaphthalenes and their methyl derivatives, phenylphenanthrenes, phenylfluoranthenes and/or phenylpyrenes results from the free radical phenylation of aromatics during organic matter combustion.

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### INTRODUCTION

Dust emitted into the atmosphere from natural and anthropogenic sources constitutes a substantial, and in some regions prevailing, pollutant of the troposphere. Some of the dust particles are of a size that enables them to be inhaled by humans (the so-called respirable dust). Therefore, they pose a real health-hazard to inhabitants of heavily dusted regions. Not only the concentration of atmospheric dust, but also its chemical and phase compositions play an important role in health hazard.

Anthropogenic air pollution in the urban and industrial agglomeration within the Silesian province has been a key ecological problem in that region and has been a subject of many studies (e.g. Warzecha, 1993; Bodzek *et al.*, 1998; Luks-Betlej and Bodzek, 2000; Wawros *et al.*, 2001).

Special attention was paid to the identification of polycyclic aromatic compounds, because many of them are

carcinogenic and mutagenic, causing irreversible changes in the structure and functioning of living organisms (Bodzek *et al.*, 1993, 1998). One of the most toxic group of compounds are polycyclic aromatic hydrocarbons (PAH) together with their oxygen, nitrogen and sulphur derivatives which naturally occur in geological environments (Killops and Massoud, 1992; Simoneit, 1993; Marynowski *et al.*, 2000, 2001; Bojakowska and Sokołowska, 2001) and are also released due to human activity (e.g. Oros and Simoneit, 2000). The problem of PAH toxicity has been studied for many years (see Zedeck, 1980; Pickering, 1999 for review), yet many problems remain unsolved. For example, it is still unknown why carcinogenic and mutagenic impact of a single PAH is significantly stronger than the impact of the same PAH, occurring at the same concentration in a mixture (Pickering, 2000).

Organic compounds formed through anthropogenic processes (e.g. combustion of coal and wastes, combustion of engine exhausts *etc.*) are adsorbed on dust particles smaller than 5 µm in diameter and can be transported over long distances by



Fig. 1. Sampling locations of the Upper Silesia region

wind. Dust particles smaller than  $1\ \mu\text{m}$  with adsorbed PAH can remain in the air from 4 to 40 days, whereas particles ranging from 1 to  $10\ \mu\text{m}$  in size reside in the atmosphere from 0.4 to 4 days (Brandys, 1990). Tropospheric dust in Upper Silesia consists of minerals characterised by high adsorption capabilities for organic phases (Manecki, 1976; Rietmeijer and Janeczek, 1997; Jabłońska, 1999; Jabłońska *et al.*, 2001). This paper characterises organic compounds adsorbed on deposited dust particles collected in three sites located outside the urban and industrial agglomeration of Upper Silesia (Fig. 1). The origin of organic matter (OM) is discussed. Particular attention is paid to poorly known phenylpolyaromatic hydrocarbons and polyphenyls.

## SAMPLES AND METHODS

**Samples.** Dust collection sites were selected to avoid a direct impact of both industrial and urban influences of the Upper Silesia agglomeration. Sampling locations included (Fig. 1):

— Ustroń, a town located in the foothills of the Carpathians (Beskidy Mts.) some 80 km south of the Upper Silesia agglomeration.

— Wielowieś, a village located NW of the Upper Silesia agglomeration. Wielowieś is considered by the local health authorities as a “clean-air” reference site for the province.

— Sączów, a village adjacent to the Upper Silesia agglomeration.

Prevailing winds in that part of Poland are from western directions, therefore both Ustroń and Wielowieś do not have significant air pollution from the Upper Silesia agglomeration for most of the year. In all of the selected locations, coal-fired domestic furnaces and coal-fired heat-generating plants are major dust emitters. This was clearly shown in Wielowieś, where the amount of gypsum and barite in dust increases dramatically in winter, during the heating period. Both those sulfates are formed as a result of increased emission of  $\text{SO}_2$  from the local heat-generating power plant (Jabłońska *et al.*, 2001).

Samples were collected between January and March 2000 by the method described by Jabłońska *et al.* (2001). Fourteen dust samples were analysed in this study, including 5 samples from Wielowieś, 5 samples from Ustroń and 4 samples from Sączów.

**Methods.** The deposited dusts were Soxhlet-extracted in pre-extracted thimbles with dichloromethane. Extracts were further separated using preparative pre-washed TLC plates coated with silica gel (Merck,  $20 \times 20 \times 0.25\ \text{cm}$ ). Prior to separation, the TLC plates were activated at  $120^\circ\text{C}$  for one hour. The plates were loaded with the *n*-hexane soluble fraction and developed with *n*-hexane. Bands comprising aliphatic ( $R_f$  — 0.4–1.0), aromatic ( $R_f$  — 0.05–0.4) and polar ( $R_f$  — 0.0–0.05) fractions were collected. Furthermore, polar fractions were again developed with *n*-hexane/benzene mixture (V:V; 6:4) on the second TLC plates coated with silica gel (Merck,  $20 \times 20 \times 0.25\ \text{cm}$ ). Four sub-fractions were obtained. The aromatic oxygen and nitrogen compounds occurred in the 2–3 fractions ( $R_f$  — 0.05–0.5). The aliphatic and aromatic fractions as well as sub-fractions 2 and 3 were analysed in detail.

GC-MS analysis was carried out with a *HP5890 II* gas chromatograph, equipped with a fused silica capillary column ( $60\ \text{m} \times 0.25\ \text{mm}$  i.d.), coated with 95% methyl/5%phenylsilicone phase (HP-5, 0.25  $\mu\text{m}$  film thickness). Helium was the carrier gas used. The GC oven was programmed from 35 to  $300^\circ\text{C}$  at a rate of  $3^\circ\text{C}\ \text{min}^{-1}$ . The gas chromatograph was coupled with a *HP 5971A* mass selective detector (MSD). The MS was operated with an ion source temperature of  $200^\circ\text{C}$ , an ionisation energy of 70 eV, and a cycle time of 1 sec in the mass range 40–600 Daltons.

**Authentic standards.** Most of the used standards are commercially available compounds. We gratefully acknowledge Dr. R. Meyer zu Reckendorf for providing the authentic standards of 1-phenylpyrene, 2-phenylfluoranthene, benzonaphthofurans, benzoanthrone, cyclopenta(*def*)phenanthrenone and xanthone. We also acknowledge Prof. J. Andersson for the kind gift of the standards: benzo[*b*]naphtho[2,1-*d*]thiophene and benzo[*b*]naphtho[1,2-*d*]thiophene. The results of the synthesis of 1-phenyl-naphthalene, *o*-terphenyl and 1,1'-binaphthalene, and of the thermal experiment with montmorillonite showing all possible isomers of the above mentioned compounds was published elsewhere (Marynowski *et al.*, 2001). 9-phenylphenanthrene was synthesized by Grignard reaction of 9-bromophenanthrene (Aldrich) with phenylmagnesium bromide.

**Quantitation and identification.** Abundances of selected PAH were calculated by comparing the peak area of the internal standard (IS; 9-phenylanthracene) with peak area of the in-

Table 1

Content of soluble organic matter in selected deposited dusts

Samples	Deposited dust [g]	Soluble organic matter [mg]	Soluble organic matter [%]	Fractions [%]		
				Al	Ar	Pol
SĄCZÓW (SACZ-I-III/2000)	0.07212	1.95	2.70	16	10	74
WIELOWIEŚ (WIE-I-III/2000)	0.07854	1.69	2.16	22	30	48
USTROŃ (UST-I-III/2000)	0.05106	0.52	1.02	16	25	59

dividual polycyclic aromatic hydrocarbons obtained from the GC-FID chromatograms.

