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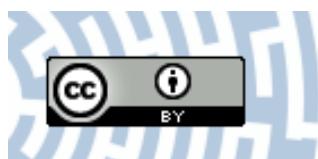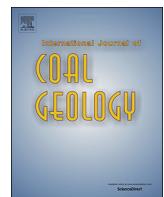
Application of organic environmental markers in the assessment of recent and fossil organic matter input in coal wastes and river sediments: A case study from the Upper Silesia Coal Basin (Poland)

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ABSTRACT

Various types of coal waste material (fresh, self-heated, soil-covered) and river sediments polluted by coal dust were studied. Characteristic geochemical features of recent vegetation input in river sediments were identified, e.g. the dominance of *n*-alkanols and *n*-alkanoic acids over *n*-alkanes. In the river sediments, several coal-related compounds were also found, e.g. *n*-alkylbenzenes, acetophenone and methylated phenols. The occurrence of sterols, stanols, vanillin, and methylbenzoic, benzeneacetic, oxalic, succinic and levulinic acids in coal waste samples (with the exception of fresh coal wastes) may indicate primitive soil-forming processes related to vegetation and moss cover. These compounds were also commonly identified in river sediments. Their distribution, characteristic of extant (as opposed to fossil) organic matter, was confirmed by several applied geochemical ratios, such as the EOP index (even-over-odd predominance) of fatty acids, (Σn-*alkanoic acid* + Σ*long chain n-alkanes*)/Σ*short chain n-alkanes* or (Σn-*alkanoic acids* + Σn-*alkanols*)/Σn-*alkanes* and various CPI (carbon preference indexes of *n*-alkanes).

1. Introduction

In Upper Silesia, coal mining has had a significant impact on the original landscape, marring it with hundreds of coal waste dumps. The enormous volume of coal wastes has led to widespread pollution in the environment. Generally, in the Upper Silesian Coal Basin, types of coal range from sub-bituminous to high-volatile bituminous; sapropelic coals occur only rarely (Kotarba et al., 2002). For the presented study, river sediments (polluted by coal dust and coal ash) and coal waste samples were collected. Biomarkers preserved in both sample types appear to be useful indicators for identification of an organic-matter (OM) origin (Nádudvari and Fabiańska, 2015; Nádudvari et al., 2018). For example, *n*-fatty acids can serve as useful indicators of OM origin because they are precursors of aliphatic hydrocarbons, which represent some of the main components of petroleum and coal bitumen, which in turn forms via decarboxylation and reduction reactions (Cooper and Bray, 1963; Kawamura and Ishiwatari, 1985; Dong et al., 1993). In addition, *n*-fatty acids, which are present in recent plant tissues, may be important components of OM involving all types of kerogen. Typical features of cutin and suberin in higher vascular plants include elevated concentrations of long-chain *n*-alkanoic acids (n-C_{22} to n-C_{32}) and *n*-

alkanols, with a notable predominance of even chain homologues and the occurrence of certain hydroxy, dicarboxylic, and diterpenoid acids, as well as long-chain (n-C_{40} to n-C_{64}) saturated alkyl (wax) esters (Gillan and Sandstrom, 1985; Mita et al., 1998; Cooper, 1990).

In conjunction with this study, it is important to mention that the spontaneous soil-forming processes which are generally possible on coal waste dumps under the influence of vegetation and other paedo-genetic factors (Wiegleb and Felinks, 2001; Frouz et al., 2008; Alday et al., 2012; Zhang et al., 2015) can be accelerated by adding various waste products, e.g. composts, lignohumate, organic waste, or salvaged materials. Such improvements are important in the successful re-cultivation of coal wastes (Sydnor and Redente, 2002; Mercuri et al., 2005). Fresh coal waste contains no extant organic material, but is rich in fossil OM. Over time, fossil OM, along with inorganic matter, may undergo so-called 'secondary' processes such as weathering, self-heating, water washing, chelatisation and complexation of soil mineral compounds, and migration and translocation of organo-mineral compounds (e.g. Nádudvari et al., 2018). Thus, soil formation is determined by the quality of the OM and soil biota (Kononova, 1966; Emmer and Sevnik, 1994; Bradshaw, 1997; Abakumov, 2008). In soil formation, humic acids, e.g. di- and tri-hydroxyalkanoic acids, α-, β- and ω-

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hydroxy fatty acids, and alkanoic, α- and β-alkanedioic, and phenolic acids, along with *n*-alkanols and sterols, play a key role (Fiorentino et al., 2006). Humic acids, insoluble in water, do not migrate intensively in the soil profile; hence they are the most important components for the formation of soil aggregates through the process of organo-mineral stabilisation. Furthermore, they can act as useful indicators of soil development processes (Kögel-Knabner et al., 2008).

