You have downloaded a document from
RE-BUŚ
repository of the University of Silesia in Katowice

**Title:** Differences in the Occurrence of Polycyclic Aromatic Hydrocarbons and Geochemical Markers in the Dust Emitted from Various Coal-Fired Boilers

**Author:** Monika Fabiańska, B. Kozielska, J. Konieczyński

**Citation style** Fabiańska Monika, Kozielska B., Konieczyński J. (2017). Differences in the Occurrence of Polycyclic Aromatic Hydrocarbons and Geochemical Markers in the Dust Emitted from Various Coal-Fired Boilers. "Meteoritics and Planetary Science" iss. 3 (2017), s. 2585-2595.
doi: 10.1021/acs.energyfuels.6b03030

Uznanie autorstwa - Użycie niekomercyjne - Bez utworów zależnych Polska - Licencja ta zezwala na rozpowszechnianie, przedstawianie i wykonywanie utworu jedynie w celach niekomercyjnych oraz pod warunkiem zachowania go w oryginalnej postaci (nie tworzenia utworów zależnych).

UNIWERSYTET ŚLĄSKI
W KATOWICACH
Biblioteka Uniwersytetu Śląskiego
Ministerstwo Nauki i Szkolnictwa Wyższego

energy&fuels
Article
pubs.acs.org/EF

Downloaded via UNIV OF SILESIA on April 6, 2020 at 10:44:16 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

# Differences in the Occurrence of Polycyclic Aromatic Hydrocarbons and Geochemical Markers in the Dust Emitted from Various Coal-Fired Boilers

M. Fabiańska,*[,†] B. Kozielska,[‡] and J. Konieczyński[§]

[†]Faculty of Earth Sciences, University of Silesia, 60 Będzińska Street, 41-200 Sosnowiec, Poland

[‡]Silesian University of Technology, Faculty of Energy and Environmental Engineering, Department of Air Protection, 22B Konarskiego Street, 44-100 Gliwice, Poland

[§]Institute of Environmental Engineering, Polish Academy of Sciences, 34 M. Skłodowskiej-Curie Street, 41-819 Zabrze, Poland

**ABSTRACT:** Organic compounds occurring in emitted fly ashes from bituminous coal and bituminous coal and biomass combustion in various boilers were qualitatively and quantitatively analyzed. Gas chromatography with a flame ionization detector (GC-FID) was applied to polycyclic aromatic hydrocarbons (PAHs) and gas chromatography−mass spectrometry (GC-MS) for geochemical markers, such as *n*-alkanes, acyclic isoprenoids, steranes, pentacyclic triterpenoids (hopanes and moretanes), alkyl PAHs, and biomass markers. It was found that distributions of geochemical markers and presence are well preserved in fly ash. Particularly in fly ash from boilers of older types, thermal changes are small and mainly affect compounds of low molecular weight whereas, in fly ash from a fluidized bed combustion boiler, most geochemical markers were destroyed. It is possible that high molecular weight compounds survived the high temperature process when adsorbed in unburned or coked coal and/or biomass particles included in the dust emitted. PAH group profiles were made, while PAHs diagnostic indices and geochemical marker ratios were calculated and compared with literature data. Fly ash from coal and biomass combustion contains the highest PAH concentrations and shows the highest values of toxic equivalence (TEQ) factors among all boilers investigated. The results indicate that, whereas the distributions and ratios of geochemical markers are close to those of bituminous coals and can be applied to indicate source fuels in particulate matter, there are high differences between the values of diagnostic ratios found in this project and literature data. This indicates that PAH diagnostic ratios should be applied with care and confirmed by other data, e.g., those from geochemical markers, which may be recommended for research on the type of emission sources of particulate matter into the air.

## 1. INTRODUCTION

Combustion of coal in different types of boilers and stoves for energy and heat production leads to emission into the atmosphere in the form of large amounts of gaseous pollutants and fly ash. It has been proven that the influence of pollutants from coal furnaces in both atmospheric and indoor air is dangerous to health. Chemical analyses and biological tests identify polycyclic aromatic hydrocarbons (PAHs) as a group of compounds which determine the mutagenic and carcinogenetic effects of the emission from coal combustion.[1] The presence of alkyl derivatives from three- and four-ring PAHs (demonstrating strong mutagenic properties) in the smoke from home furnaces indicates the importance of indoor air quality.[2] PAHs coming from coal combustion nearly always occur in solid form in the air and are adsorbed on the surface of soot and dust particles, whose diameters are less than 10 $\mu$m,[3] which constitute the respirable dust. Considering the energy production from coal as the main source of PAH emissions, it should be noted that there is an essential difference in the emission of these compounds between different types of furnaces.

The organic compounds occurring in the dust particles in the air are specific tracers of the emissions from sources such as fossil fuel and biomass combustion, operations of industrial installations,[4] and coal coking.[5] The researchers determined selected PAHs in the dust emitted from energy boilers and in gaseous and solid phases in coal flue gases from home furnaces.[6,7] They also determined the emission factors for the PAH sum and assessed the percentage of the PAH groups according to the number of rings in a molecule.[8]

Research into the participation of the emission sources in air pollution with PAHs has been conducted over a long period of time. In the process, the profiles of the PAHs present in the particulate matter have been compared,[9] as well as used, for example, to determine diagnostic ratios based on the analysis of PAHs.[10−12] The researchers compared the occurrence of PAHs, either in the summer and heating seasons in terms of the dust present in the air of cities with different economic development stages,[13,14] or in urban, suburban, roadside, and agricultural air.[15−21] The seasonal variability of the PAH and *n*-alkane levels in PM10, as well as the spatial distribution, indicates that coal combustion is the dust source in the investigated city in China.[22]

The research conducted so far did not resolve the issue concerning each of the main PAH emission sources. Although classified as persistent organic pollutants (POPs) to varying degrees, PAHs are subjected to biological and photodegradative

**Received:** November 14, 2016
**Revised:** January 31, 2017
**Published:** February 7, 2017

© 2017 American Chemical Society

DOI: 10.1021/acs.energyfuels.6b03030
*Energy Fuels* 2017, 31, 2585−2595

decomposition,[23,24] such that research into PAH content alone does not lead to satisfactory results. The breakthrough was the use of geochemical markers, which are substances associated with PAHs but are much more stable. Geochemical marker applications provide information on the origin of organic matter, as well as the way in which migration and degradation occur in the environment. Many of these geochemical markers have a link with the kind of fuel combusted (bituminous coal, lignite, hydrocarbon engine fuels, biomass, wood). He et al.[25] investigated atmospheric dust in Singapore using *n*-alkanes, PAHs, and carboxylic acids as diagnostic indicators and organic markers.

Analysis of dust sample extracts found group components of organic matter, i.e., PAHs, hopanes, steranes, and *n*-alkanes, and identified the characteristic indicators. Using a model based on the mass balance of molecular markers (based on the chemical balance MM-CMB) allowed for assessing the relative contribution of emission source groups.[26] This required careful selection of the sources tested and identification of organic compounds, whose distribution was investigated in samples taken from the source and the air.[27]

In Poland, the primary dust emission from different sources is still very high compared to the other European countries and causes relatively high PM concentrations in urban air. In particular, this concerns densely populated industrial cities in the Upper Silesian region. Apart from traffic and industrial emission, there is a considerable input from domestic furnaces and power plants due to the high share of biomass and bituminous coal in energy production.[28−30]

The scientific objective of the research was to assess the co-occurrence of PAHs and biomarkers in the fly ash emitted from bituminous coal, lignite combustion, and cofiring of bituminous coal and forest biomass. The well-known persistence of PAHs and some biomarkers encourages research into the occurrence of both compound groups in solid fuel combustion products in typical furnaces used in heat and power production. The furnaces differ in construction and combustion mode. The differences result in different combustion conditions, which affect the type and amount of the solid and gaseous combustion products. The expected effect of the research was in determining the level and profiles of the selected PAHs and biomarkers with consideration of the combustion mode and the degree of coalification of the fuel.

## 2. EXPERIMENTAL SECTION

Fly ash was emitted from power plants located in Southern Poland, where Upper Silesian bituminous coal or bituminous coal/biomass fuel was combusted in different types of boilers as follows: traveling grate water and steam boilers (TGW and TGS, respectively), pulverized coal-fired steam boilers (PC), and fluidized bed combustion boiler (FBC). In the latter, only the composite fuel of bituminous coal with forest biomass was combusted. The boiler plants were equipped with dedusting cyclones or multicyclones with forced fuel gas flow. Bituminous coal combusted in the power plant was also sampled as a representative of Upper Silesia bituminous coals, commonly combusted in these boilers. However, the results were also compared with geochemical features of coals investigated previously.[31] The detailed boiler characteristics are given in Table 1.

Samples of fly ash were determined following the reference procedure[32] and the Regulation of the Minister for the Environment.[33] The measurement is based on the principle of isokinetic partial sampling of investigated gas flow and separating the particulate matter on the filter. Fly ash contained in the flue gas was sampled behind the dedusting device using the EMIOTEST gravimetric dust meter, which is equipped with a dust aspiration probe with inner dust filtration using the Whatman grade QMA quartz fiber filters, with a diameter of 4.7 cm. Filters were weighed both before and after sampling by a sensitive microbalance (Sartorius). The balance sensitivity was ±0.01 g.

Dust collected on filters was extracted with dichloromethane (DCM) in an ultrasonic bath. Extracts were percolated, washed, and helium-dried. Every extract was divided into two parts: one for PAH investigation on the GC-FID and the second for biomarkers using GC-MS.

The fly ash extracts were analyzed on a Clarus 500 PerkinElmer gas chromatograph (PerkinElmer, Inc., Waltham, MA, USA) equipped with an autosampler. The compounds were separated on a capillary column (Restek RTX-5, 5% phenyl methyl siloxane, 30 m × 0.32 mm × 0.25 $\mu$m). The carrier gas (helium) flow in the column was maintained at the constant rate of 1.5 $cm^3$/min. The 3 $\mu$L samples were introduced using splitless injection, with the temperature of the injector at 240 °C. A flame ionization detector (FID) was used. For the PAH analysis, the initial temperature of the oven (60 °C) was held for 4 min, after which the temperature grew at 10 °C/min to 280 °C, and then was held for 14 min. The flow rates of hydrogen and air in the detector were 45 $cm^3$/min and 450 $cm^3$/min, respectively; the FID's temperature was 280 °C. The calibration curves for the quantitative analysis were prepared for 16 standard PAHs. The linear correlation between the peak surface areas and PAH concentrations was checked within the range 1−20 $\mu$g/mL (correlation coefficients: 0.99, PAH Mix PM-611, Ultra Scientific standard, at the concentration 100 $\mu$g/mL for each PAH in DCM). The analysis of each campaign sample series was accompanied by a blank sample analysis. The application of the whole analytical procedure involved a clean quartz fiber filter. The blank result was used to adjust the PAH concentration, but only if the blank exceeded 10% of the PAH concentration.