Identification of individual structures was performed by:

- comparison of retention times of the standards with retention times of the identified substances;
- comparison of mass spectra of the identified compounds with mass spectra from Wiley's MS library;
- comparison of retention indices and chromatograms of PAH as well as polycyclic aromatic compounds published by Lee *et al.* (1979); White and Lee (1980); Radke *et al.* (1982, 1986, 1990); Grimmer *et al.* (1985); Wise *et al.* (1986, 1988); Alexander *et al.* (1991); Simoneit and Fetzer (1996); Meyer zu Reckendorf (1997, 2000); Clegg *et al.* (1997); Bodzek *et al.* (1997); Allen *et al.* (1998); Kang *et al.* (1998); Mardrignac *et al.* (1998); Wilkes *et al.* (1998a, b); Marynowski *et al.* (2001).

## RESULTS

**Fractionation.** The soluble organic matter (SOM) was separated into three fractions: aliphatic — Al, aromatic — Ar and polar + asphaltenes — Pol.

The percentage of soluble organic matter in deposited dust samples was estimated (Table 1), and after separation of samples, the percentage of individual fractions was calculated (Table 1). Most of the samples show the highest percentage in the polar fraction (48–74%), whereas, both aliphatic and aromatic fractions occur at comparable percentages of 10–30% (Table 1).

**Aliphatic fraction.** All samples analysed contain a homologous series of *n*-alkanes in the range of *n*-C<sub>14</sub> to *n*-C<sub>39</sub> (the maximum range was noted in the sample UST-I-III/2000) showing a clearly bimodal distribution with the maximum at *n*-C<sub>19</sub> and *n*-C<sub>29</sub> (Fig. 2A). Two characteristic isoprenoids: pristane (Pr) and phytane (Ph), which are common in sedimentary organic matter e.g. petroleum, hard coal and brown coal, are also present in all samples. The distribution of *n*-alkanes shows predominance of the concentration of high molecular weight *n*-alkanes with an odd number of carbon atoms in the chain (especially *n*-C<sub>25</sub>, *n*-C<sub>29</sub>, *n*-C<sub>31</sub>) over the concentrations of *n*-alkanes with an even number of carbon atoms (Fig. 2A). This is a characteristic feature for immature terrestrial organic matter (Tissot and Welte, 1984), and was also observed in products of terrestrial organic matter incomplete combustion (for review see Simoneit, 2002).

Samples from Ustroń (UST-I-III/2000), Wielowieś (WIE-I-III/2000) and Sączów (SACZ-I-III/2000) contain hopane

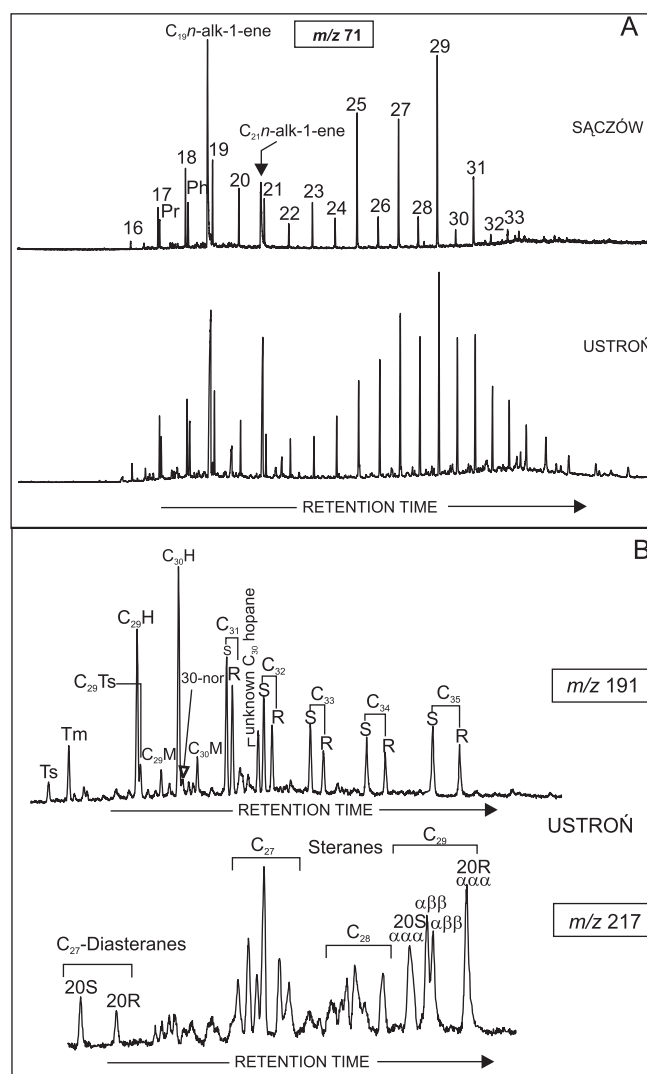


Fig. 2. GC-MS ion chromatograms showing distribution. A: *m/z* 71 — *n*-alkanes from Sączów and Ustroń samples; numbers above the peaks represent the number of carbon atoms in the molecule, Pr — pristane, Ph — phytane; B: *m/z* 191 — hopanes from sample Ustroń; Ts — 18, 21, 22, 29, 30-trisnorhopane, Tm — 17, 21, 22, 29, 30-trisnorhopane, C<sub>29</sub>H — 17, 21, 30-norhopane, C<sub>29</sub>Ts — 18, 30-norhopane, C<sub>29</sub>M — 17, 21, 30-normoretane, C<sub>30</sub>H — 17, 21, 30-norhopane, 30-nor — 17, 21, 30-norhopane, C<sub>30</sub>M — 17, 21, 30-normoretane, C<sub>31</sub>–C<sub>35</sub> — 17, 21, 30-homohopanes with 20S and 20R stereoisomeric configuration, and *m/z* 217 — steranes from sample Ustroń with C<sub>27</sub>-diasteranes and C<sub>27</sub>, C<sub>28</sub> and C<sub>29</sub>-steranes

Table 2

Concentrations of selected PAH identified in the deposited dusts from Ustroń (UST-I-III/2000), Wielowieś (WIE-I-III/2000) and Sączów (SACZ-I-III/2000) samples

Compound		Concentration [ g/g]		
		Ustroń	Sączów	Wielowieś
IS	9-phenylanthracene	—	—	—
P	phenanthrene	66.6	40.1	79.5
A	anthracene	6.9	1.7	3.8
Fl	fluoranthene	142.4	115.9	167.9
Py	pyrene	121.6	101.3	147.4
B[c]P	benzo[c]phenanthrene	14.5	11.5	17.9
B[a]A	benzo[a]anthracene	49.0	30.6	52.6
Ch+Tr	chrysene + triphenylene	78.9	64.0	94.6
BFl	benzofluoranthenes	109.8	81.8	145.5
B[e]P	benzo[e]pyrene	52.0	37.2	61.6
B[a]P	benzo[a]pyrene	64.3	56.4	75.0
widctIparIPy	indeno(1,2,3- <i>cd</i> )pyrene	45.9	33.2	53.6
BPe	benzo( <i>ghi</i> )perylene	50.5	38.9	58.9

group compounds (characteristic ion trace —  $m/z$  191), the biological precursors, of which were prokaryotic organisms and steranes ( $m/z$  217) originating from eucariota (Fig. 2B). Organic connections of that kind are commonly described for sedimentary organic matter (Peters and Moldowan, 1993). There are two compounds with an odd number of carbon atoms, i.e.  $n$ -alk-1-enes- $C_{19}$  and  $-C_{21}$  that are particularly interesting. They were identified in all of the samples. Only trace amounts of tricyclic diterpanes, specific for terrestrial OM, were detected in one sample (WIE-I-III/2000).

**Aromatic fraction and polar NSO compounds.** Polycyclic aromatic hydrocarbons, including strongly carcinogenic compounds, were found in all samples examined (Appendix 1). Oxygen and nitrogen compounds found in the samples investigated are listed in (Appendix 2). Concentrations of selected PAH in samples UST-I-III/2000 and WIE-I-III/2000 are shown in Table 2. Concentrations of individual compounds vary from sample to sample. The highest concentration levels of polycyclic aromatic hydrocarbons were found in samples collected in Wielowieś (WIE-I-III/2000); slightly lower concentrations were observed in the dust samples collected in Ustroń (UST-I-III/2000) and Sączów (SACZ-I-III/2000). The TICs (total ion chromatograms) of the aromatic fractions are shown in Figure 3.