General formation of soil crust can be observed one or two years after initial coal waste dumping. Under favourable conditions e.g., if the wastes contain carboniferous clays and are rich in fossil OM, colonisation by a large number of various algae, cyanobacterial groups, and mosses would be favoured. Later, these types of dumps can be more easily covered by vascular plants (Lukešová et al., 2014). These type of soil-forming processes occurred at the Wełnowiec dump despite self-heating.

The aim of the research was to learn how vegetation, water washing, or self-heating affects characteristic features of geochemical markers occurring in coal wastes, thus helping to distinguish coal-related compounds in river sediments. The distribution of such vegetation markers as *n*-alkanes, *n*-alkanoic acids, *n*-alkanols, and sterols can constitute a clear sign of the presence of extant plants. Their occurrence can indicate initial soil-forming processes taking place on coal waste dumps, using river sediments as reference material. Furthermore, one part of a secondary process in coal wastes, called self-heating, can influence the distribution of studied compounds, e.g. polar compounds (phenols), aliphatic (*n*-alkanes) and aromatic (*n*-alkylbenzenes) hydrocarbons. The article is a continuation of previous researches, see Nádudvari and Fabiańska (2015); Nádudvari and Fabiańska (2016a), covering a range of the new compounds to find their applicability in geochemical investigations. According to our knowledge polar compounds were not applied in the research of coal wastes subjected to self-heating or river sediments containing coal dust.

2. Samples and methods

The river sediments were given names according to the form AN_Mxx and they were studied with details in Nádudvari and Fabiańska (2015) and Nádudvari et al. (2018). Two of them are borehole samples: DR2_1, taken from a depth of approximately 1 m from a river bed containing gravelly sediment, and DR2_2, taken from the bank of the river at a depth of 1.7 m in typically gravelly sediment (Fig. 1). SZ_F_12 and SZ_F_13 are fresh coal wastes, dumped several weeks prior to sampling, taken from the Szczygłowice dump (Fig. 1; see the earlier publication by Nádudvari and Fabiańska, 2016a). Additional samples include self-heated coal wastes AN8 and AN9 (taken from the Anna dump), WE2 and WE5 (taken from the Wełnowiec dump), CZ7 (taken from the Czerwionka-Leszczyny dump) (see Nádudvari and Fabiańska, 2016a, 2016b), and RC7, consisting of expelled pyrolytic bitumen from the Rymer dump coal wastes. Details are given in Nádudvari and Fabiańska (2016b).

2.1. Extraction and derivatisation

Powdered samples (ca 18–20 g) were extracted using dichloromethane with an accelerated Dionex ASE 350 solvent extractor. The extracts of the samples were converted to trimethylsilyl (TMS) derivatives via a reaction with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), 1% trimethylchlorosilane, and pyridine for three hours at 70 °C. The excess reagent was then removed under blowdown with dry nitrogen and the sample mixture was dissolved in an equivalent volume of dehydrated *n*-hexane.

2.2. Gas chromatography-mass spectrometry

Gas chromatography-mass spectrometry (GC–MS) analyses were carried out using an Agilent Technologies 7890A gas chromatograph and an Agilent 5975C Network mass spectrometer with a Triple-Axis detector (MSD) at the Faculty of Earth Sciences, Sosnowiec, Poland. Helium (grade 6.0) was used as a carrier gas at a constant flow of 2.6 ml/min. Separation was obtained on fused silica capillary column, DB-5 (60 m × 0.25 mm i.d.; film thickness 0.25 μm) coated with a chemically bonded phase (5% phenyl, 95% methylsiloxane), for which the GC oven temperature was programmed from 45 (1 min) to 100 °C at 20 °C/min, then to 300 °C (held for 60 min) at 3 °C/min, with a solvent delay of 10 min. The GC column outlet was connected directly to the ion source of the MSD. The GC–MS interface was set at 280 °C, while the ion source and the quadrupole analyser were set at 230 and 150 °C, respectively. Mass spectra were recorded from 45 to 550 da (0–40 min), and 50 to 700 da (> 40 min). The MS was operated in the electron impact mode, with an ionisation energy of 70 eV. For quality control, these samples were compared with the originals using PAH diagnostic ratios such as phenanthrene/anthracene; fluoranthene/pyrene; benz[*a*]anthracene/(benz[*a*]anthracene + chrysene); benzo[*a*]pyrene/benzo[*ghi*]perylene; and indeno[1,2,3-*cd*]pyrene/(indeno[1,2,3-*cd*]pyrene + benzo[*ghi*]perylene). The calculated error varied, but was consistently under 2% (Nádudvari et al., 2018).