Prior to the GC-MS analyses for the biomarker content, the extracts were not separated into compound groups, due to the low extractability. An Agilent gas chromatograph 6890 with a DB-35 column (60 m × 0.25 mm i.d, 0.25 $\mu$m stationary phase film), coupled with an Agilent Technology mass spectrometer 5973, was used. The experimental conditions were as follows: carrier gas = He; temperature = 50 °C (isothermal for 2 min); heating rate = up to 175 °C at 10 °C/min, to 225 °C at 6 °C/min, and, finally, to 300 °C at 4 °C/min. The final temperature (300 °C) was held for 20 min. The mass spectrometer was operated in the EI ionization mode (70 eV) and scanned from 50 to 650 Da. Data were acquired in a full scan mode and processed with Hewlett-Packard Chemstation software. The compounds were identified by their mass spectra, the comparison of peak retention times with those of standard compounds, and literature data.[34,35] The objective of the GC-MS analyses was to find geochemical markers, which were characteristic of bituminous coal combustion. The distribution of biomarkers, such as *n*-alkanes, diterpenes, steranes and pentacyclic triterpenes, and several groups of aromatic hydrocarbons, such as naphthalene, biphenyl, and phenanthrene aliphatic derivatives, were investigated. All biomarker parameters were calculated using peak areas acquired in the manual integration mode.

**Table 1. Boiler Types with Their Characteristics**

| Boiler code | Boiler description | Fuel type | Max continuous rating | Gross efficiency |
|---|---|---|---|---|
| TGW | a traveling grate water boiler equipped with a multicyclone | bituminous coal | 29.2 MW | 82% |
| TGS | a traveling grate steam boiler equipped with a multicyclone | bituminous coal | 9.7 kg/s | 83% |
| PC | a pulverized coal-fired steam boiler equipped with an electrofilter | bituminous coal | 58 kg/s | 89% |
| FBC | a fluidized bed combustion boiler equipped with an electrofilter | bituminous coal and forest biomass | 119 kg/s | 90.7% |

The analyses were carried out in the laboratory of the Faculty of Earth Sciences, University of Silesia.

## 3. RESULTS AND DISCUSSION

The contents of organic substances in the fly ash from the combustion of coal or bituminous coal/forests biomass in the studied boilers do not exceed 9.1% (wt.). Most organic compounds in the fly ash from the PC boiler are 9.1 wt % on average. For the remaining boilers, that is, TGW, TGS, and FBC, the values are in the following range: 0.4−2.7% (wt), 0.6−0.9% (wt), and 0.2−2.5% (wt), respectively.

### 3.1. General composition of fly ash extracts.

The following compound groups, derived from combusted bituminous coal, have been identified in the PM extracts: *n*-alkanes ($m/z$ = 71) and *iso*-alkanes, acyclic isoprenoids ($m/z$ = 71, 183), mostly pristane (Pr) and phytane (Ph), steranes ($m/z$ = 217), in some cases accompanied by diasteranes ($m/z$ = 259), and tri- and pentacyclic triterpenoids (hopanes and moretanes) ($m/z$ = 191). Diterpenes ($m/z$ = 123) were present in a small number of extracts in low concentrations, which is a common feature in Pennsylvanian/Mississippian coals, particularly those from Upper Silesia.[36]

Among aromatic hydrocarbons, the following were identified: alkylbenzenes ($m/z$ = 95) and polycyclic aromatic hydrocarbons and their alkyl derivatives. Particular attention has been given to distributions of methyl- ($m/z$ = 142), dimethyl- ($m/z$ = 156), trimethyl- ($m/z$ = 170), and tetramethylnaphthalenes ($m/z$ = 184), methyl- ($m/z$ = 192), and dimethylphenanthrenes ($m/z$ = 206), biphenyl ($m/z$ = 154) and methylbiphenyls ($m/z$ = 168), methylchrysenes ($m/z$ = 242) and methylpyrenes ($m/z$ = 216), and a series of unsubstituted PAHs including compounds with two-six rings, among them, acenaphthene (Acy), acenaphthylene (Ace), anthracene (An), benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[g,h,i]perylene (BghiP), chrysene (Ch), dibenzo[a,h]-anthracene (DBA), fluoranthene (Fl), fluorene (F), naphthalene (Na), phenanthrene (Phe), pyrene (Py), and indeno[1,2,3-cd]pyrene (IP).

Apart from geochemical compounds in some samples, compounds of biochemical origin were found, particularly in fly ash from composite biomass/bituminous coal fuels, in which they are the dominant organic compound group. Among them were long-chain aliphatic alcohols, ketones, methyl esters of fatty acids ($m/z$ = 74), farnesol ($m/z$ = 69, 136,), levoglucosan (1,6-anhydro-*β*-D-glucopyranose) ($m/z$ = 60, 144), squalene ($m/z$ = 69, 410), vitamin E, and *β*-sitosterol, together with phenol derivatives, such as cresols ($m/z$ = 108), xylenols ($m/z$ = 122 + 14$n$), and guaiacol ($m/z$ = 124).

### 3.2. PAHs.

The composition of the combustion products is determined by the conditions of the process. Improper combustion parameters may lead to significant emissions of PAHs.[37] On the other hand, efficient combustion in the majority of cases, especially coal combustion in power plants, results in a very low emission of PAHs.[38] For example, PAH

**Table 2. Contents of ∑PAHs, TEQ, comPAHs/∑PAHs, cancPAHs/∑PAHs, and Diagnostic Ratios for 16 Priority PAHs from Stationary Sources Based on Literature Data[a]**

| Source | Power plant [this study] | | | | | Power plant Chorzów, Poland[7] | Heating station Shenyang, China[41] | Power plant Fushun, China[41] | Combined heat and power plant Anhui, China[40] | Power plant Huainan, China[39] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Extracted sample | fly ash | | | | | fly ash (PM10 fraction) | fly ash (PM10 fraction) | | fly ash | fly ash | | |
| Fuel | coal | | | coal/biomass | raw coal | coal | coal | | pulverized coal | coal | raw coal | coal combustion |
| Boiler* | TGW | TGS | PC | FBC | C | FBC | ** | ** | FBC mean | ** | ** | |
| ∑PAHs μg/g | 32.72 | 65.21 | 21.36 | 110.8 | 37.53 | 172.44 | 611.02 | 696.49 | 22.10 | 0.93−1.38 | 37.62 | |
| TEQ μg/g | 5.71 | 35.42 | 2.69 | 103.2 | 1.15 | 29.94 | 70.66 | 72.60 | 0.28 | 0.22−0.69 | 18.20 | |
| comPAHs/∑PAHs | 0.91 | 0.78 | 0.94 | 0.49 | 0.29 | 0.61 | 0.75 | 0.70 | 0.35 | 0.49−0.61 | 0.63 | ~1[42−45] |
| cancPAHs/∑PAHs | 0.73 | 0.52 | 0.72 | 0.55 | 0.17 | 0.46 | 0.47 | 0.42 | 0.05 | 0.29−0.38 | 0.53 | |
| [BaA]/([BaA]+[Ch]) | 0.85 | 0.81 | | | 0.28 | 0.09 | 0.54 | 0.60 | 0.51 | | 0.55 | 0.46[46]<br>0.5[47]<br>0.2−0.35[48] |
| [Phe]/([Phe]+[An]) | 0.42 | 0.36 | | 0.78 | 0.82 | 0.67 | 0.42 | 0.42 | 0.90 | | 0.55 | 0.24[3,49] |
| [Fl]/([Fl]+[Py]) | | 0.32 | 0.55 | | 0.58 | 0.40 | 0.58 | 0.61 | 0.42 | 0.60−0.65 | 0.26 | 0.57[46,49]<br>>0.5[50−52] |
| [BaP]/([BaP]+[Ch]) | 0.57 | 0.41 | 0.17 | | 0.22 | 0.30 | 0.44 | 0.42 | 0.27 | 0.35−0.54 | 0.40 | 0.18−0.49[50]<br>0.46[46]<br>0.5[47,49] |
| [An]/([An]+[Phe]) | 0.58 | 0.64 | | 0.22 | 0.18 | 0.33 | 0.58 | 0.58 | 0.10 | | 0.45 | |
| [BaA]/[Ch] | 5.59 | 4.16 | | | 0.39 | 0.10 | 1.29 | 1.53 | 1.04 | 0.44 | 0.54 | |
| [BbF/[BkF] | | 1.41 | | | 2.22 | 1.74 | 1.57 | 1.83 | 6.80 | 1.83−3.50 | | 3.5−3.9[53]<br>3.53−3.87[54,55] |

[a] TEQ = 0.001 × ([Na]+[Acy]+[Ace]+[F]+[Phe]+[Fl]+[Py])+0.01 × ([An]+[Ch]+[BghiP])+0.1 × ([BaA]+[BbF]+[BkF]+[IP])+1 × [BaP]+5 × [DBA]; the values 0.001, 0.01, 0.1, and 1 are the toxic equivalence factors (TEF) for specific PAHs.[56] comPAHs: sum of combustion PAHs including Fl, Py, Ch, BbF, BkF, BaA, BaP, IP, and BghiP.[57,58] cancPAHs: sum of carcinogenic PAHs including BaA, Ch, BbF, BkF, BaP, IP, and DBA.[57,59] *Boiler acronyms are explained in Table 1. **No data.

DOI: 10.1021/acs.energyfuels.6b03030
Energy Fuels 2017, 31, 2585−2595

emissions from coal-fired power plants are characterized by the absence of five or more ring PAHs, whereas phenanthrene, fluorene, and fluoranthene dominated.[38] In this work, the content of all 16 PAHs in coal fly ash is 21.36−65.21 $\mu$g/g, depending on the boiler type (Table 2). The lowest value was found in the PC boiler, for which the residence time of the grain was 1−6 s, while the temperature of combustion was 1,400−1,600 °C. Other authors have reported even lower values.[39,40] Only fly ash (PM10 fraction) derived from the heating station and power plant in Liaoning Province, China, contained 611−696 $\mu$g/g for 16 PAHs.[41] For comparison, PAH sums in dust from a coke production plant were 5,321−7,056 $\mu$g/g (Anshan, China[41]) and 1,323−15,914 $\mu$g/g (Radlin, Poland[5]).