Unsubstituted PAH prevail in the aromatic fraction of all samples. Those mainly are: fluoranthene, pyrene, phenanthrene, chrysene and triphenylene, benzofluoranthenes, benzo(*a*)pyrene, benzo(*e*)pyrene, indeno(1,2,3-*cd*)pyrene and benzo(*ghi*)perylene (Table 2, Appendix 1 and Fig. 3). Additionally, significant concentrations of carcinogenic  $C_{22}H_{14}$  PAH ( $m/z$  278) (see Table 2) and  $C_{24}H_{14}$  PAH ( $m/z$  302) (up to 35  $\mu\text{g/g}$  of

dust for naphtho[2,3-*k*]fluoranthene) were found together with numerous aromatic hydrocarbons. They include rarely identified compounds, which contribute to an anthropogenic pollution of the environment and are of unknown toxicity (Appendix 1), e.g.: polyphenyls and phenyl-polyaromatic hydrocarbons, i.e.: terphenyls, phenylnaphthalenes, phenylphenanthrenes, phenylpyrenes and/or phenylfluoranthene (see Appendix 1 and Fig. 4). Aromatic sulphur compounds are represented by: dibenzothiophene and their methyl derivatives, benzonaphthothiophenes and their methyl derivatives, as well as phenanthro[4,5-*bcd*]thiophene and four unidentified isomers of dinaphthothiophene (Appendix 1).

The highest concentrations of dibenzofuran and its methyl derivatives (up to 45  $\mu\text{g}$  per g of dust) and dinaphthofurans (up to 25  $\mu\text{g}$  per g of dust) were observed in sub-fractions 3–5. Lower quantities of aromatic ketones and quinones (up to 15  $\mu\text{g}$  per 1 g of dust), compounds of higher polarity found in sub-fractions 6–7, were also identified (Appendix 2). The highest concentrations measured were of benzantrone, a highly carcinogenic and mutagenic ketone. Benzantrone is the major polycyclic aromatic ketone found in the emission from all combustion sources (Spitzer and Takeuchi, 1995).

The most frequently occurring nitrogen compounds in the sub-fractions 5–7 include carbazole and their methyl derivatives, benzocarbazoles and their methyl derivatives (up to 5  $\mu\text{g}$  per g of dust) as well as acridine and benzochinoline (about 2  $\mu\text{g}$  per g of dust) (Appendix 2).

No occurrence of polychlorinated biphenyls, polychlorinated terphenyls as well as polychlorinated dibenzofurans and dioxins, highly toxic anthropogenic pollutants (Lang, 1992; Grochowalski and Chrzęszcz, 1997), was observed.

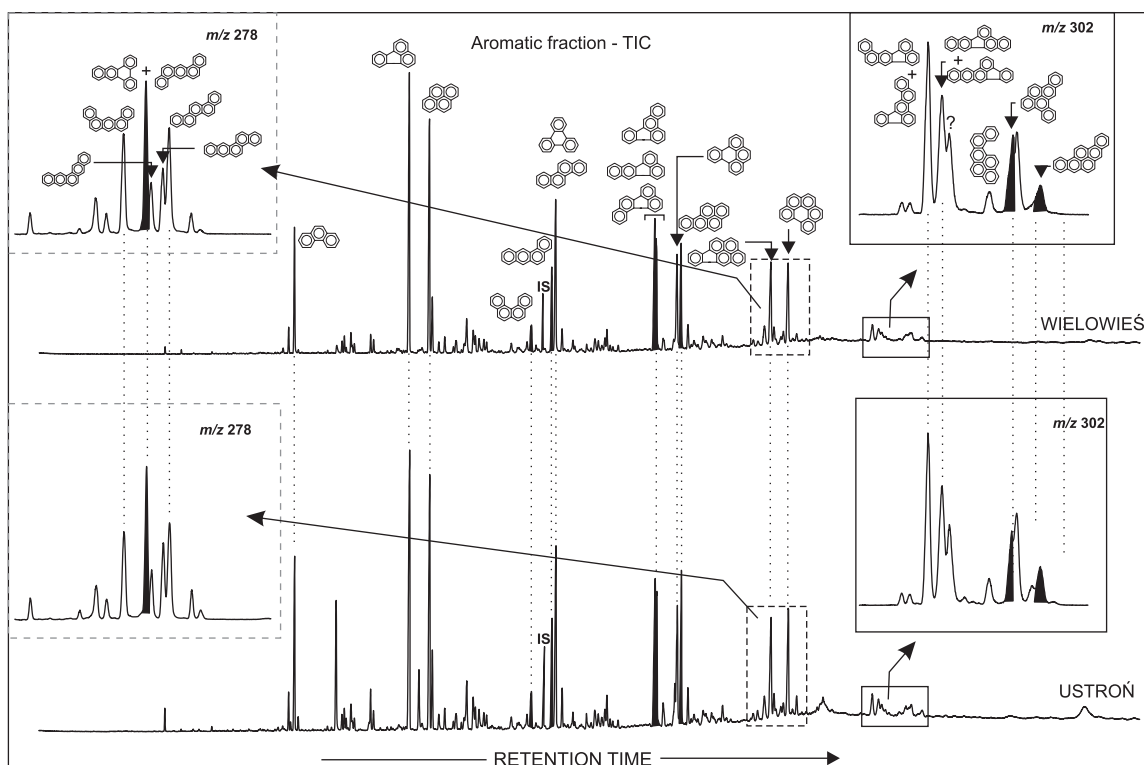


Fig. 3. GC-MS chromatograms (TIC) of aromatic fractions from Wielowieś and Ustroń sites with identification of the most abundant compounds

Additionally, ion chromatograms of  $C_{22}H_{14}$  PAHs ( $m/z$  278) and  $C_{24}H_{14}$  PAHs ( $m/z$  302) are shown in the selected frames; carcinogenic compounds are marked as shaded peaks; IS — internal standard

## DISCUSSION

The odd-to-even carbon number predominance in the high molecular weight *n*-alkanes (especially *n*- $C_{25}$ , *n*- $C_{29}$ , *n*- $C_{31}$ ) suggests significant input of terrestrial organic matter from incomplete combustion of coals and/or from the recent plant material (especially Sączów sample — Fig. 2A). Two even carbon numbered *n*-alk-1-enes:  $C_{19}$  and  $C_{21}$  are probably products of incomplete coal combustion. The *n*-alk-1-enes are formed primarily by thermal dehydration of *n*-alkanols (not detected) and from *n*-alkanes by oxidation during incomplete combustion (Oros and Simoneit, 2000). Relatively high concentrations of steranes ( $m/z$  217) in the aliphatic fraction of the analysed samples (Fig. 2B) suggest that part of extractable organic matter may be genetically related to a diesel engine exhaust and/or paved road dust, (for comparison see: Schauer *et al.*, 1996; Fraser *et al.*, 1999; Briker *et al.*, 2001). The distribution of the hopanes series ( $m/z$  191) is not typical for coals, because the  $C_{33}$  to  $C_{35}$  carbon atoms homohopanes occur in relatively high concentrations (Fig. 2B). Those homohopanes are usually detected in crude oils generated from the source rocks deposited under highly anoxic conditions (e.g. Peters and Moldowan, 1993; Köster *et al.*, 1997).

The molecular composition of aliphatic hydrocarbons suggests that the investigated pollutants were emitted from various sources, mainly due to incomplete combustion of coals, recent

terrestrial plants and diesel engine exhausts and/or asphalt (*sensu* Takada *et al.*, 1990).

Distribution of PAH in samples from Wielowieś and Ustroń shows striking similarity to the PAH distribution described from the air particulate materials of St. Louis and Washington (Wise *et al.*, 1986). For example, fluoranthene, pyrene, phenanthrene, chrysene and/or triphenylene, benzo(a)pyrene, benzo(e)pyrene, indeno(1,2,3-*cd*)pyrene and benzo(*ghi*)perylene are predominant compounds in the aromatic fraction of the investigated air particulate samples described by Wise *et al. op. cit.*, and in our samples (Fig. 3).