3. Results and discussion

In the studied area, the predominant sources of OM are coal and coal wastes, accompanied, in the case of river sediments, by recent vegetation and urban wastes. In the following section, the particular sources are discussed, along with an indication of the main organic compounds generated by individual sources.

3.1. Aliphatic hydrocarbons

Elevated relative percentages of *n*-alkanes (ranging from C_{11} to C_{34}) were found in the coal waste samples and in AN_M9 compared with other sediments. Typically, short-chain *n*-alkanes dominated over long-chain *n*-alkanes in coal wastes (both fresh and self-heated coal wastes, except for the Wełnowiec samples) (Tables 1 and 2). The reason for the dominance of short-chain over long-chain *n*-alkanes differs between fresh (0.29–0.51) and self-heated (0.02–0.19 for AN8, AN9, CZ7, RC7 and 0.94–6.80 for WE2, WE5) coal wastes (Table 3). It is a common feature for short-chain *n*-alkanes to dominate in unaltered coal wastes where water-washing and biodegradation have not influenced the organic material (Fabiańska and Kurkiewicz, 2013; Nádudvari and Fabiańska, 2016a). However, in the case of self-heated coal wastes, the distribution reflects macromolecule cracking and the expulsion of short-chain *n*-alkanes (*n*-C_{11} to *n*-C_{18}), a process which can be seen in the AN8, AN9, CZ7, and RC7 samples (Table 3). The distribution maximum depends on the range of heating temperatures (Misz-Kennan et al., 2007; Nádudvari and Fabiańska, 2016a, 2016b). The origin of short-chain *n*-alkanes (e.g. *n*-C_{17} to *n*-C_{18}) in fossil OM is associated with microorganisms, including phytoplankton settled in terrestrial organic material deposited in deltaic environments (Gelpi et al., 1970; Grimalt and Albaigés, 1987; Meyers, 1997; Fabiańska et al., 2003, 2008). However, long-chain *n*-alkanes with carbon numbers from *n*-C_{25} to *n*-C_{35} and odd carbon preponderance are related to higher terrestrial plants (Eglinton and Hamilton, 1967). Carbon Preference Index values e.g. CPI(*n*-C_{24}-C_{34}), or CPI(*n*-C_{25}-C_{31}) can distinguish coal wastes.