In 1 g of raw coal, there was approximately 37.53 $\mu$g of 16 selected PAHs, with the highest content of phenanthrene, i.e., 8.45 $\mu$g (22.51%). Investigated fly ash, derived from bituminous coal combustion in a variety of boilers, contained an average of 65.2 $\mu$g (TGS), 32.7 $\mu$g (TGW), and 21.4 $\mu$g (PC) of the sum of 16 PAHs in 1 g of fly ash. These figures are lower than those presented by Kong et al.[41] In their research for fly ash from heating plants, power plants, and steelworks, where coal was used, they received the following results of the sum of PAHs: 620.14 $\mu$g/g, 708.66 $\mu$g/g, and 290.20 $\mu$g/g, respectively.

In the case of bituminous coal and forest biomass cofiring in the FBC boiler, the dust contained 110.85 $\mu$g/g of the total PAHs; BbF > Phe > DBA > Fl in the largest quantities. In the fly ash from coal combustion in boilers with a mechanical grate (TGW and TGS) and a steam boiler (PC), the PAHs profiles are similar. The highest contents are shown by four-ring PAHs (on average 64−80%) (Figure 1). Quite a different profile was observed for raw bituminous coal (C). In this case, 71% are two- and three-ring PAHs, 21% are four-ring PAHs, and the rest are five- and six-ring PAHs. Fly ash from the cofiring of coal with biomass in the FBC boiler had the highest content of five- and six-ring PAHs (>50%), while 34% had two-three rings, and those with four rings <20%.

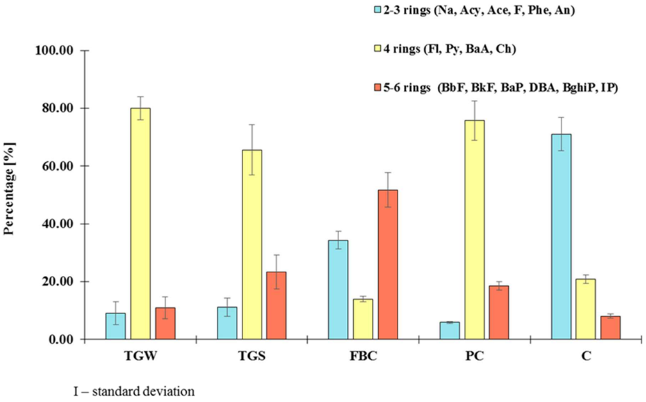

**Figure 1.** Average percentage of two-, three-, four-, five-, and six-ring PAHs in emitted fly ashes and raw coal (C).

In Table 2, TEQ, cancPAH/$\sum$PAH, comPAH/$\sum$PAH, and diagnostic ratio (DR) values were calculated for this study and also in others reported in the literature. The highest value of TEQ was found for coal/biomass combustion in the FBC boiler, that is, 103.2 $\mu$g/g, whereas the PAH sum was 110.8 $\mu$g/g, while Kozielska and Konieczyński,[7] in their study concerning the content of $\sum$PAHs in fly ash for a FBC boiler, fired with bituminous coal, reported the content of $\sum$PAHs and TEQ to be about 172 $\mu$g/g and 30 $\mu$g/g, respectively.

ComPAH/$\sum$PAH values for bituminous coal fly ash are in the range 0.78−0.94 for Polish power plants and 0.35−0.77 for Chinese power plants, findings which differ from those reported in the literature. On the other hand, cancPAH/$\sum$PAH values are in the range 0.5−0.7 and >05 for fly ashes from Chinese stationary sources. Similar values were found for particulate matter.[21] It is remarkable that, for each DR value, the ranges are wide and often differ from the oft-cited data in the literature.

### 3.3. Geochemical markers in coal fly ash: *n*-alkanes and acyclic isoprenoids.

These compounds dominate in extracts of bituminous coal fly ash, with monomodal smooth distributions comprising compounds from $n$-C$_{14}$ to $n$-C$_{35}$ (Figure 2). Long chain $n$-alkanes (>$n$-C$_{23}$) clearly show higher contents than short-chain $n$-alkanes, as reflected in the values of the ratio of long- to short-chain $n$-alkanes ($\sum 2/\sum 1$ > 1.5, Table 3). For a more detailed investigation of the $n$-alkane distribution type, a triangle diagram has been applied showing relative percentage contents of $n$-C$_{14}$−C$_{18}$, $n$-C$_{19}$−C$_{24}$, and $n$-C$_{25}$−C$_{36}$ $n$-alkanes (Figure 3). The group of the lightest $n$-alkanes had the lowest contents with 1.5−10.2% (5.1% on average), the medium-chain had 11.6−42.3% (26.9% on average), and the longest $n$-alkanes occurred in the highest contents, which were 48.4−88.2% (68.0% on average). The enrichment in long-chain $n$-alkanes is obvious when we compare coal (C) and fly ash samples. There is also an influence of the boiler type on $n$-alkane distributions, resulting

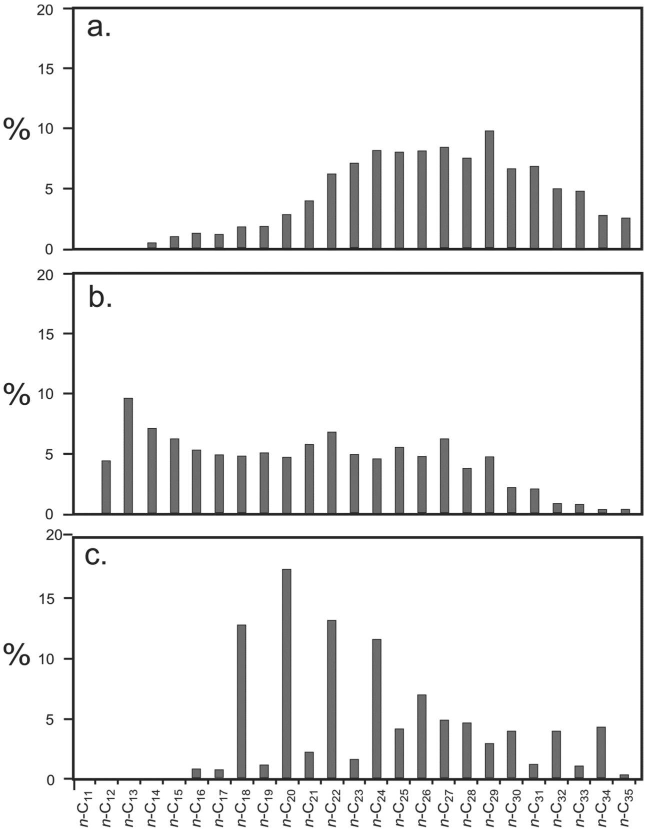

**Figure 2.** Representative $n$-alkane profiles in the extracts: (A) bituminous coal fly ash (TGS); (B) raw bituminous coal (C); (C) bituminous coal/biomass combustion (FBC).

Table 3. Values of Geochemical Ratios Based on Aliphatic Geochemical Markers Found in Extracts of Emitted Fly Ash and Raw Coal[a]

| Sample | CPI(1) | $\sum2/\sum1$(2) | $n$-$C_{23}$/ $n$-$C_{31}$(3) | $C_{11-18}$ %(4) | $C_{19-24}$ %(5) | $C_{25-37}$ %(6) | Pr/Ph(7) | Pr/ $n$-$C_{17}$(8) | Ph/ $n$-$C_{18}$(9) | Ts/ (Ts+Tm)(10) | $C_{31}$S/(S+R)(11) | $C_{29}$Ts/ ($C_{29}$+$C_{29}$Ts)(12) | $\beta\alpha/(\alpha\beta+\beta\alpha)$(13) | $C_{29}$ 20S/(S+R)(14) | $C_{29}\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$(15) | $C_{27}$ $\alpha\alpha\alpha$/ $C_{29}$ $\alpha\alpha\alpha$(16) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TGW-1 | 1.05 | 4.24 | 2.26 | 2.7 | 34.5 | 62.8 | 1.29 | 1.53 | 0.50 | 0.49 | 0.61 | 0.10 | 0.10 | 0.36 | 0.34 | 0.97 |
| TGW-2 | 1.16 | 5.36 | 2.01 | 1.7 | 32.6 | 65.7 | 1.12 | 0.83 | 0.58 | 0.47 | 0.63 | 0.09 | 0.09 | 0.49 | 0.40 | |
| TGW-3 | 1.11 | 5.47 | 1.32 | 1.9 | 30.5 | 67.6 | 1.75 | 1.29 | 0.47 | | 0.56 | 0.07 | 0.07 | 0.30 | 0.36 | |
| TGW-4 | 1.38 | 6.19 | 0.68 | 1.3 | 28.9 | 69.8 | 0.87 | 1.95 | 0.73 | 0.69 | 0.60 | 0.12 | 0.12 | 0.46 | 0.36 | 0.87 |
| **TGW aver.** | **1.18** | **5.31** | **1.57** | **1.9** | **31.6** | **66.5** | **1.26** | **1.40** | **0.57** | **0.55** | **0.60** | **0.095** | **0.10** | **0.40** | **0.37** | **0.92** |
| TGS-1 | 1.56 | 1.02 | 0.6 | 6.6 | 20.6 | 72.8 | 1.75 | 0.98 | 0.39 | | 0.59 | 0.12 | 0.35 | | | |
| TGS-2 | 1.14 | 0.95 | 0.77 | 7.5 | 23.6 | 68.9 | 1.56 | 1.02 | 0.51 | | 0.59 | 0.17 | 0.26 | 0.42 | 0.31 | |
| TGS-3 | 1.11 | 3.38 | 0.60 | 5.8 | 20.5 | 73.8 | 1.93 | 1.11 | 0.51 | | 0.56 | 0.22 | 0.20 | | | |
| TGS-4 | 1.05 | 2.55 | 0.87 | 8.7 | 24.1 | 67.2 | 1.67 | 0.95 | 0.56 | | 0.58 | | | | | |
| TGS-5 | 1.03 | 5.82 | 0.24 | 4.3 | 11.6 | 84.1 | 1.84 | 1.23 | 0.58 | | 0.65 | 0.21 | 0.07 | | | |
| TGS-6 | 1.16 | 6.54 | 1.04 | 5.2 | 28.4 | 66.4 | 1.61 | 1.06 | 0.41 | | 0.63 | | | | | |
| **TGS aver.** | **1.18** | **3.38** | **0.69** | **6.35** | **21.5** | **72.2** | **1.70** | **1.06** | **0.49** | | **0.60** | **0.18** | **0.22** | **0.42** | **0.31** | |
| PC | 1.17 | 6.96 | 1.25 | 1.5 | 26.6 | 71.9 | 0.96 | 0.58 | 0.52 | 0.66 | 0.64 | 0.13 | 0.22 | 0.35 | 0.46 | |
| FBC-1 | | | | | | | | | | | | | | | | |
| FBC-2 | 0.60 | 1.43 | 0.44 | 11.1 | 41.3 | 47.6 | 0.07 | 2.9 | 19.8 | | | | | | | |
| FBC-3 | 0.54 | 1.08 | 1.28 | 14.5 | 46.7 | 38.7 | 0.07 | 12.8 | 34.5 | | | | | | | |
| FBC-4 | 0.70 | 1.20 | 0.94 | 13.2 | 43.8 | 43.0 | 0.04 | 2.62 | 33.3 | | | | | | | |
| FBC-5 | 0.98 | 1.53 | 1.08 | 12.5 | 36.7 | 50.8 | 0.09 | 5.51 | 28.7 | | | | | | | |
| **FBC aver.** | **0.71** | **1.31** | **0.94** | **12.8** | **42.1** | **45.0** | **0.07** | **5.96** | **29.08** | | | | | | | |
| C | 1.41 | 0.68 | 2.42 | 37.6 | 31.4 | 31.0 | 6.56 | 3.62 | 0.54 | 0.74 | 0.50 | | 0.26 | 0.32 | 0.35 | 1.08 |