Distribution and concentration of PAHs in our samples is also similar to the PAH levels in coal-fired residential furnaces (Grimmer *et al.*, 1985), where fluoranthene and pyrene reach the highest concentrations (compare with Table 2).

Highly carcinogenic PAH, including benzo(a)anthracene, benzo(*c*)phenanthrene, benzo(a)pyrene, dibenz(*a,h*)anthracene (Pickering *et al.*, 1999) were observed in all of the samples we investigated. The latest studies show that a large part of PAH with  $C_{24}H_{14}$  molecular formula ( $m/z$  302), including dibenz(*a,e*)pyrene, dibenz(*a,i*)pyrene, dibenz(*a,h*)pyrene, naphtho(2,1-*a*)pyrene, are compounds of high mutagenicity (probable exceeding that of benzo(a)pyrene) and must be considered during monitoring of environmental pollution (Allen *et al.*, 1998). The presence of the above mentioned compounds was observed in the dust samples examined during this study (Fig. 3 and Appendix 1). However, their con-

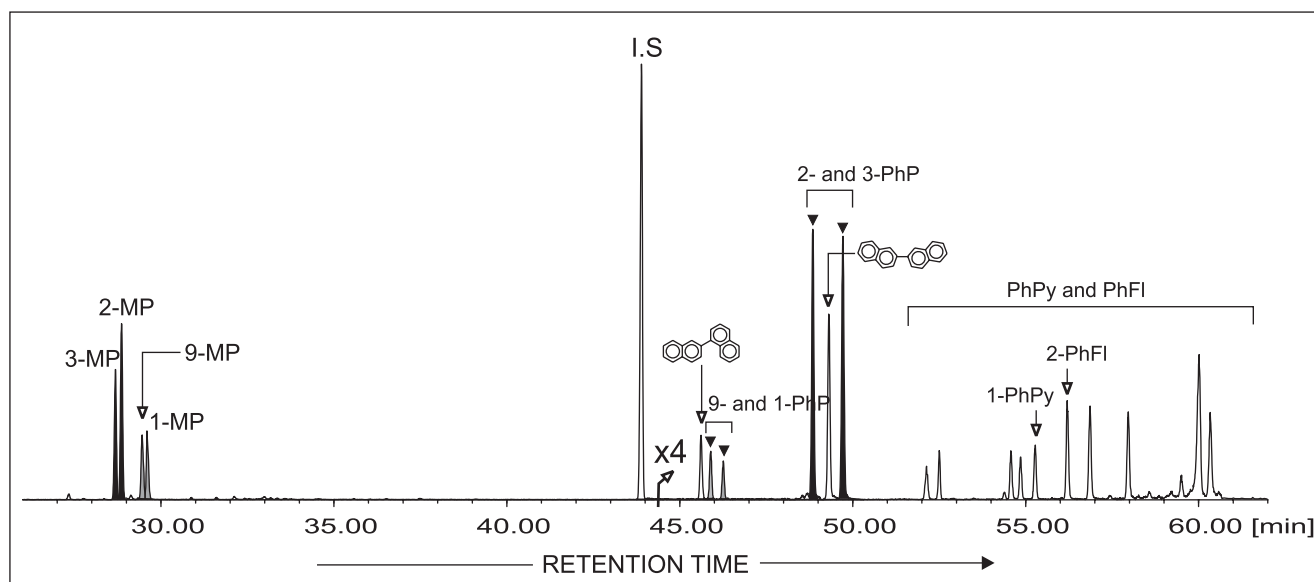


Fig. 4. Partial summed mass chromatogram ( $m/z$  192 +  $m/z$  254 +  $m/z$  278) of the aromatic fraction isolated from Wielowieś sample revealing the distribution of MP — methylphenanthrenes, PhP — phenylphenanthrenes and PhFI — phenylfluoranthenes and/or PhPy — phenylpyrenes; more stable isomers of the methyl- and phenylphenanthrenes are shaded in black, less stable isomers — in grey; note the reverse distribution of individual isomers of methylphenanthrenes in relation to phenylphenanthrenes on the HP-5 stationary phase

centrations are 10 to 20 times lower than concentrations of benzo(*a*)pyrene or benzo(*fluoranthene*s).

We observed the presence of numerous phenyl-PAH derivatives and polyphenyls (Fig. 4 and Appendix 1) occurring in various but relatively low concentrations, which do not exceed 30  $\mu\text{g}$  per g of dust. Phenylphenanthrenes and binaphthyls are the prevailing phenylpolyaromatic hydrocarbons. They were previously identified in geological samples (Marynowski *et al.*, 2001). Genesis of phenylpolyaromatic hydrocarbons may be related to free radical phenylation of PAH. Processes of that kind occur during combustion of sedimentary organic matter (Meyer zu Reckendorf, 1997, 2000), but they are also possible in geological systems (Marynowski *et al.*, 2002).

The observed oxygen compounds can be divided into the following two main groups:

- compounds genetically related to the primary organic matter, i.e. dibenzofuran and its methyl derivatives, and dinaphthofurans;

- secondary compounds formed by oxidation of PAH during combustion and photo-oxidation processes, mainly ketones and quinones, (e.g. fluorenone and phenanthroquinone). They were formed in the phenanthrene oxidation processes, or benzofluorenones — products of benzofluorene oxidation (Allen *et al.*, 1997). However, aromatic aldehydes and ketones e.g. fluoren-9-ones, benzofluoren-9-ones, naphthofluoren-9-ones, naphthaldehydes, alkylnaphthylketones, benzaldehydes, alkylphenylketones, 1-indanones and 1-tetralones have also been identified in geological samples (Posidonia Shale, Hils Syncline, Germany). They may be formed by inter- and/or intramolecular acylations and formylations, cyclisation reactions of functionalised biphenyls and phenylnaphthalenes as well as oxidation of aromatic hydrocarbons (Wilkes *et al.*, 1998*a, b*).

Nitrogen compounds of the carbazole and azaarene groups (Appendix 2) are probably directly related to the source organic

matter, as they are commonly known from sedimentary organic matter (e.g. Bakel and Philp, 1990; Clegg *et al.*, 1997). Most of the organic compounds occurring in the samples examined containing heteroatoms are highly toxic (e.g. Allen *et al.*, 1997; Bleeker *et al.*, 1998, 1999).

## CONCLUSIONS

Organic matter adsorbed on deposited dusts in places located outside the urban and industrial agglomeration of the Upper Silesia region results from several unrelated emission sources. High concentrations of carcinogenic PAH in the dust samples from Wielowieś and Ustroń localities are mainly due to emissions caused by incomplete coal combustion in the residential furnaces. The terrestrial origin of the source organic matter is proved by predominance of long-chain, odd carbon numbered *n*-alkanes in the investigated samples, especially in Sączów.

Relatively high concentrations of steranes and, untypical for coals, high concentrations of  $\text{C}_{33}$  to  $\text{C}_{35}$  carbon atoms homohopanes in the aliphatic fraction of the samples suggest that part of the extractable organic matter may be genetically related to the diesel engine exhaust and/or paved road dust.

Aromatic compounds of sulphur, nitrogen and oxygen were identified in the dusts in addition to PAH. Most of those compounds are carcinogenic and/or mutagenic. The most dangerous of them are those, which are formed during the coal combustion processes (i.e. high molecular weight  $\text{C}_{24}\text{H}_{14}$  PAHs e.g.: dibenz(*a,e*)pyrene, dibenz(*a,i*)pyrene, dibenz(*a,h*)pyrene, naphtho(2,1-*a*)pyrene) and during photo-oxidative decomposition of PAH (i.e. aromatic ketones and quinones). The occurrence of polyphenyls and phenyl-polyaromatic hydrocarbons such as terphenyls, phenylnaphthalenes, phenylphenanthrenes,

phenylfluoranthenes and/or phenylpyrenes is related to free-radical phenylation of aromatics during coal combustion.