CPI(*n*-C_{24}-C_{34}) = 1.02–1.49; CPI(*n*-C_{25}-C_{31}) = 0.94–1.60) from almost all river sediments CPI(*n*-C_{24}-C_{34}) = 2.72–9.26; CPI(*n*-C_{25}-C_{31}) = 2.46–8.89; see Table 3). In river sediments, long-chain *n*-alkanes dominated, with a predominance of odd-over-even in the range *n*-C_{25} to *n*-C_{31}, showing a bimodal distribution. Commonly *n*-C_{27} and *n*-C_{29}*n*-alkanes occurred with abundant relative percentages in relation to others, with the exception of only one sample (AN_M62), in which *n*-C_{31} was dominant (Tables 1 and 2). Typically, *n*-alkanes from higher terrestrial plants (trees, roots, shrubs, epicuticular waxes in plant leaves) are characterised by a strong odd-over-even carbon preference,
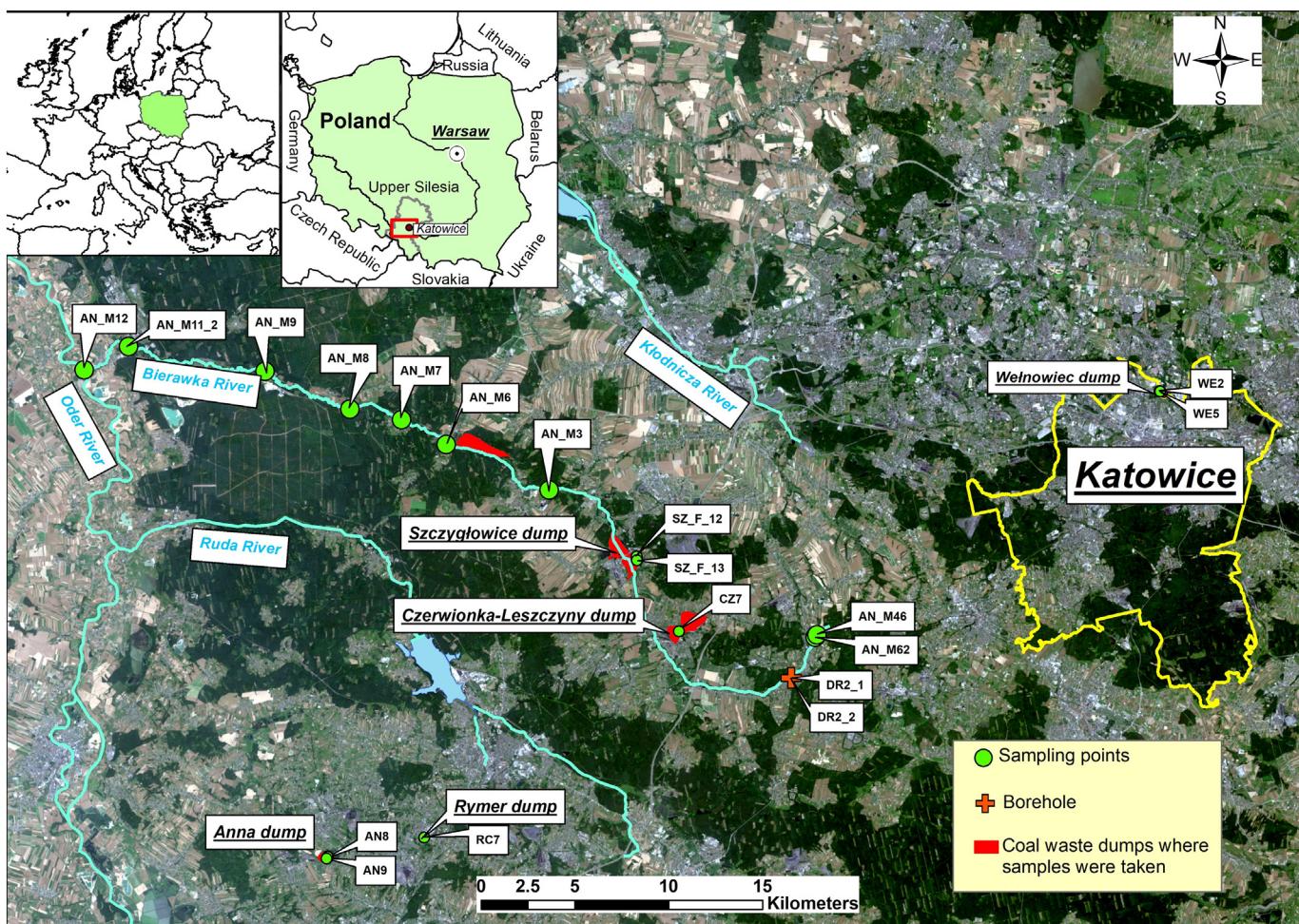
Fig. 1. Sampling points in the coal waste dumps and along the Bierawka River (background map: Sentinel-2, 2016; source: https://earthexplorer.usgs.gov/).

especially n-C_{27} and n-C_{29} alkanes, while n-alkanes from grasses and mosses are characterised by a maximum at n-C_{31} (Eglinton and Hamilton, 1967; Rieley et al., 1991; Ficken et al., 2000; Pancost et al., 2002; Bi et al., 2005; Bingham et al., 2010). Fig. 2A and B distinctly separate coal wastes, river sediments mixed with coal particles with long-chain n-alkane input from recent vegetation, and samples where n-alkanes related to terrestrial plants were dominant.

3.2. Polar compounds

Polar compounds were identified in both sample groups, i.e. in river sediments and coal wastes. The main groups of compounds are: sterols, stanols, phenols, n-alkanoic- and benzenedicarboxylic acid, 4-hydroxybenzaldehyde, acetophenones, and benzoic and methylbenzoic acids. However, the distributions of the listed compounds varied according to the type of samples studied.