[a] Empty cells indicate compounds not detected; or compounds detected but at concentrations too low to calculate a parameter value. (1) CPI = $0.5[(n\text{-}C_{25}+n\text{-}C_{27}+n\text{-}C_{29}+n\text{-}C_{31}+n\text{-}C_{33})/(n\text{-}C_{24}+n\text{-}C_{26}+n\text{-}C_{28}+n\text{-}C_{30}+n\text{-}C_{32})] + [(n\text{-}C_{25}+n\text{-}C_{27}+n\text{-}C_{29}+n\text{-}C_{31}+n\text{-}C_{33})/(n\text{-}C_{26}+n\text{-}C_{28}+n\text{-}C_{30}+n\text{-}C_{32}+n\text{-}C_{34})]$; Carbon Preference Index; $m/z$ = 71; thermal maturity parameter.[61] (2) $\sum2/\sum1 = [\sum(\text{from } n\text{-}C_{23} \text{ to } n\text{-}C_{37})]/[\sum(\text{from } n\text{-}C_{11} \text{ to } n\text{-}C_{22})]$; $m/z$ = 71; source indicator.[64] (3) $n$-$C_{23}$/$n$-$C_{31}$.[65] (4-6) Relative percentage contents of a sum of $n$-alkanes in a given range. (7) Pr/Ph = pristane/phytane; parameter of environment oxicity (with exception of coals); $m/z$ = 71.[66] (8) Pr/$n$-$C_{17}$ = pristane/$n$-heptadecane; $m/z$ = 71.[67] (9) Ph/$n$-$C_{18}$ = phytane/$n$-octadecane; $m/z$ = 71.[67] (10) Ts/(Ts+Tm) = 18α(H)-22,29,30-trisnorneohopane/(18α(H)-22,29,30-trisnorneohopane + 17α(H)-22,29,30-trisnorhopane); $m/z$ = 191; thermal maturity parameter.[63] (11) $C_{31}$S/(S+R) = 17α(H),21β(H)-29-homohopane 22S/(17α(H),21β(H)-29-homohopane 22S+17α(H),21β(H)-29-homohopane 22R); $m/z$ = 191; thermal maturity parameter.[63] (12) $C_{29}$Ts/($C_{29}$+$C_{29}$Ts = 18α-30-norneohopane/(18α-30-norneohopane + 17α(H),21β(H)-30-norhopane); $m/z$ = 191, thermal maturity parameter.[68] (13) $C_{30}$βα/(αβ+βα) = 17β(H),21α(H)-29-hopane $C_{30}$/(17α(H),21β(H)-29-hopane $C_{30}$+17β(H),21α(H)-29-hopane $C_{30}$); $m/z$ = 191, thermal maturity parameter.[68] (14) $C_{29}$ 20S/(S+R) = 5α(H),14α(H),17α(H) $C_{29}$ sterane 20S/(5α(H),14α(H),17α(H) $C_{29}$ sterane 20S + 5α(H),14α(H),17α(H) $C_{29}$ sterane 20R); $m/z$ = 217, thermal maturity parameter.[68] (15) $C_{29}$αββ/(ααα + αββ) = 5α(H),14β(H),17β(H)$C_{29}$ steranes/(5α(H),14α(H),17α(H) $C_{29}$ steranes + 5α(H),14β(H),17β(H) $C_{29}$ steranes); $m/z$ = 217, thermal maturity parameter.[68] (16) $C_{27}$ ααα/$C_{29}$ ααα a sum of cholestanes $C_{27}$ ααα/a sum of stigmastanes $C_{29}$ ααα, $m/z$ = 217, source indicator.[69]

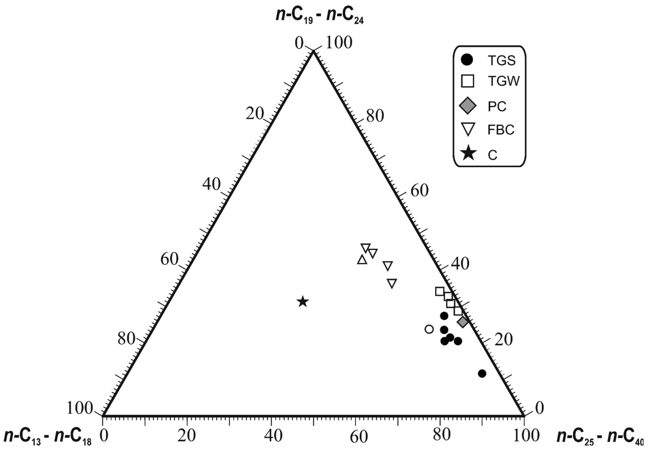

**Figure 3.** Relative percentage contents of $n$-C$_{14}$–C$_{18}$, $n$-C$_{19}$–C$_{24}$, and $n$-C$_{25}$–C$_{36}$ $n$-alkanes.

in significant changes compared to bituminous coal extracts, both analyzed in this project and investigated previously.[31] The distinguishing feature of TGS fly ash is the higher percentage of lightest $n$-alkanes (~6–9%), compared to 1–2% for TGW and PC fly ash. The difference is probably caused by differences in the quality of combustion, i.e. the possible presence of oxygen depletion zones within the older boiler types. This leads to better preservation of the original pattern of geochemical markers distributions due to the presence of unburnt or only slightly charred particles of coal.[60]

The $n$-alkanes distributions in TGW, PC, and TGS fly ash showed only slight odd-over-even carbon atom number predominance with the carbon preference index (CPI) values in the range 1.00–1.56 (Table 3). This corresponds to the ranks of coals combusted.[31,36,61,62] Fly ash from the modern FBC boiler (year: 2003) was particularly poor in all geochemical compounds, with $n$-alkane distributions highly differing from those derived from combustion in TGW, TGS, and PC boilers (Figure 3). The distributions are shorter, with higher contents shown by medium-chain compounds (42.3% on average) and FBC samples showing a high degree of similarity. CPI values are all <1.0 (0.54–0.99), indicating the predomination of even carbon atom number $n$-alkanes, a feature unknown in bituminous coals.[63] In this case, $n$-alkanes most probably come from combusted biomass, whereas most bituminous coal components were destroyed during combustion in this modern and efficient boiler.

Acyclic isoprenoids, which included pristane and phytane, occurred in all fly ash extracts. In organic geochemistry, these compounds are applied to assess the oxygen level in the environment of organic matter depositional, oil-kerogen, and oil–oil correlations.[63,66,67,70,71] Here, these ratios are used to assess changes caused by temperature during combustion. In the fly ash investigated from TGW, TGS, and PC boilers, the average values of their ratios were as follows: Pr/Ph = 1.44, Pr/$n$-C$_{17}$ = 1.11, and Ph/$n$-C$_{18}$ = 0.59 (Table 3). There was a significant decrease of Pr/Ph values for fly ash from coal/biomass combustion in the FBC boiler (0.06 on average), compared to bituminous coal fly ash, possibly due to more advanced thermal destruction of lighter pristane than phytane (Figure 4a). Ph/$n$-C$_{18}$ and Pr/$n$-C$_{17}$ values for TGW, TGS, and PC boilers are in the range of common bituminous coals/kerogen III Upper Silesia coals investigated previously,[31,62] as is seen in the diagram of Pr/$n$-C$_{17}$ vs Ph/$n$-C$_{18}$, with a relatively slight shift caused by combustion (Figure 4a). However, the FBC samples show unusually high values of Pr/$n$-C$_{17}$ (29.07 on average) and moderately high values of Pr/$n$-C$_{17}$ (5.96 on average) caused by thermal removal of $n$-octadecane and/or input of the phytane chain from such sources as acyclic isoprenoids present in biomass (Figure 4b).