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## REFERENCES

- ALEXANDER R., NGO S. H. and KAGI R. I. (1991) — Identification and analysis of trimethylbiphenyls in petroleum. *J. Chrom. A.*, **538**: 424–430.
- ALLEN J. O., DURANT J. L., DOOKERAN N. M., TAKHIZADEH K., LAFLEUR A. L., SMITH K. A. and SAROFIM A. F. (1997) — Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. *Environ. Sc. Technol.*, **31**: 2064–2070.
- ALLEN J. O., DOOKERAN N. M., TAKHIZADEH K., PLUMER E. F., LAFLEUR A. L., SAROFIM A. F. and SMITH K. A. (1998) — Measurement of C<sub>24</sub>H<sub>14</sub> polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. *Environ. Sc. Technol.*, **32**: 1928–1932.
- BAKEL A. J. and PHILP R. P. (1990) — The distribution and quantitation of organonitrogen compounds in crude oils and rock pyrolysates. In: *Advances in Organic Geochemistry 1989* (eds. B. Durand and F. Behar). *Org. Geochem.*, **16**: 353–367.
- BLEEKER E. A. J., Van Der GEEST H. G., KRAAK M. H. S., De VOOGT P. and ADMIRAL W. (1998) — Comparative ecotoxicity of NPAHs to larvae of the midge. *Aquatic Toxicol.*, **41**: 51–62.
- BLEEKER E. A. J., Van Der GEEST H. G., KLAMER H. J. C., De VOOGT P., WIND E. and KRAAK M. H. S. (1999) — Toxic and genotoxic effects of azaarenes: Isomers and metabolites. *Polycyc. Arom. Comp.*, **13**: 191–203.
- BODZEK D., TYRPIEŃ K. and WARZECHA L. (1993) — Identification of oxygen derivatives of polycyclic aromatic hydrocarbons in airborne particulate matter of Upper Silesia (Poland). *Int. J. Environ. Anal. Chem.*, **52**: 75–85.
- BODZEK D., JANOSZKA J., DOBOSZ C., WARZECHA L. and BODZEK M. (1997) — Determination of polycyclic aromatic compounds and heavy metals in sludges from biological sewage treatment plants. *J. Chromatograph. A*, **774**: 177–192.
- BODZEK D., LUKS-BETLEJ K. and JANOSZKA B. (1998) — Occurrence of PAHs in various elements of environment in Zabrze (Upper Silesia, Poland). *Water, Air and Soil Pollution*, **103**: 91–100.
- BOJAKOWSKA I. and SOKOŁOWSKA G. (2001) — Polycyclic aromatic hydrocarbons in crude oils from Poland. *Geol. Quart.*, **45**: 81–86.
- BRANDYS J. (1990) — Chemiczne substancje toksyczne w środowisku — wielopierścieniowe węglowodory aromatyczne. Oddział PAN w Krakowie: 163–176.
- BRIKER Y., RING Z., IACHELLI A., MCLEAN N., RAHIMI P. M. and FAIRBRIDGE C. (2001) — Diesel fuel analysis by GC-FIMS: aromatics, *n*-paraffins and isoparaffins. *Energy and Fuels*, **15**: 23–37.
- CLEGG H., WILKES H. and HORSFIELD B. (1997) — Carbazole distributions in carbonate and clastic source rocks. *Geochim. Cosmochim. Acta*, **61**: 5335–5345.
- DOBROSIEWICZ K., LUKS-BETLEJ K. and BODZEK D. (2000) — Concentration of polycyclic aromatic hydrocarbons and base cations in the air and drinking water of the Silesian Rehabilitation Centre, Poland. *Water, Air and Soil Pollution*, **118**: 101–113.
- FRASER M. P., CASS G. R. and SIMONEIT B. R. T. (1999) — Particulate organic compounds emitted from motor vehicle exhaust and in the urban atmosphere. *Atmos. Environ.*, **33**: 2715–2724.
- GRIMMER G., JAKOB J., DETTBARN G. and NAUJACK K. W. (1985) — Determination of polycyclic aromatic hydrocarbons, azaarenes, and thiaarenes emitted from coal fired residential furnaces by gas chromatography/mass spectrometry. *Fresenius' Z. Anal. Chem.*, **332**: 595–602.
- GROCHOWALSKI A. and CHRZĄSZCZ R. (1997) — PCDDs/Fs in suspended particulate matter in ambient air from Krakow City, Poland. *Organohal. Comp.*, **32**: 76–80.
- JABŁOŃSKA M. (1999) — Phase composition of atmospheric dust in selected cities of the Upper Silesia Industrial Region. Ph.D. Thesis, University of Silesia, Faculty of Earth Sciences.
- JABŁOŃSKA M., RIETMEIJER F. J. M. and JANECZEK J. (2001) — Fine-grained barite in coal fly ash from the Upper Silesian Industrial Region. *Environ. Geol.*, **40**: 941–948.
- KANG J., CAO C. and LI Z. (1998) — Quantitative structure — retention relationship studies for predicting the gas chromatography retention indices of polycyclic aromatic hydrocarbons. Quasi-length of carbon chain and pseudo-conjugated system surface. *J. Chrom. A.*, **799**: 361–367.
- KILLOPS S. D. and MASSOUD M. S. (1992) — Polycyclic aromatic hydrocarbons of pyrolytic origin in ancient sediments: evidence for Jurassic vegetation fires. *Org. Geochem.*, **18**: 1–7.
- KÖSTER J., Van KAAM-PETERS H. M. E., KOOPMANS M. P., De LEEUW J. W. and SINNINGHE DAMSTÉ J. S. (1997) — Sulphurisation of homohopanooids: effects on carbon number distribution, speciation, and 22S/22R epimer ratios. *Geochim. Cosmochim. Acta*, **61**: 2431–2452.
- LANG V. (1992) — Polichlorinated biphenyls in the environment. *J. Chrom. A.*, **585**: 1–43.
- LEE M. L., VASSILAROS D. L., WHITE C. M. and NOVOTNY M. (1979) — Retention indices for programmed-temperature capillary-column gas chromatography of polycyclic aromatic hydrocarbons. *Anal. Chem.*, **51**: 768–773.
- LUKS-BETLEJ K. and BODZEK D. (2000) — Determination of tri-, tetrachloromethanes and trichloroethane by using microextraction with GC-ECD detection. *Chem. Anal. (Warsaw)*, **45**: 45–51.
- MANECKI A. (1976) — Aeromineralogy–mineralogy of atmospheric dust. *Miner. Polon.*, **7**: 91–97.
- MARDRIGNAC J., BEHAR F., ALBRECHT P., BRIOT P. and VANDERBRUCKE M. (1998) — Quantitative extraction of nitrogen compounds in oils: atomic balance and molecular composition. *Ener. Fuel*, **12**: 1342–1355.
- MARYNOWSKI L., NARKIEWICZ M. and GRELOWSKI C. (2000) — Biomarkers as environmental indicators in a carbonate complex, example from the Middle to Upper Devonian, Holy Cross Mts., Poland. *Sediment. Geol.*, **137** (3–4): 187–212.
- MARYNOWSKI L., CZECHOWSKI F. and SIMONEIT B. R. T. (2001) — Phenylanthracenes and polyphenyls in Palaeozoic source rocks of the Holy Cross Mountains, Poland. *Org. Geochem.*, **32**: 69–85.
- MARYNOWSKI L., ROSPONDEK M. J., MEYER ZU RECKENDORF R. and SIMONEIT B. R. T. (2002) — Phenylidibenzofurans and phenyldibenzothiophenes in marine sedimentary rocks and hydrothermal petroleum. *Org. Geochem.*, **33**: 701–714.
- MEYER ZU RECKENDORF R. (1997) — Identification of phenyl-substituted polycyclic aromatic compounds in ring furnace gases using GC-MS and GC-AED. *Chromatographia*, **45**: 173–182.
- MEYER ZU RECKENDORF R. (2000) — Phenyl-substituted polycyclic aromatic compounds as intermediate products during pyrolytic reactions involving coal tars, pitches and related materials. *Chromatographia*, **52**: 67–76.
- MOTOHASHI N., MEYER R., MOLNÁR J., PÁRKÁNYI C. and FANG X. (1995) — Chromatographic determination of benz[*c*]acidines and related compounds in airborne carcinogens. *J. Chrom. A.*, **710**: 117–128.