3.2.1. n-Alkanoic acids

A common feature of river sediments in comparison with coal wastes was the appearance of n-alkanoic acids (ranging from n-C_6 to n-C_{32}) with elevated relative abundances (Tables 1 and 2, Fig. 3). The applied EOP index (even-over-odd predominance) points to the dominance of even long-chain n-alkanoic acids (n-C_{20} to n-C_{26}) in river sediments (Table 3). Typically, high concentrations and notable predominance of even long-chain (n-C_{22} to n-C_{32}) compounds are characteristic of higher-vascular-plant cutin and suberin (Mita et al., 1998). Notably, n-hexadecanoic (palmitic), n-octadecanoic (stearic), and oleic acids were dominant in several river sediment samples, e.g.

DR2_1 and AN_M11_2 (see Table 1). These compounds can be generated by both bacteria and higher plants (Hedges et al., 1997; Summons et al., 2013; Walley et al., 2013; Huang et al., 2016). Application of n-alkanoic acids for different geochemical ratios calculated from the total ion chromatograms, such as (Σn-alkanoic acids + Σlong chain n-alkanes)/ Σshort chain n-alkanes, for river sediments 2.21–300.98, for coal wastes 0.18–11.25; or (Σn-alkanoic acids + Σn-alkanols)/Σn-alkanes, for river sediments 0.34–23.66, for coal wastes 0.01–0.58, closely reflected the vegetation/soil input to the sediments and Wełnowiec samples (Table 3). The previously mentioned ratio values of the AN_M9 sample differ from those of the other sediments (Table 3; Fig. 2C) because this sample is characterised by an elevated level of inertinite (the sample contained many coal particles), as described in Nádudvari and Fabiańska (2015; sample no. m29(2)). The ternary diagram (Fig. 4) shows clear separation of the coal samples from the extant organic material deposited in the river; as in the case of recent OM, n-alkanoic acids were dominant over n-alkanes. The exceptions are the WE2 and WE5 samples, where additional n-alkanoic acids derive from recent vegetation related to initial soil formation on the coal waste dump.

3.2.2. Other acids/aromatic acids

Polar compounds that typically occurred in river sediments included glycerol, α-tocopherol, tyrosol, and the following acids: pimaric, isopimaric, β-hydroxybutyric, and palmitoleic (Table 1). Glycerol, palmitoleic acid, and α-tocopherol are commonly present in higher plants, e.g. in leaves or roots (Gerber et al., 1988; Xing and Chin, 2000; Fernández-Marín et al., 2014). Among drilled samples, DR2_2 showed slight differences in comparison to other river sediments, since this

Table 1

Calculated relative percentages of identified compounds (TMS: trimethylsilyl derivatives) based on the integrated peak areas of the corresponding ion chromatograms.