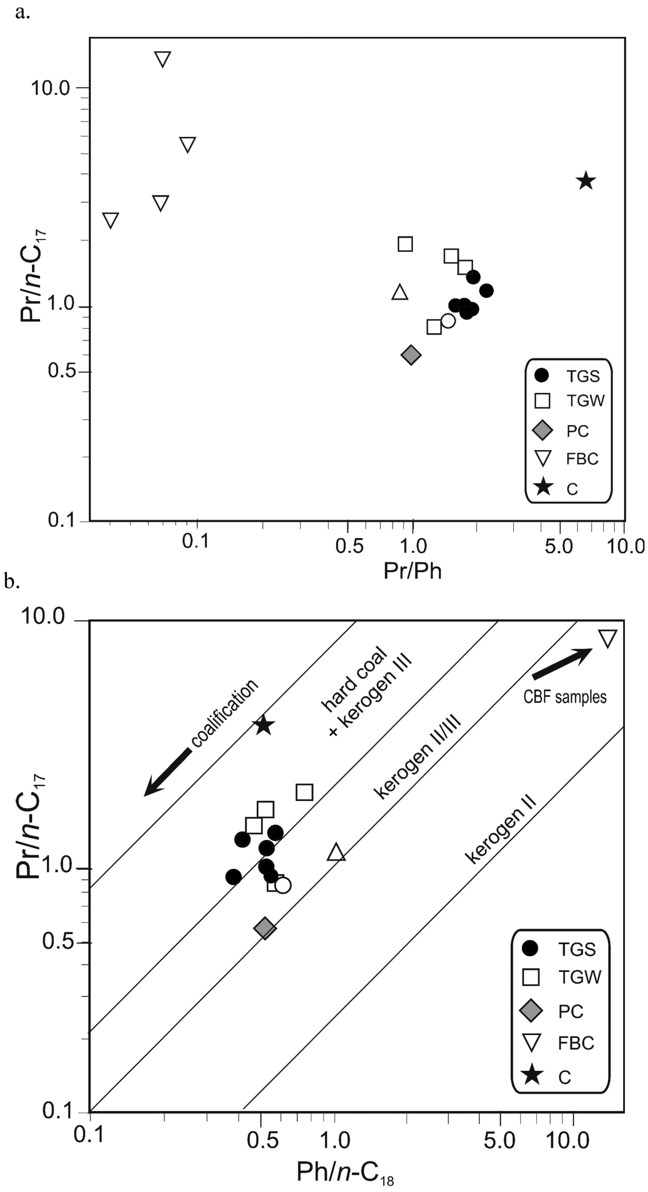

**Figure 4.** (a) Pr/Ph vs Pr/$n$-C17 diagram; (b) Pr/$n$-C$_{17}$ vs Ph/$n$-C$_{18}$ diagram.[72]

*Pentacyclic triperpanes.* Hopanes and moretanes ($m/z$ = 191) occurred in fly ash extracts in the range of 18$\alpha$(H)-22,29,30-trisnorneohopane (Ts) to 17$\alpha$(H),21$\beta$(H)-29-pentakishomohopane (C$_{35}\alpha\beta$); however, in most cases, the distributions ended at 17$\alpha$(H),21$\beta$(H)-29-trishomohopane (C$_{33}\alpha\beta$) (Figure 5). This feature is common in most humic coals and kerogen III (terrestrial organic matter), and was previously found in coals from the Upper Silesian Coal Basin.[31,36,62] The highest contents were shown by 17$\alpha$(H),21$\beta$-(H) hopanes ($\alpha\beta$), with only one moretane C$_{30}$ $\beta\alpha$ present in higher contents. Hopanes with a biological $\beta\beta$ configuration were not identified, which indicated geochemically mature organic matter (Figure 5). The specific feature of TGS fly ash

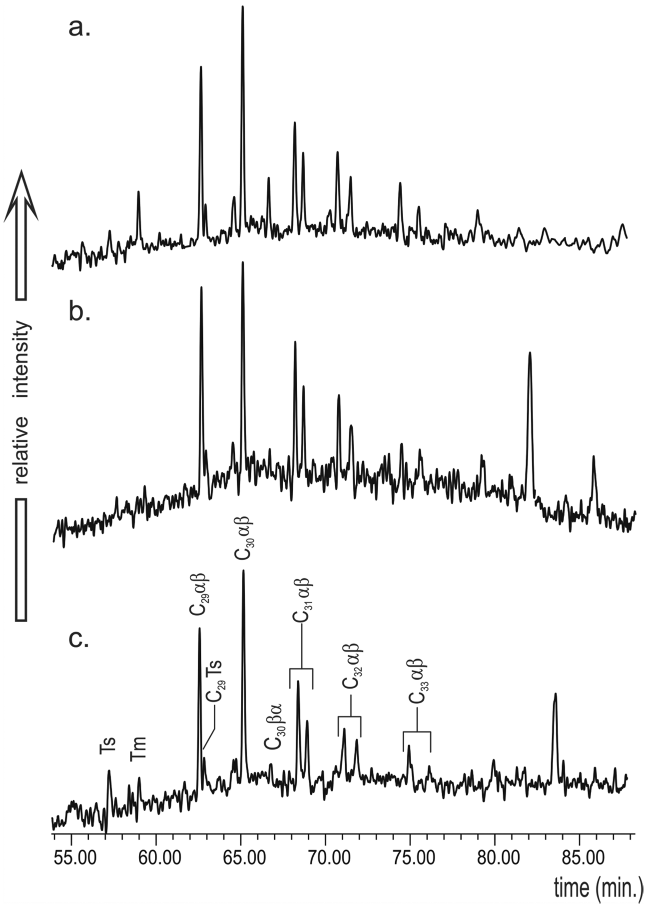

**Figure 5.** Pentacyclic triterpene distribution in bituminous coal fly ash extracts.

hopane distributions is the absence of Ts, as well as the occasional removal of Tm (17α(H)-22,29,30-trisnorhopane), possibly due to thermal destruction in combustion. Ts contents were also lowered in some TGW fly ash. The similar tendency was found in laboratory pyrolysis of Upper Silesian coals, in which Ts relative contents decreased compared to Tm.[73] However, such behavior is opposite to that shown during catagenesis of organic matter in a deposit where Tm tends to decrease in concentration with increasing maturity.[63] These results may indicate that maturation in the lithosphere causes Tm to Ts conversion rather than thermal destruction of Tm. Although hopanes occurred in the total amount of fly ash from coal combustion, they were generally absent in fly ash from coal/biomass combustion (FBC) whereas the best preserved hopane distributions were found in TGW fly ash extracts. This indicates that geochemical markers tend to be found in fly ash from boilers of lower efficiency.

Several geochemical maturity ratios, based on hopanes and moretanes, were calculated to assess the maturity level of source fuel (Table 3). Values of 17α(H),21β(H)-29-homohopane 22S (geochemical diastereomer) in relation to the sum of 17α(H),21β(H)-29-homohopane 22S and 17α(H),21β(H)-29-homohopane 22R were in the range 0.52−0.64. This corresponds to vitrinite reflectance $R_o$ = 0.7−0.8% (middle catagenesis), which is the typical range for bituminous coals from Upper Silesia.[31,60] At this stage in the thermal evolution of organic matter, both diastereomers are in a state of thermodynamic equilibrium, while the index value is close to about 0.60.

Values of Ts/(Ts + Tm) (Table 3) were in the range of 0.47−0.74. The above-mentioned loss of Ts and Tm impairs the value of this parameter; hence, the relatively low-rank coal utilized by the steam boiler (PC sample) shows the highest value of this indicator. The values of 17β(H) and 21α(H)-29-hopane $C_{30}$ to the total sum of 17α(H) 21β(H)-29-hopane $C_{30}$ and 17β(H),21α(H)-29-hopane $C_{30}$ for fly ash from bituminous coal combustion ranged from 0.07 to 0.35. 18α-30-Norneohopane was a rarely appearing compound because the thermal maturity of fuels used was too low.[63] Values of 18α-30-norneohopane ($C_{29}$Ts) in relation to the sum 18α-30-norneohopane and 17α(H),21β(H)-30-norhopane ($C_{29}$Ts/($C_{29}$ + $C_{29}$Ts)) were in the range 0.07−0.22. The values of maturity ratios, based on hopanes and moretanes, correspond to the thermal evolution stage of combusted coal, confirming that the essential characteristics of geochemical distribution pentacyclic triterpenes did not change under the influence of the combustion process, with the exception of the loss of Ts and Tm.

On the basis of the distribution of the three groups of pentacyclic triterpenes, $C_{29}$, $C_{30}$, and $C_{31}$, their relative percentages were calculated (Figure 6). In most fly ash from bituminous coal combustion, norhopanes ($C_{29}$) showed the lowest relative contents, and homohopanes ($C_{31}$) showed the highest. There is no real influence of the boiler type on relative percentage contents, since all samples are plotted close to each other.

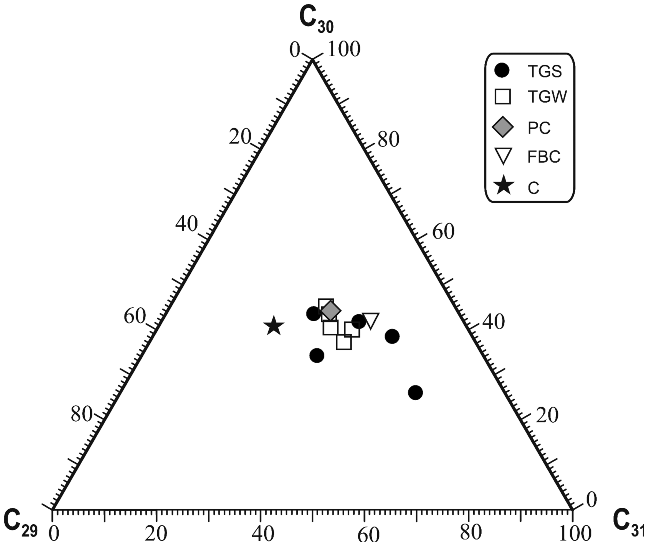

**Figure 6.** Relative percentage concentrations of $C_{29}$, $C_{30}$, and $C_{31}$ pentacyclic triterpenes.

Summarizing, pentacyclic triperpanes, due to relatively limited changes caused by the thermal influence of combustion, the preserved distribution type, and ratio values, should be considered good indicators of fossil fuel emission of fly ash into the air. It is possible that such good preservation is caused by the sorption of these heavy molecular weight compounds in only partially combusted particles of bituminous coal or its coked remains. This general thermal resistance of pentacyclic triterpanes has also been found in experiments of organic matter pyrolysis and concerns both free and bound compounds.[74]

*Steranes.* Steranes were only found in a few fly ash samples from bituminous coal combustion. Their contents are mostly very low; thus, their distributions are difficult to interpret. Relative percentages of stigmastanes ($C_{29}$) and cholestanes

($C_{27}$) are close to each other, such that their ratio values oscillate around 1.0 (Table 3), confirming the objections raised by several authors relating to the differentiation of the distribution of the compounds according to the type of kerogen.[63,75,76] Values of $C_{29}$ sterane 20S in relation to the sum of 20S and 20R steranes were in a range from 0.30 to 0.49 for the coal fly ash, which does not reach its upper limit; this is the same as the ratio of the sum of $5\alpha(H),14\beta(H),17\beta(H)$ $C_{29}$ steranes to the sum of all stigmastanes (0.31−0.46, Table 3). As in the case of pentacyclic triterpenes, steranes were absent in FBC fly ash, and also in some TGS samples. There are two possible explanations of sterane absence in fly ash: (i) their absence or low concentrations in a large number of Upper Silesia coals,[31] and (ii) their thermal stability lower than that of pentacyclic triterpanes, as found in pyrolysis experiments.[74] The latter explanation seems to be more valid, since power plants utilize mixtures of bituminous coals from different mines and coal seams. This leads to a more uniform composition of fuel combusted than that found in selected seams.