- MÖSSNER S. G. and WISE S. A. (1999) — Determination of polycyclic aromatic sulfur heterocycles in fossil fuel-related samples. *Anal. Chem.*, **71**: 58–69.
- OROS D. R. and SIMONEIT B. R. T. (2000) — Identification and emission rates of molecular tracers in coal smoke particulate matter. *Fuel*, **79**: 515–536.
- PETERS K. E. and MOLDOWAN J. M. (1993) — The biomarker guide. *Interpreting Molecular Fossils in Petroleum and Ancient Sediments*. Englewood Cliffs, New Jersey, Prentice Hall.
- PICKERING R. W. (1999) — A toxicological review of polycyclic aromatic hydrocarbons. *J. Toxicol. Cut and Ocular*, **18**: 101–135.
- PICKERING R. W. (2000) — Toxicity of polyaromatic hydrocarbons other than Benzo(a)pyrene. A Review; *J. Toxicol. Cut and Ocular*, **19**: 55–67.
- RADKE M., WILLSCH H., LEYTHAEUSER D. and TEICHMÜLLER M. (1982) — Aromatic components in coal: relation of distribution pattern to rank. *Geochim. Cosmochim. Acta*, **46**: 1831–1848.
- RADKE M., WELTE D. H. and WILLSCH H. (1986) — Maturity parameters based on aromatic hydrocarbons: influence of the organic matter type. In: *Advances in Organic Geochemistry*, 1985 (eds. D. Leythaeuser and J. Rullkötter). *Org. Geochem.*, **10**: 51–63.
- RADKE M., GARRIGUES P. and WILLSCH H. (1990) — Methylated dicyclic and tricyclic aromatic hydrocarbons in crude oils from the Handil field, Indonesia. *Org. Geochem.*, **15**: 17–34.
- RADKE M., VRIEND S. P. and RAMANAMPISOA L. R. (2000) — Alkyldibenzofurans in terrestrial rocks: Influence of organic facies and maturation. *Geochim. Cosmochim. Acta*, **64**: 275–286.
- RIETMEIJER F. J. M. and JANECZEK J. (1997) — An analytical electron microscope study of airborne industrial particles in Sosnowiec, Poland. *Atmos. Environ.*, **31**: 1941–1951.
- SCHAUER J. J., ROGGE W. F., HILDEMAN L. M., MAZUREK M. A., CASS G. R. and SIMONEIT B. R. T. (1996) — Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ.*, **30**: 3837–3855.
- SIMONEIT B. R. T. (1993) — Hydrothermal alteration of organic matter in marine and terrestrial systems. In: *Organic Geochemistry. Principles and Applications* (eds. M. H. Engel and S. A. Macko): 397–418. Plenum Press, New York.
- SIMONEIT B. R. T. (2002) — Biomass burning — a review of organic tracers for smoke from incomplete combustion. *App. Geochem.*, **17**: 129–162.
- SIMONEIT B. R. T. and FETZER J. C. (1996) — High molecular weight polycyclic aromatic hydrocarbons in hydrothermal petroleum from the Gulf of California and Northeast Pacific Ocean. *Org. Geochem.*, **24**: 1065–1077.
- SPITZER T. and TAKEUCHI T. (1995) — Determination of benzantrone in environmental samples. *J. Chrom. A.*, **710**: 109–116.
- STRACHAN M. G., ALEXANDER R. and KAGI R. I. (1988) — Trimethylnaphthalenes in crude oils and sediments: effects of source and maturity. *Geochim. Cosmochim. Acta*, **52**: 1255–1264.
- TAKADA H., ONDA T. and OGURA N. (1990) — Determination of polycyclic aromatic hydrocarbons in urban street dusts and their source materials by capillary gas chromatography. *Environmental Sc. Tech.*, **24**: 1179–1186.
- TISSOT B. P. and WELTE D. H. (1984) — *Petroleum Formation and Occurrence*. 2nd edn. Springer Verlag, Berlin.
- TROLIO R., GRICE K., FISHER J. S., ALEXANDER R. and KAGI R. I. (1999) — Alkylbiphenyls and alkyldiphenylmethanes as indicators of petroleum biodegradation. *Org. Geochem.*, **30**: 1241–1253.
- Van AARSSSEN B. G. K., BASTOW T. P., ALEXANDER R. and KAGI R. I. (1999) — Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. *Org. Geochem.*, **30**: 1213–1227.
- WARZECHA L. (1993) — Separation and analysis of azaarenes from Upper Silesia airborne particulate matter. *Chem. Anal. (Warsaw)*, **38**: 571–583.
- WAWROS A., TALIK E. and PASTUSZKA J. S. (2001) — Investigations of aerosols from Swietochlowice, Pszczyna and Kielce by XPS method. *J. All. Comp.*, **328**: 171–174.
- WHITE C. M. and LEE M. L. (1980) — Identification and geochemical significance of some aromatic components of coal. *Geochim. Cosmochim. Acta*, **44**: 1825–1832.
- WILKES H., CLEGG H., DISKO U., WILLSCH H. and HORSFIELD B. (1998a) — Fluoren-9-ones and carbazoles in the Posidonia Shale, Hils Syncline, Northwest Germany. *Fuel*, **77**: 657–668.
- WILKES H., DISKO U. and HORSFIELD B. (1998b) — Aromatic aldehydes and ketones in the Posidonia Shale, Hils Syncline, Germany. *Org. Geochem.*, **29**: 107–117.
- WISE S. A., BENNER B. A., CHESLER S. N., HILPERT L. R., VOGT C. R. and MAY W. E. (1986) — Characterization of the polycyclic aromatic hydrocarbons from two standard reference material air particulate samples. *Anal. Chem.*, **58**: 3067–3077.
- WISE S. A., BENNER B. A., BYRD G. D., CHESLER S. N., REBBERT R. E. and SCHANTZ M. M. (1988) — Determination of polycyclic aromatic hydrocarbons in a coal tar standard reference material. *Anal. Chem.*, **60**: 887–894.

## APPENDIX 1

Polycyclic aromatic hydrocarbons and their methyl- and phenyl- derivatives as well as aromatic sulphur compounds identified in the samples analyzed (with the elution order on the HP-5, 60m capillary column)

<i>m/z</i>	Identified compounds	Relative intensity	I(Rt)	ID	References
128	naphthalene	+	200.00	u	Troilio <i>et al.</i> , 1999
142	2-methylnaphthalenes	+	220.22	u	
142	1-methylnaphthalenes	+	223.01	u	
154	biphenyl	++	236.39	u	
168	2-methylbiphenyl	traces	239.57	ms	
156	dimethylnaphthalenes (the most of isomers)	+	–	u, ms	
154	acenaphthene	+	243.16	u	
168	diphenylmethane	+	249.09	ms	
170	trimethylnaphthalenes (the most of isomers)	+	–	ms	
166	fluorene	++	269.94	u	