Identified compounds	m/z	River sediments		River sediments borehole samples		River sediments							Fresh coal wastes		Self-heated coal wastes					
		AN_M46	AN_M62	DR2_1	DR2_2	AN_M3	AN_M6	AN_M7	AN_M8	AN_M9	AN_M11_2	AN_M12	SZ_F_12	SZ_F_13	AN8	AN9	WE2	WE5	CZ7	RC7
n-Undecane	71	-	-	-	-	-	-	-	-	-	-	-	0.37	0.02	-	-	-	-	-	-
n-Dodecane	71	-	-	-	-	-	-	-	-	-	-	-	1.22	0.16	-	-	-	-	-	-
n-Tridecane	71	-	-	-	-	-	-	0.02	-	0.04	-	-	2.72	1.01	0.35	0.69	-	-	-	-
n-Tetradecane	71	-	0.02	-	-	0.02	-	0.13	0.03	0.38	0.05	0.02	4.22	2.78	1.61	2.11	-	-	0.06	10.47
n-Pentadecane	71	-	0.06	-	-	0.10	-	0.31	0.06	1.33	0.16	0.18	5.04	6.01	3.36	3.95	-	-	0.30	11.58
n-Hexadecane	71	-	0.13	-	-	-	0.04	0.50	0.16	2.14	0.28	0.38	5.62	11.42	5.03	5.10	-	-	0.91	18.50
n-Heptadecane	71	0.15	0.24	-	-	0.36	0.05	0.82	0.38	3.21	0.44	0.66	6.29	7.03	6.87	5.16	0.14	0.70	2.82	3.99
Pristane	71	0.06	0.22	-	-	0.80	0.09	1.91	0.34	10.13	1.07	1.29	5.92	13.39	4.26	2.34	0.13	1.01	8.25	5.39
n-Octadecane	71	0.06	0.12	-	-	0.51	0.19	0.99	0.14	4.05	0.51	0.77	6.79	1.35	8.05	4.63	0.23	1.88	7.27	1.16
Phytane	71	0.07	0.31	-	-	0.23	0.09	0.43	0.46	1.39	0.26	0.33	1.16	9.14	0.88	0.36	0.05	4.00	3.29	0.88
n-Nonadecane	71	0.09	0.37	-	0.11	0.60	0.51	1.03	0.47	3.76	0.54	0.79	6.34	5.33	7.86	4.25	0.47	6.66	15.91	0.15
n-Eicosane	71	0.10	0.44	0.08	0.12	0.57	0.70	0.99	0.45	3.90	0.57	0.76	5.89	3.55	5.81	3.47	0.98	9.31	16.36	-
n-Heneicosane	71	0.22	0.37	0.07	1.94	0.73	0.95	1.24	0.38	5.09	0.78	1.05	5.77	2.98	3.97	2.25	2.47	11.32	13.31	-
n-Docosane	71	0.15	0.50	0.11	0.42	0.70	0.92	1.09	0.49	4.51	0.74	0.90	5.05	2.87	2.34	1.12	3.66	11.99	9.07	-
n-Tricosane	71	0.51	0.44	0.09	2.55	0.88	1.35	1.45	0.47	4.80	0.83	1.31	4.80	2.83	1.40	0.77	5.60	9.87	6.58	-
n-Tetracosane	71	0.24	0.88	0.16	0.50	0.80	1.15	1.21	0.92	4.84	0.68	0.93	4.51	2.56	0.90	0.59	7.18	4.32	4.32	-
n-Pentacosane	71	1.63	0.54	0.15	1.67	1.70	2.19	2.57	0.57	5.41	1.18	2.32	4.05	2.33	0.76	0.53	8.50	4.12	0.99	-
n-Hexacosane	71	0.42	1.57	0.24	0.47	1.03	1.26	1.14	1.85	4.92	0.70	0.99	3.49	2.12	0.69	0.47	8.46	2.65	0.73	-
n-Heptacosane	71	2.83	0.63	0.13	5.13	2.82	4.53	4.62	0.66	5.53	1.88	4.92	3.18	1.58	0.69	0.53	8.63	1.11	0.29	-
n-Octacosane	71	0.48	4.41	0.53	0.44	1.01	1.25	1.10	2.49	3.89	0.63	0.98	2.45	1.38	0.42	0.37	6.81	0.92	0.35	-
n-Nonacosane	71	3.71	0.52	0.12	3.70	3.00	5.50	4.69	0.44	4.60	1.88	4.87	1.99	0.92	0.38	0.35	5.40	0.42	0.08	-
n-Tricontane	71	0.52	6.94	0.28	0.35	0.77	0.89	0.71	2.43	2.14	0.43	0.64	1.27	0.65	0.22	0.20	3.19	0.37	-	-
n-Hentriacontane	71	2.68	0.51	-	3.17	2.28	4.36	2.28	0.36	1.94	1.15	2.76	1.03	0.44	0.18	0.16	2.15	0.20	-	-
n-Dotriacontane	71	0.33	2.70	-	-	0.53	0.42	0.35	0.86	0.98	0.24	0.50	0.67	0.35	0.11	0.10	1.02	-	-	-
n-Tritriacontane	71	1.07	-	-	-	0.72	1.32	0.62	-	0.91	0.36	0.91	0.49	0.31	0.09	0.09	0.61	-	-	-