*Aliphatic derivatives of aromatic compounds.* Alkyl aromatic compounds were present in a wide range of derivatives in fly ash. Figure 7 shows the distribution of aliphatic derivatives of naphthalene found in the range from methyl- to tetramethylnaphthalenes. Meanwhile, Figure 8 shows the distributions of alkylphenanthrenes ($C_1$−$C_2$), and Figure 9 shows the distributions of methyl biphenyls, methyl chrysenes, and pyrenes. There is significant dependence of alkyl PAH occurrence on the boiler type. Fly ash from biomass/bituminous coal combustion, i.e. the most modern FBC boiler, did not contain alkylnaphthalenes and methyl biphenyls; the same was true for some TGW boiler samples, despite the wide occurrence of these compounds in most Upper Silesian coals[31,62] and in bituminous coal (C) investigated here. Methyl phenanthrenes were found in most fly ash extracts. The occurrence of methyl pyrenes was similar to that of methyl phenanthrenes, whereas methyl chrysenes were rare in the fly ash investigated. Distributions of lighter compounds generally showed a significantly higher impact of combustion temperature than distributions of higher molecular weight substances. Alkylaromatic hydrocarbon distributions were the best preserved in the TGS than TGW fly ash, the opposite to the tendency found for aliphatic geochemical markers. The reason for this may be in differences in molecular weights of these compounds groups, i.e. much heavier steranes and hopanes (and less volatile) than alkyl aromatic hydrocarbons and differing combustion conditions in both boilers.

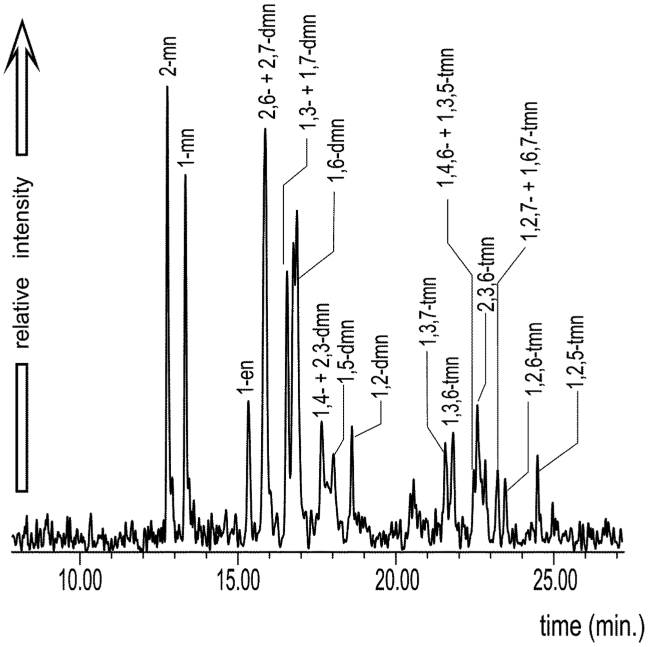

**Figure 7.** Distributions of aliphatic derivatives of naphthalene bituminous coal fly ash extracts.

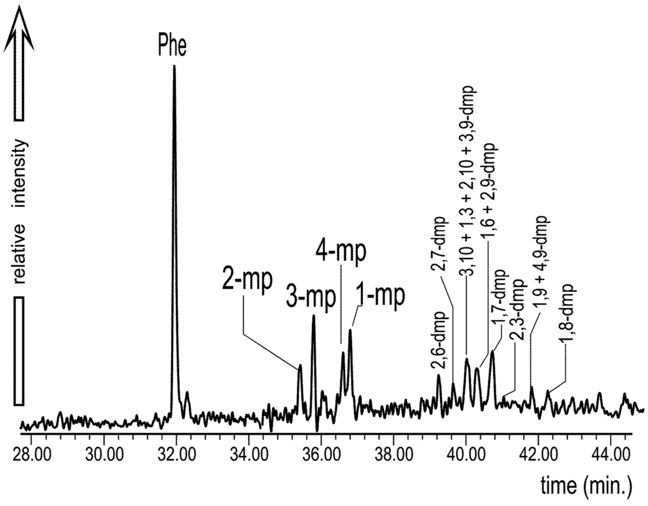

**Figure 8.** Distributions of aliphatic derivatives of phenanthrene in bituminous coal fly ash extracts.

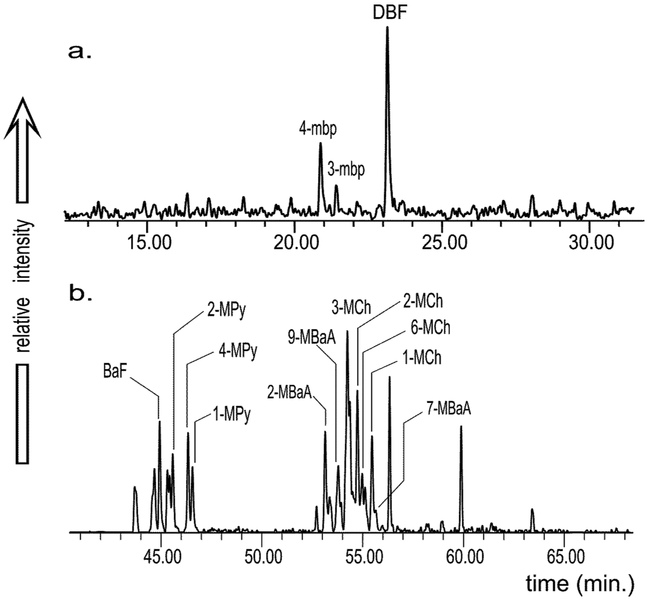

**Figure 9.** Distribution of methyl biphenyls, methyl chrysenes, and methyl pyrenes in bituminous coal fly ash extracts.

The average values of alkylnaphthalene ratios were as follows: methylnaphthalene ratio (MNR) = 0.78, dimethylnaphthalene ratio (DMR) = 2.01, trimethylnaphthalene ratio 1 (TNR-1) = 2.64, TNR-2 = 1.42, and TNR-5 = 0.48. The contents of methyl-, dimethyl-, and trimethylnaphthalenes varied relative to each other, while, in most of the lighter sample compounds, they occurred in lower concentrations, as shown in Figure 7.

Table 4. Values of Geochemical Ratios Based on Alkyl Aromatic Hydrocarbons' Geochemical Markers Found in Extracts of Emitted Fly Ash and Raw Coal[a]

| Sample | MNR(1) | DNR-1(2) | TNR-1(3) | TNR-2(4) | TNR-5(5) | MPI-3(6) | MPI-1(7) | DMPR(8) | MPyR(9) | MChR(10) | (3-MB + 4MB)/DBF(11) | Rc [%](12) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **TGW-1** | | | | | | 1.24 | 0.5 | 0.60 | 0.58 | | | 0.70 |
| **TGW-2** | | | | | | 1.76 | 0.26 | | 0.81 | | | 0.56 |
| **TGW-3** | | | | | | | | | | | | |
| **TGW-4** | | | | | | | | | | | | |
| **TGW aver.** | | | | | | **1.50** | **0.38** | **0.60** | **0.70** | | | **0.63** |
| **TGS-1** | 0.66 | 2.33 | 3.70 | 1.68 | 0.54 | 1.56 | 0.40 | | 0.38 | | 0.38 | 0.64 |
| **TGS-2** | 0.8 | 2.07 | | | | 0.93 | 0.26 | 0.44 | 0.50 | | 0.74 | 0.55 |
| **TGS-3** | 0.78 | | 1.66 | 1.10 | 0.43 | 1.19 | 0.28 | | | | 0.49 | 0.57 |
| **TGS-4** | 0.79 | 1.55 | 1.18 | 1.10 | 0.46 | 0.86 | 0.23 | | 0.62 | | 0.53 | 0.54 |
| **TGS-5** | | | | | | 1.01 | 0.25 | | 0.38 | | 0.54 | 0.55 |
| **TGS-6** | 1.12 | | 0.32 | 0.59 | 0.51 | 1.80 | 0.42 | 0.46 | 0.56 | 1.56 | | 0.65 |
| **TGS aver.** | **0.83** | **1.98** | **1.72** | **1.12** | **0.49** | **1.23** | **0.31** | **0.45** | **0.49** | **1.56** | **0.54** | **0.58** |
| **PC** | | | | | | **1.02** | **0.45** | **0.38** | **0.53** | **0.22** | | **0.67** |
| **FBC-1** | | | | | | | | | | | | |
| **FBC-2** | | | | | | | | | | | | |
| **FBC-3** | | | | | | | | | | | | |
| **FBC-4** | | | | | | | | | | 0.51 | | |
| **FBC-5** | | | | | | | | | 0.55 | | | 0.56 |
| **FBC aver.** | | | | | | | | | **0.55** | **0.51** | | **0.56** |
| **C** | **1.35** | **3.04** | **10.2** | **2.36** | **0.63** | **1.00** | **0.65** | **0.64** | **-** | **0.38** | **0.35** | **0.79** |