<i>m/z</i>	Identified compounds	Relative intensity	I(Rt)	ID	References
168	3- and 4-methylbiphenyls	++	–	ms	Troilio <i>et al.</i> , 1999
182	dimethylbiphenyls (the most of isomers)	+	–	ms	Troilio <i>et al.</i> , 1999
184	tetramethylnaphthalenes (the most of isomers)	+	–	ms	van Aarssen <i>et al.</i> , 1999
180	methylfluorenes (4 isomers)	++	–	ms	
196	trimethylbiphenyls (the most of isomers)	+	–	ms	Alexander <i>et al.</i> , 1991
184	dibenzothiophene	++	295.59	u	
178	phenanthrene	++++	300.00	u	
178	anthracene	++	301.38	u	
210	tetramethylbiphenyls (the most of isomers)	+	–	ms	
198	1-methyldibenzothiophene	+	310.67	u	Radke <i>et al.</i> , 1986
204	1-phenylnaphthalene	++	312.59	ms	Marynowski <i>et al.</i> , 2001
198	2- + 3-methyldibenzothiophenes	+	313.83	u	Radke <i>et al.</i> , 1986
230	<i>o</i> -terphenyl	+	317.42	u	Marynowski <i>et al.</i> , 2001
192	3-methylphenanthrene	+++	317.58	u	Radke <i>et al.</i> , 1982
198	4-methyldibenzothiophene	+	317.78	u	Radke <i>et al.</i> , 1986
192	2-methylphenanthrene	+++	319.03	ms	Radke <i>et al.</i> , 1982
192	2-methylanthracene	++	321.14	ms	
190	4H-cyclopenta[ <i>del</i> ]phenanthrene	+++	321.96	ms	
192	4- and/or 9-methylphenanthrene	+++	322.78	ms	Radke <i>et al.</i> , 1982
192	1-methylphenanthrene	+++	323.52	ms	Radke <i>et al.</i> , 1982
204	2-phenylnaphthalene	+++	330.45	u	Marynowski <i>et al.</i> , 2001
206	dimethylphenanthrenes (the most of isomers)	++	–	ms	Radke <i>et al.</i> , 1990
202	fluoranthene	++++	344.49	u	
218	methyl derivatives of 1-phenylnaphthalene	++	–	ms	
208	phenanthro[4,5- <i>bcd</i> ]thiophene	++	349.17	ms	
202	pyrene	++++	351.91	u	
220	trimethylphenanthrenes (the most of isomers)	+	–	ms	Radke <i>et al.</i> , 1990
216	methylfluoranthenes + benzofluorenes	++(+)	–	u,ms	
216	methylpyrenes + benzofluorenes	++(+)	–	u,ms	
218	methyl derivatives of 2-phenylnaphthalene	++	–	ms	
232	dimethylphenylnaphthalenes	+	–	ms	
242	9-phenylfluorene	+	256.00	u	
230	<i>m</i> -terphenyl	+(+)	356.74	u	Marynowski <i>et al.</i> , 2001
230	<i>p</i> -terphenyl	+(+)	362.40	u	Marynowski <i>et al.</i> , 2001
242	phenylfluorene (unknown isomer)	+(+)	370.67	ms	
230	dimethyl derivatives of <i>m/z</i> 202	++	–	ms	
234	benzo[ <i>b</i> ]naphtho[2,1- <i>d</i> ]thiophene	+(+)	389.16	u	Mössner and Wise, 1999
226	benzo[ <i>ghi</i> ]fluoranthene	+++	390.28	ms	Wise <i>et al.</i> , 1986
228	benzo[ <i>c</i> ]phenanthrene*	+++	391.07	u	Wise <i>et al.</i> , 1986
234	benzo[ <i>b</i> ]naphtho[1,2- <i>d</i> ]thiophene	+	392.51	u	Mössner and Wise, 1999
254	<b>IS (9-phenylanthracene)</b>	+++(+)	394.37	u	
234	benzo[ <i>b</i> ]naphtho [2,3- <i>d</i> ]thiophene	+	395.59	ms	Mössner and Wise, 1999
228	benz[ <i>a</i> ]anthracene*	+++(+)	398.69	u	
228	chrysene + triphenylene	+++(+)	400.00	u,ms	
228	naphthacene	+	402.86	u	
242	methyl derivatives of <i>m/z</i> 228	++	–	ms	
254	1,2'-binaphthyl	+	403.93	u	Marynowski <i>et al.</i> , 2001
240	methyl derivatives of <i>m/z</i> 226	++	–	ms	
254	9-phenylphenanthrene	+(+)	405.36	u	
254	phenylphenanthrene (unknown isomer)	+(+)	407.50	ms	
256	dimethyl derivatives of <i>m/z</i> 228	+	–	ms	
254	phenylphenanthrene (unknown isomer)	+(+)	422.50	ms	
254	2,2'-binaphthyl	+	425.00	u	Marynowski <i>et al.</i> , 2001
254	phenylphenanthrene (unknown isomer)	+(+)	427.50	ms	
256	dimethyl derivatives of <i>m/z</i> 228	+	–	ms	
278	phenylpyrene or phenylfluoranthene	+	441.42	ms	
252	benzo[ <i>b</i> ]fluoranthene	+++(+)	443.11	u	Wise <i>et al.</i> , 1986
252	benzo[ <i>j</i> ]fluoranthene + benzo[ <i>k</i> ]fluoranthene*	+++(+)	444.06	u	Wise <i>et al.</i> , 1986
252	benzo[ <i>a</i> ]fluoranten*	+(+)	446.88	u	Wise <i>et al.</i> , 1986
252	benzo[ <i>e</i> ]pyrene	+++(+)	452.70	u	Wise <i>et al.</i> , 1986
252	benzo[ <i>a</i> ]pyrene*	+++(+)	454.57	u	Wise <i>et al.</i> , 1986
278	phenylpyrene or phenylfluoranthene	+	455.36	ms	
278	phenylpyrene or phenylfluoranthene	+	457.14	ms	
252	perylene	++	457.63	u	Wise <i>et al.</i> , 1986
278	1-phenylpyrene	+	457.93	u	
266	methyl derivatives of <i>m/z</i> 252	++	–	ms	