n-Tetratriacontane	71	-	-	-	-	-	-	-	-	0.55	-	-	0.38	-	0.08	0.08	0.36	-	-	-
n-Hexanoic acid TMS	117	0.01	0.01	0.02	0.01	0.01	-	-	0.01	0.02	-	0.01	0.04	0.01	0.02	0.01	-	0.01	0.01	-
n-Heptanoic acid TMS	117	0.03	0.01	0.03	0.01	0.01	0.02	0.02	0.01	0.02	0.01	0.01	-	0.01	0.05	0.02	0.01	0.01	0.01	-
n-Octanoic acid TMS	117	0.07	0.02	0.04	0.02	0.04	0.02	0.04	0.02	0.06	0.26	0.05	-	0.02	0.08	-	0.05	0.07	0.01	-
n-Nonanoic acid TMS	117	0.08	0.06	0.07	0.04	0.05	0.07	0.11	0.06	0.13	0.09	0.06	-	-	-	-	0.10	0.18	0.04	-
n-Decanoic acid TMS	117	0.04	0.03	0.05	0.03	0.07	0.05	0.18	0.07	0.11	0.58	0.08	-	-	-	-	0.12	0.24	-	-
n-Undecanoic acid TMS	117	0.23	0.04	0.02	0.01	0.02	0.03	0.16	0.05	0.11	0.03	0.04	-	-	-	-	0.15	0.27	-	-
n-Dodecanoic acid TMS	117	0.08	0.06	0.39	0.09	0.13	0.14	0.09	0.15	0.25	5.93	0.23	-	-	0.10	-	0.20	0.38	-	-
n-Tridecanoic acid TMS	117	0.72	0.03	0.05	0.03	0.06	0.07	0.33	0.08	0.19	0.05	0.09	-	-	0.10	-	0.22	0.30	-	-
n-Tetradecanoic acid TMS	117	0.31	0.12	1.71	0.22	0.38	0.56	0.18	0.41	0.48	4.67	0.63	-	-	0.10	0.07	0.45	0.49	0.08	-
n-Pentadecanoic acid TMS	117	4.34	0.08	0.35	0.08	0.18	0.32	1.21	0.29	0.41	0.37	0.28	-	-	0.09	0.11	0.46	0.36	0.36	-
n-Hexadecanoic acid TMS	117	0.21	0.69	26.00	1.22	2.83	4.09	0.51	2.24	2.43	21.81	4.76	0.59	0.40	0.35	0.31	3.96	1.51	0.53	0.45
n-Heptadecanoic acid TMS	117	1.36	0.07	0.40	0.07	0.17	0.19	7.97	0.21	0.50	0.72	0.30	-	-	0.04	0.94	1.11	0.36	0.28	-
Oleic acid TMS	117	1.58	-	3.71	0.08	0.97	0.82	0.50	0.16	0.91	16.18	1.33	-	-	-	-	-	-	-	-
n-Octadecanoic acid TMS	117	0.11	0.31	23.03	2.56	2.22	2.00	4.66	0.94	2.39	14.32	3.33	-	-	0.04	0.51	2.74	0.77	-	0.08
n-Nonadecanoic acid TMS	117	0.79	0.05	0.13	0.25	0.12	0.13	0.28	0.15	0.38	0.14	0.18	-	-	0.04	0.49	0.88	0.26	-	0.16
n-Eicosanoic acid TMS	117	0.30	0.18	1.66	0.60	0.78	0.91	1.92	1.07	0.69	0.40	1.29	-	-	0.02	0.11	1.31	0.33	-	-
n-Heneicosanoic acid TMS	117	3.27	0.11	0.15	0.18	0.27	0.32	0.56	0.52	0.35	0.14	0.43	-	-	-	0.08	0.87	0.20	-	-
n-Docosanoic acid TMS	117	1.04	0.55	1.44	3.72	2.05	2.50	4.03	4.03	0.78	0.73	3.31	-	-	-	0.02	2.02	0.34	0.05	-
n-Tricosanoic acid TMS	117	6.08	0.25	0.35	0.51	0.88	1.15	1.15	2.15	0.41	0.29	1.20	-	-	-	0.05	1.11	0.19	0.03	-
n-Tetracosanoic acid TMS	117	0.78	1.26	1.39	5.40	4.34	4.26	4.03	7.19	0.81	1.01	4.80	-	-	-	0.04	1.67	0.28	0.08	-
n-Pentacosanoic acid TMS	117	3.73	0.38	0.23	0.58	0.92	0.91	0.72	1.62	0.36	0.17	0.76	-	-	-	-	0.30	0.14	0.03	-
n-Hexacosanoic acid TMS	117	0.53	2.19	0.53	2.73	4.16	4.27	0.33	7.11	0.65	0.58	3.28	-	-	-	-	0.51	0.20	0.07	-
n-Heptacosanoic acid TMS	117	0.64	0.31	-	0.65	0.78	0.65	0.47	1.35	0.28	0.12	0.57	-	-	-	-	0.11	0.10	-	-
n-Octacosanoic acid TMS	117	3.58	1.92	0.36	3.84	4.26	3.03	1.92	6.93	0.55	0.41	2.67	-	-	-	-	0.35	0.16	0.05	-
n-Nonacosanoic acid TMS	117	0.37	0.37	0.03	0.58	0.52	0.31	-	1.18	0.18	-	-	-	-	-	-	-	-	-	-