[a] Empty cells indicate compounds not detected; or compounds detected but concentrations too low to calculate a parameter value. (1)MNR = 2-methylnaphthalene/1-methylnaphthalene; *m/z* = 142; thermal maturity.[79] (2)DNR-1 = (2,6-dimethylnaphthalene + 2,7-dimethylnaphthalene)/1,5-dimethylnaphthalene; *m/z* = 156, thermal maturity.[79] (3)TNR-1 = (1,3,7-trimethylnaphthalene + 2,3,6-trimethylnaphthalene)/(1,3,5-trimethylnaphthalene + 1,4,6-trimethylnaphthalene + 1,3,6-trimethylnaphthalene); *m/z* = 170, thermal maturity.[79] (4)TNR-2 = (1,3,7-trimethylnaphthalene + 2,3,6-trimethylnaphthalene)/(1,3,5-trimethylnaphthalene + 1,4,6-trimethylnaphthalene + 1,3,6-trimethylnaphthalene); *m/z* = 170, thermal maturity.[79] (5)TNR-5 = 1,2,5-trimethylnaphthalene/(1,2,5-trimethylnaphthalene + 1,2,7-trimethylnaphthalene + 1,6,4-trimethylnaphthalene); *m/z* = 170, source.[79] (6)MPI-3 = (2-methylphenanthrene + 3-methylphenathrene)/(1-methylphenathrene + 9-methylphenathrene); *m/z* = 192; thermal maturity.[79] (7)MPI-1 = 1.5(2-methylphenanthrene + 3-methylphenanthrene)/(phenanthrene + 1-methylphenanthrene + 9-methylphenanthrene); thermal maturity.[79] (8)DMPR = dimethylphenanthrene ratio ([3,5-+2,6-+2,7-DMP]/[1,3-+3,9-+2,10-+3,10-+1,6-+2,9-+2,5-DMP]), *m/z* = 206; thermal maturity.[79] (9)MChR = 2-methylchrysene/(methylbenzoanthracenes + 2-methylchrysene + 6-methylchrysene + 1-methylchrysene), *m/z* = 242, thermal maturity.[80] (10)MPyR = 2-methylpyrene/(1-methylpyrene+2-methylpyrene); *m/z* = 216, thermal maturity parameter.[80] (11)MBR = (3-methylbiphenyl + 4-methylbiphenyl)/dibenzofurane; *m/z* = 168; thermal maturity parameter.[81] (12)$R_c$ = 0.60 MPI-1 + 0.40.[79]

Alkylphenanthrenes (*m/z* = 192), accompanied by methyl anthracenes, were found in all coal fly ash samples. Their average values for the dust from the burning coals were as follows: methylphenanthrene index 1 (MPI-1) = 0.37, MPI-3 = 1.28, and dimethylphenenthrene ratio (DMPR) = 0.50 (Table 4). However, the MPI values for some fly ash are clearly too low, perhaps due to the low concentration of isomers, which led to the integration error. The other possible explanation is phenanthrene release and/or formation due to organic matter heating. Generally, petrogenic materials such as bituminous coals or crude oil show a pattern of alkylated PAHs distributions where $C_1$−$C_3$ PAHs are more abundant than unsubstituted ($C_0$) and $C_4$ PAHs or—when degraded—the pattern is $C_0 < C_1 < C_2 < C_3 < C_4$. However, in pyrogenic materials alkyl PAHs show the opposite distribution pattern: $C_0 \gg C_1 > C_2 > C_3 > C_4$, here reflected in the decrease of MPI-1 values.[77]

The distribution of alkyl biphenyls included biphenyl (*m/z* = 154) and methyl- and dimethyl biphenyls (*m/z* = 168 and 182) (Figure 9). The latter compounds, however, occurred at such low concentrations that their interpretation was not possible. Values for the methylbiphenyl/dibenzofuran ratio (Table 4) are within the range 0.04−0.90. Such a wide range for bituminous coals with similar geochemical characteristics to each other and the coalification stage indicates a low degree of reliability concerning the values obtained from this ratio. This is due to the low molecular weights of these compounds. As it was in the case of methyl naphthalenes having similar molecular weights, combustion tends to remove them.

The distribution of methyl pyrenes (*m/z* = 216) comprises 2-, 4-, and 1-metylopyrene (Figure 9). These compounds are quite well preserved in the fly ash. As was the case with other groups of compounds, biomass/bituminous coal combustion fly ash contained only small amounts of them, with the exception of one sample (FBC5). Methyl pyrene ratio values were 0.55 on average (Table 4). The methyl chrysene (*m/z* = 242) distribution comprised 3-, 2-, 6-, and 1-methylchrysene, with 2-, 9-, and 7-methylbenzo[a]anthracene observed in the same chromatogram (Figure 9). The average methylchrysene ratio value was 0.72 (Table 4).

DOI: 10.1021/acs.energyfuels.6b03030
Energy Fuels 2017, 31, 2585−2595

*Biomass markers.* In the FBC boiler, fly ash from biomass/coal combustion compounds, which derived from biomass, predominated. Apart from *n*-alkanes described previously, these extracts contained a wide range of polysubstituted phenolic compounds, ketones, fatty acids and their methyl esters. However, levoglucosan, which is a commonly applied indicator for cellulose combustion,[4,78] was not found, possibly due to very good combustion parameters in this modern boiler. All lighter biomarkers were absent in these samples for the same reason.

While phenolic compounds derive from lignin thermal destruction, bituminous coal also produces these substances when pyrolyzed, since vitrinite originates from lignin and, at moderate coalification, phenolic structures are still present in its macromolecule.[82,83] Thus, in order to indicate biomass combustion, it is better to use heavier and more characteristic compounds, such as guaiacol derivatives or eugenol.

## 4. CONCLUSIONS

Fly ash from coal and biomass cofiring contains the highest PAH concentrations, as well as indicates the highest TEQ values among all boilers investigated. It is a significant problem from a municipal and health hazard point of view. Fly ash from bituminous coal combustion in different types of boilers is rich in four-ring PAHs (approximately 70%), whereas the source fuel (i.e., raw bituminous coal) is rich in three-ring PAHs. There are high differences between the values of diagnostic ratios found in this project and the literature data, such that these ratios should be applied in order to identify emission sources with care; alternatively, additional indicators, such as biomarkers, should be applied.

Studies have shown that the distributions of geochemical markers and biochemical markers, as well as the distribution of the majority of aromatic hydrocarbons and their aliphatic derivatives in fly ash, which is emitted from a variety of boilers combusting bituminous coal and composite fuel, show a significant similarity to combusted coal. In the fly ash extracts, several groups of organic compounds were identified, whose presence or characteristic distribution can be considered as an indicator of the contamination source. These compounds include the following biomarkers: *n*-alkanes in the range of compounds from 11 to 38 carbon atoms in a molecule and accompanying *iso*-alkanes; acyclic isoprenoids, pristane and (mainly) phytane, and steranes in the range from $C_{27}$ (cholestanes) to $C_{29}$ (stigmastanes); pentacyclic triterpenoids (hopanes and moretanes); and alkyl derivatives of aromatic hydrocarbons, including alkylnaphthalenes, alkylphenanthrenes, alkylpyrenes, and alkylchrysenes, showing a distribution characteristic for the source fuels, as well as markers for solid biofuels, namely, polysubstituted phenol derivatives, fatty acids, and their esters.

It has been found that the thermal changes in the distributions and presence of biomarkers, caused by combustion, are small and mainly affect compounds of low molecular weight. It is possible that high molecular weight compounds survived the high temperature process when adsorbed in unburned or coked coal and/or biomass particles included in the dust emitted. The results confirm the thesis concerning the general preservation of the geochemical features of the source fuel in organic matter of fly ash, particularly with respect to compounds of high molecular mass, and indicate the usefulness of these compounds in research on the type of emission sources of particulate matter into the air.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: monika.fabianska@us.edu.pl.

### ORCID

M. Fabiańska: 0000-0002-8270-9384

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This research was supported by the Polish Ministry of Science and Higher Education, Grant No. N523 751840.

## REFERENCES

(1) IARC. *Monographs on the Evaluation of Carcinogenic Risks to Humans* **2012**, *100E*, 515−538.

(2) Zhang, J.; Smith, K. R. *Environ. Health Perspect.* **2007**, *115* (6), 848−855.

(3) Guo, H.; Lee, S. C.; Ho, K. F.; Wang, X. M.; Zou, S. C. *Atmos. Environ.* **2003**, *37* (38), 5307−5317.

(4) Simoneit, B. R. T. *Appl. Geochem.* **2002**, *17* (3), 129−162.

(5) Kozielska, B.; Konieczyński, J. *Fuel* **2015**, *144*, 327−334.

(6) Kozielska, B.; Konieczyński, J. *Environ. Technol.* **2007**, *28* (8), 895−903.

(7) Kozielska, B.; Konieczyński, J. *Environ. Technol.* **2008**, *29* (11), 1199−1207.

(8) Geng, C.; Chen, J.; Yang, X.; Ren, L.; Yin, B.; Liu, X.; Bai, Z. *J. Environ. Sci. (China)* **2014**, *26* (1), 160−166.

(9) Mueller, J. F.; Hawker, D. W.; Connell, D. W. *Chemosphere* **1998**, *37* (7), 1369−1383.

(10) Dvorská, A.; Lammel, G.; Klánová, J. *Atmos. Environ.* **2011**, *45* (2), 420−427.

(11) Herlekar, M.; Joseph, A. E.; Kumar, R.; Gupta, I. *Aerosol Air Qual. Res.* **2012**, *12* (6), 1247−1260.

(12) Agudelo-Castañeda, D. M.; Teixeira, E. C. *Atmos. Environ.* **2014**, *96*, 186−200.

(13) Panther, B. C.; Hooper, M. A.; Tapper, N. J. *Atmos. Environ.* **1999**, *33* (24−25), 4087−4099.

(14) Mohanraj, R.; Solaraj, G.; Dhanakumar, S. *Environ. Sci. Pollut. Res.* **2011**, *18* (5), 764−771.

(15) Wu, S. P.; Tao, S.; Liu, W. X. *Chemosphere* **2006**, *62* (3), 357−367.

(16) Ladji, R.; Yassa, N.; Balducci, C.; Cecinato, A.; Meklati, B. Y. *Sci. Total Environ.* **2009**, *408* (2), 415−24.

(17) Martellini, T.; Giannoni, M.; Lepri, L.; Katsoyiannis, A.; Cincinelli, A. *Environ. Pollut.* **2012**, *164*, 252−58.

(18) Křůmal, K.; Mikuška, P.; Večeřa, Z. *Atmos. Environ.* **2013**, *67*, 27−37.

(19) Mirante, F.; Alves, C.; Pio, C.; Pindado, O.; Perez, R.; Revuelta, M. A.; Artiñano, B. *Atmos. Res.* **2013**, *132−133*, 345−61.

(20) Kozielska, B.; Rogula-Kozłowska, W.; Pastuszka, J. S. *Int. J. Environ. Pollut.* **2013**, *53* (3−4), 245−264.

(21) Kozielska, B.; Rogula-Kozłowska, W.; Klejnowski, K. *Atmosphere* **2015**, *6* (1), 1−20.