<i>m/z</i>	Identified compounds	Relative intensity	I(Rt)	ID	References
278	2-phenylfluoranthene	+(+)	463.43	u	
266	methyl derivatives of <i>m/z</i> 252	+(+)	–	ms	
278	phenylpyrene or phenylfluoranthene	+(+)	463.43	ms	
266	methyl derivatives of <i>m/z</i> 252	+(+)	–	ms	
278	phenylpyrene or phenylfluoranthene	+(+)	467.68	ms	
266	methyl derivatives of <i>m/z</i> 252	+	–	ms	
278	phenylpyrene or phenylfluoranthene	+(+)	473.75	ms	
284	dinaphthothiophene	+	482.46	ms	Grimmer <i>et al.</i> , 1985
276	indeno[1,2,3- <i>cd</i> ]fluoranthene	+(+)	484.67	ms	Grimmer <i>et al.</i> , 1985
278	naphtho[1,2- <i>a</i> ]anthracene	+(+)	485.71	ms	Grimmer <i>et al.</i> , 1985
264	n.i.	++	–	–	
278	n.i.	+	–	–	
128	naphthalene	+	200.00	u	
142	2-methylnaphthalenes	+	220.22	u	
142	1-methylnaphthalenes	+	223.01	u	
154	biphenyl	++	236.39	u	
168	2-methylbiphenyl	traces	239.57	ms	Troilio <i>et al.</i> , 1999
156	dimethylnaphthalenes (the most of isomers)	+	–	u,ms	
154	acenaphthene	+	243.16	u	
168	diphenylmethane	+	249.09	ms	Troilio <i>et al.</i> , 1999
170	trimethylnaphthalenes (the most of isomers)	+	–	ms	Strachan <i>et al.</i> , 1988
166	fluorene	++	269.94	u	
168	3- and 4-methylbiphenyls	++	–	ms	Troilio <i>et al.</i> , 1999
182	dimethylbiphenyls (the most of isomers)	+	–	ms	Troilio <i>et al.</i> , 1999
184	tetramethylnaphthalenes (the most of isomers)	+	–	ms	van Aarssen <i>et al.</i> , 1999
180	methylfluorenes (4 isomers)	++	–	ms	
196	trimethylbiphenyls (the most of isomers)	+	–	ms	Alexander <i>et al.</i> , 1991
184	dibenzothiophene	++	295.59	u	
178	phenanthrene	++++	300.00	u	
178	anthracene	++	301.38	u	
210	tetramethylbiphenyls (the most of isomers)	+	–	ms	
198	1-methyldibenzothiophene	+	310.67	u	Radke <i>et al.</i> , 1986
204	1-phenylnaphthalene	++	312.59	ms	Marynowski <i>et al.</i> , 2001
198	2- + 3-methyldibenzothiophenes	+	313.83	u	Radke <i>et al.</i> , 1986
284	dinaphthothiophene	+	486.76	ms	Grimmer <i>et al.</i> , 1985
276	dibenz[ <i>k,mno</i> ]fluoranthene	++	489.20	ms	Grimmer <i>et al.</i> , 1985
278	n.i.	++	489.60	–	
284	dinaphthothiophene	+	490.59	ms	Grimmer <i>et al.</i> , 1985
276	indeno(1,2,3- <i>cd</i> )pyrene*	+++(+)	493.82	ms	Wise <i>et al.</i> , 1986
278	dibenz[ <i>ac</i> ]anthracene + dibenz[ <i>ah</i> ]anthracene*	++	495.92	ms	Wise <i>et al.</i> , 1986
278	pentaphene	+	496.83	ms	Wise <i>et al.</i> , 1986
278	benzo[ <i>b</i> ]chrysene	+(+)	498.84	ms	Wise <i>et al.</i> , 1986
278	picene + benzo[ <i>a</i> ]naphthacene	++	500.00	u,ms	Wise <i>et al.</i> , 1986
276	benzo[ <i>ghi</i> ]perylene*	+++(+)	501.38	u	Wise <i>et al.</i> , 1986
278	n.i.	+	–	–	
276	anthanthrene	++	505.29	ms	Wise <i>et al.</i> , 1986
292	methyl derivatives of <i>m/z</i> 278, (about 30 isomers)	++	–	ms	
290	methyl derivatives of <i>m/z</i> 276, (about. 13 isomers)	++	–	ms	
300	coronene	++	529.07	u	
302	n.i.	+	–	–	
302	n.i.	+	–	–	
302	naphtho[1,2- <i>b</i> ]fluoranthene + naphtho[1,2- <i>k</i> ]fluoranthene *	+++	536.50	ms	Allen <i>et al.</i> , 1998
302	naphtho[2,3- <i>b</i> ]fluoranthene + dibenzo[ <i>bk</i> ]fluoranthene *	++	538.50	–	Allen <i>et al.</i> , 1998
302	n.i.	++	–	–	
302	naphtho[2,3- <i>k</i> ]fluoranthene *	+	543.09	–	Allen <i>et al.</i> , 1998
302	naphtho[2,3- <i>e</i> ]pyrene\	+(+)	547.69	ms	Allen <i>et al.</i> , 1998
302	dibenz[ <i>a,e</i> ]pyrene	++	551.53	ms	Allen <i>et al.</i> , 1998
302	dibenz[ <i>a,l</i> ]pyrene + naphtho[2,3- <i>e</i> ]pyrene *	++	553.00	ms	Allen <i>et al.</i> , 1998
302	naphtho[2,3- <i>a</i> ]pyrene	+	555.50	ms	Allen <i>et al.</i> , 1998
302	dibenz[ <i>a,i</i> ]pyrene *	+	556.47	ms	Allen <i>et al.</i> , 1998
326	unknown PAHs (at least 8 isomers)	+	–	ms	

I(Rt) — retention index for selected compounds; ID — identification by means of mass spectrum (ms), original standard (u); \* — star denotes compounds of well known carcinogenic activity (after Brandys, 1994; Pickering *et al.*, 1999 and Pickering *et al.*, 2000); n.i. — not identified; I.S. — internal standard; references — helpful in identification of some compounds

## APPENDIX 2

Aromatic nitrogen and oxygen compounds identified in the samples investigated  
(with the elution order on the HP-5, 60 m capillary column)

<i>m/z</i>	Identified compounds	Relative intensity (regarding to IS)	ID	References
139	4-nitrophenol	++	u	
153	methyl derivatives of 4-nitrophenol (at least 2 isomers)	+	ms	
168	dibenzofuran	+	u	
180	fluorenone	+	u	
182	methyl dibenzofuran	++	ms	Radke <i>et al.</i> , 2000
182	methyl dibenzofuran	++	ms	Radke <i>et al.</i> , 2000
182	methyl dibenzofuran	+	ms	Radke <i>et al.</i> , 2000
179	benzo( <i>h</i> )chinoline	+	u	Bodzek <i>et al.</i> , 1997
179	acridine	+	u	Bodzek <i>et al.</i> , 1997
179	benzo( <i>f</i> )chinoline	+	u	Bodzek <i>et al.</i> , 1997
194	anthrone	+	ms	Bodzek <i>et al.</i> , 1997
167	carbazole	++	u	
181	1-methylcarbazole	+	ms	
181	3-methylcarbazole	+	ms	Clegg <i>et al.</i> , 1997
181	2-methylcarbazole	+	ms	Clegg <i>et al.</i> , 1997
196	xanthone	+	u	Clegg <i>et al.</i> , 1997
181	4-methylcarbazole	+	ms	
208	9,10-anthracenedione	+	ms	Clegg <i>et al.</i> , 1997
195	dimethylcarbazoles (the most of isomers)	+	ms	
204	cyclopenta( <i>def</i> )phenanthrene	+	u	Clegg <i>et al.</i> , 1997
222	methyl derivatives of <i>m/z</i> 208 (at least 3 isomers)	+	ms	
203	azapyrenes/azafluoranthenes (5 compounds)	+	ms	
218	benzo[ <i>b</i> ]naphtho[2,1- <i>d</i> ]furan	+++	u	
218	benzo[ <i>b</i> ]naphtho[1,2- <i>d</i> ]furan	++	ms	
218	benzo[ <i>b</i> ]naphtho[2,3- <i>d</i> ]furan	++	u	
218	benzo[ <i>k</i> ]xanthene	++	ms	
232	methyl derivatives of <i>m/z</i> 218	++	ms	
230	11 <i>H</i> -benzo[ <i>a</i> ]fluorene-11-one	+	ms	
230	7 <i>H</i> -benzo[ <i>c</i> ]fluorene-7-one	+	ms	Wilkes <i>et al.</i> , 1998 <i>a</i>
229	benzacridine and/or azachrysene	+	ms	Wilkes <i>et al.</i> , 1998 <i>a</i>
230	11 <i>H</i> -benzo[ <i>b</i> ]fluorene-11-one	+	ms	Motohashi <i>et al.</i> , 1995
229	benzacridine and/or azachrysene	+	ms	Wilkes <i>et al.</i> , 1998 <i>a</i>
229	benzacridine and/or azachrysene	+	ms	Motohashi <i>et al.</i> , 1995
229	benzacridine and/or azachrysene	+	ms	Motohashi <i>et al.</i> , 1995
217	benzo[ <i>a</i> ]carbazole	+	ms	Motohashi <i>et al.</i> , 1995
229	benzacridine and/or azachrysene	+	ms	Clegg <i>et al.</i> , 1997
230	benzanthrone	++	u	Motohashi <i>et al.</i> , 1995
217	benzo[ <i>b</i> ]carbazole	+	ms	Spitzer and Takeuchi, 1995
217	benzo[ <i>c</i> ]carbazole	+	ms	Clegg <i>et al.</i> , 1997
244	methyl derivatives of <i>m/z</i> 230	+	ms	Clegg <i>et al.</i> , 1997
231	methylbenzocarbazoles	+	ms	
258	benz[ <i>a</i> ]anthracene-7,12-dione	+	ms	
258	naphthacene-5,12-dione	+	ms	
268	dinaphthofuranes (about 4 isomers)	++	ms	
253	aza- <i>m/z</i> 252	+	ms	
241	dibenzocarbazoles (?)	+	ms	
279	dibenzacridines (at least 3 isomers)	+	ms	
280	dibenzanthracenones and/or benzochrysenones	+	ms	

ID — identification by means of mass spectrum (ms); original standard (u); references — helpful in identification of some compounds