(22) Xie, M.; Wang, G.; Hu, S.; Han, Q.; Xu, Y.; Gao, Z. *Atmos. Res.* **2009**, *93* (4), 840−848.

(23) Kim, D.; Kumfer, B. M.; Anastasio, C.; Kennedy, I. M.; Young, T. M. *Chemosphere* **2009**, *76* (8), 1075−1081.

(24) Riva, M.; Robinson, E. S.; Perraudin, E.; Donahue, N. M.; Villenave, E. *Environ. Sci. Technol.* **2015**, *49* (9), 5407−5416.

(25) He, J.; Zielinska, B.; Balasubramanian, R. *Atmos. Chem. Phys.* **2010**, *10* (23), 11401−11413.

(26) Hasheminassab, S.; Daher, N.; Schauer, J. J.; Sioutas, C. *Atmos. Environ.* **2013**, *79*, 529−39.

(27) Schauer, J. J.; Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. *Atmos. Environ.* **1996**, *30* (22), 3837−3855.

(28) Klejnowski, K.; Kozielska, B.; Krasa, A.; Rogula-Kozłowska, W. *Arch. Environ. Prot.* **2010**, *36*, 65−72.

(29) Rogula-Kozłowska, W.; Kozielska, B.; Klejnowski, K. *Bull. Environ. Contam. Toxicol.* **2013**, *91* (3), 349−355.

(30) Rogula-Kozłowska, W.; Klejnowski, K.; Rogula-Kopiec, P.; Ośródka, L.; Krajny, E.; Błaszczak, B.; Mathews, B. *Air Qual., Atmos. Health* **2014**, *7*, 41−58.

(31) Fabiańska, M. J.; Ćmiel, S. R.; Misz-Kennan, M. *Int. J. Coal Geol.* **2013**, *107*, 96−111.

(32) PN-Z-04030-7:1994 Air purity protection. Research dust content - The measurement of concentration and mass flow of dust in flue gases by gravimetric method [In Polish].

(33) The Minister of Environment of 30 October 2014. On the requirements for the measurements of the emission and measurement of the amount of abstracted water. Dz.U. 2014, poz. 1542 [In Polish].

(34) Philp, R. P. Fossil fuel biomarkers. *Application and spectra*; Elsevier: Amsterdam, 1985.

(35) Wiley/NBS Registry of Mass Spectral Data, 2000.

(36) Fabiannska, M.; Bzowska, G.; Matuszewska, A.; Racka, M.; Skręt, U. *Chem. Erde* **2003**, *63* (1), 63−91.

(37) Chagger, H. K.; Jones, J. M.; Pourkashanian, M.; Williams, A. *Process Saf. Environ. Prot.* **2000**, *78* (1), 53−59.

(38) Revuelta, C. C.; De la Fuente Santiago, E.; Vázquez, J. R. *Environ. Technol.* **1999**, *20* (1), 61−68.

(39) Ruwei, W.; Jiamei, Z.; Jingjing, L.; Liu, G. *Arch. Environ. Contam. Toxicol.* **2013**, *65* (2), 193−202.

(40) Li, H.; Liu, G.; Cao, Y. *Aerosol Air Qual. Res.* **2014**, *14* (4), 1179−1188.

(41) Kong, S.; Shi, J.; Lu, B.; Qiu, W.; Zhang, B.; Peng, Y.; Zhang, B.; Bai, Z. *Atmos. Environ.* **2011**, *45* (23), 3777−3785.

(42) Ravindra, K.; Sokhi, R.; Van Grieken, R. *Atmos. Environ.* **2008**, *42* (13), 2895−921.

(43) Gogou, A.; Stratigakis, N.; Kanakidou, M.; Stephanou, E. G. *Org. Geochem.* **1996**, *25* (1−2), 79−96.

(44) Ravindra, K.; Bencs, L.; Wauters, E.; De Hoog, J.; Deutsch, F.; Roekens, E.; Bleux, N.; Berghmans, P.; Van Grieken, R. *Atmos. Environ.* **2006**, *40* (4), 771−785.

(45) Mantis, J.; Chaloulakou, A.; Samara, C. *Chemosphere* **2005**, *59* (5), 593−604.

(46) Galarneau, E. *Atmos. Environ.* **2008**, *42* (35), 8139−8149.

(47) Tang, N.; Hattori, T.; Taga, R.; Igarashi, K.; Yang, X.; Tamura, K.; Kakimoto, H.; Mishukov, V. F.; Toriba, A.; Kizu, R.; Hayakawa, K. *Atmos. Environ.* **2005**, *39* (32), 5817−5826.

(48) Akyüz, M.; Çabuk, H. *Sci. Total Environ.* **2010**, *408* (22), 5550−5558.

(49) Kong, S.; Ding, X.; Bai, Z.; Han, B.; Chen, L.; Shi, J.; Li, Z. *J. Hazard. Mater.* **2010**, *183* (1−3), 70−80.

(50) Yunker, M. B.; Macdonald, R. W.; Vingarzan, R.; Mitchell, R. H.; Goyette, D.; Sylvestre, S. *Org. Geochem.* **2002**, *33* (40), 489−515.

(51) De La Torre-Roche, R. J.; Lee, W.-Y.; Campos-Díaz, S. I. *J. Hazard. Mater.* **2009**, *163* (2−3), 946−958.

(52) Saarnio, K.; Sillanpää, M.; Hillamo, R.; Sandell, E.; Pennanen, A. S.; Salonen, R. O. *Atmos. Environ.* **2008**, *42* (40), 9087−9097.

(53) Lee, W.-J.; Wang, Y.-F.; Lin, T.-C.; Chen, Y.-Y.; Lin, W.-C.; Ku, C.-C.; Cheng, J.-T. *Sci. Total Environ.* **1995**, *159* (2−3), 185−200.

(54) Masclet, P.; Mouvier, G.; Nikolaou, K. *Atmos. Environ.* **1986**, *20* (3), 439−446.

(55) Dickhut, R. M.; Canuel, E. A.; Gustafson, K. E.; Liu, K.; Arzayus, K. M.; Walker, S. E.; Edgecombe, G.; Gaylor, M. O.; MacDonad, E. H. *Environ. Sci. Technol.* **2000**, *34* (21), 4635−4640.

(56) Nisbet, I. C. T.; LaGoy, P. K. *Regul. Toxicol. Pharmacol.* **1992**, *16* (3), 290−300.

(57) Bourotte, C.; Forti, M.-C.; Taniguchi, S.; Bícego, M. C.; Lotufo, P. A. *Atmos. Environ.* **2005**, *39* (21), 3799−3811.

(58) Hong, H.; Yin, H.; Wang, X.; Ye, C. *Atmos. Res.* **2007**, *85* (3−4), 429−441.

(59) del Rosario Sienra, M.; Rosazza, N. G.; Préndez, M. *Atmos. Res.* **2005**, *75* (4), 267−281.

(60) Külaots, I.; Hurt, R. H.; Suuberg, E. M. *Fuel* **2004**, *83* (2), 223−230.

(61) Bray, E. E.; Evans, E. D. *Geochim. Cosmochim. Acta* **1961**, *22* (1), 2−15.

(62) Kotarba, M. J.; Clayton, J. L. *Int. J. Coal Geol.* **2003**, *55* (2−4), 73−94.

(63) Peters, K. E.; Walters, C. C.; Moldowan, J. M. *The Biomarker Guide. Biomarkers and isotopes in petroleum exploration and earth history*; Cambridge University Press: United Kingdom, 2005.

(64) Tissot, B. P.; Welte, D. H. *Petroleum Formation and Occurrence*, 2nd ed.; Springer-Verlag Telos: Berlin, 1984.

(65) Pancost, R. D.; Baas, M.; Van Geel, B.; Sinninghe Damsté, J. S. *Org. Geochem.* **2002**, *33* (7), 675−690.

(66) Didyk, B. M.; Simoneit, B. R T.; Brassell, S. C.; Eglington, G. *Nature* **1978**, *272* (5650), 216−222.

(67) Leythaeuser, D.; Schwartzkopf, Th. *Org. Geochem.* **1986**, *10* (1−3), 191−197.

(68) Seifert, W. K.; Moldowan, J. M. *Biological markers in the sedimentary record*; Elsevier Science & Technology: Oxford, United Kingdom, 1986; pp 261−290.

(69) Ourisson, G.; Albrecht, P.; Rohmer, M. *Pure Appl. Chem.* **1979**, *51*, 709−729.

(70) Volkman, J. K. *Geol. Soc. Spec. Publ.* **1988**, *40*, 103−122.

(71) Palmer, S. E. Effect of biodegradation and water washing on crude oil composition. Organic Geochemistry. *Top. Geobiol.* **1993**, *11*, 511−534.

(72) Shanmugam, G. *Am. Assoc. Pet. Geol. Bull.* **1985**, *69* (8), 1241−1254.

(73) Fabiańska, M.; Matuszewska, A. *Pol. J. Appl. Chem.* **1998**, *3* (4), 259−274.

(74) Wu, L.; Geng, A. *Org. Geochem.* **2016**, *101*, 38−48.

(75) Huang, W.-Y.; Meinschein, W. G. *Geochim. Cosmochim. Acta* **1978**, *42* (9), 1391−1396.

(76) Grantham, P. J. *Org. Geochem.* **1986**, *9* (1), 1−10.

(77) Dagnag, T.; Jeannot, R. *Chromatographic Analysis of the Environment*; Taylor & Francis Group: New York, 2005; pp 1027−1102.

(78) Simoneit, B. R. T.; Schauer, J. J.; Nolte, C. G.; Oros, D. R.; Elias, V. O.; Fraser, M.; Rogge, W. F.; Cass, G. R. *Atmos. Environ.* **1999**, *33* (2), 173−182.

(79) Radke, M. In *Advances in Petroleum Geochemistry*; Welte, D., Ed.; Academic Press: New York, 1987; pp 141−202.

(80) Kruge, M. A. *Int. J. Coal Geol.* **2000**, *43* (1−4), 27−51.

(81) Radke, M.; Vriend, S. P.; Ramanampisoa, L. R. *Geochim. Cosmochim. Acta* **2000**, *64* (2), 275−286.

(82) Hatcher, P. G.; Faulon, J.-L.; Wenzel, K. A.; Cody, G. D. *Energy Fuels* **1992**, *6* (6), 813−820.

(83) Hatcher, P. G.; Clifford, D. J. *Org. Geochem.* **1997**, *27* (5−6), 251−274.