Table 1 (*continued*)

Identified compounds	m/z	River sediments		River sediments borehole samples		River sediments							Fresh coal wastes		Self-heated coal wastes					
		AN_M46	AN_M62	DR2_1	DR2_2	AN_M3	AN_M6	AN_M7	AN_M8	AN_M9	AN_M11_2	AN_M12	SZ_F_12	SZ_F_13	AN8	AN9	WE2	WE5	CZ7	RC7
n-Triacontanoic acid TMS	117	1.70	1.71	0.19	2.97	2.34	1.58	0.80	4.95	0.35	0.17	1.23	-	-	-	-	0.23	-	-	-
n-Hentriacontanoic acid TMS	117	0.17	0.17	0.08	0.16	0.28	0.10	0.10	0.54	-	-	0.16	-	-	-	-	-	-	-	-
n-Dotriacontanoic acid TMS	117	0.42	0.93	0.06	1.34	0.70	0.35	0.14	2.01	-	-	0.32	-	-	-	-	-	-	-	-
n-Dodecanol TMS	75	0.11	0.04	0.07	0.06	0.09	0.04	0.16	0.06	-	0.08	0.13	-	-	-	-	-	-	0.14	-
n-Tetradecanol TMS	75	0.14	-	0.08	0.05	0.12	-	0.15	0.04	-	0.03	0.16	-	-	-	-	-	-	0.06	-
n-Pentadecanol TMS	75	0.05	-	0.03	-	0.04	-	0.10	0.06	-	0.04	-	-	-	-	-	-	-	-	-
n-Hexadecanol TMS	75	0.30	0.04	0.27	0.08	0.37	0.21	0.54	0.15	0.16	0.13	0.45	-	-	-	-	-	0.07	0.10	-
n-Octadecanol TMS	75	0.24	0.06	0.42	0.13	0.49	0.26	0.56	0.14	-	0.17	0.60	-	-	-	-	-	-	-	-
n-Eicosanol TMS	75	0.31	0.17	0.13	0.57	0.25	0.30	0.32	0.18	-	0.10	0.39	-	-	-	-	-	-	-	-
n-Docosanol TMS	75	3.36	1.40	0.28	8.94	2.14	2.55	1.49	1.37	0.24	0.55	2.07	-	-	-	-	-	-	-	-
n-Tricosanol TMS	75	0.40	0.19	0.05	0.38	0.18	0.36	0.15	0.19	0.16	0.05	0.16	-	-	-	-	-	-	-	-
n-Tetracosanol TMS	75	4.82	2.56	0.24	11.27	4.79	4.76	1.77	2.07	-	0.55	2.21	-	-	-	-	-	-	-	-
n-Pentacosanol TMS	75	0.45	0.64	0.03	0.75	0.59	0.57	0.18	0.39	-	0.10	0.25	-	-	-	-	-	-	-	-
n-Hexacosanol TMS	75	11.96	35.72	0.40	5.76	7.74	12.40	2.43	17.60	0.31	1.37	5.00	-	-	-	-	-	-	-	-
n-Heptacosanol TMS	75	0.44	0.67	0.02	0.65	0.50	0.63	0.25	0.43	-	0.12	0.34	-	-	-	-	-	-	-	-
n-Octacosanol TMS	75	6.41	10.47	-	5.87	5.09	5.21	1.94	4.62	-	1.13	3.39	0.22	0.11	-	-	0.20	0.18	0.11	-
n-Nonacosanol TMS	75	0.43	0.93	-	0.43	0.21	0.55	0.18	0.40	-	0.16	0.26	-	-	-	-	-	-	-	-
n-Triacontanol TMS	75	2.65	8.81	-	2.33	3.17	3.34	1.02	2.47	-	0.67	1.93	-	-	-	-	-	0.13	-	-
n-Hentriacontanol TMS	75	0.12	0.42	-	0.14	0.14	0.17	0.08	0.31	-	0.04	0.10	-	-	-	-	-	-	-	-
n-Dotriacontanol TMS	75	0.74	1.76	-	-	0.90	0.87	0.31	0.89	-	0.15	0.49	-	-	-	-	-	-	-	-
Cholestan-3-ol, (3β,5β) TMS	75	0.99	-	18.46	1.25	7.28	1.81	6.55	0.39	0.54	1.93	4.31	-	-	-	-	-	-	-	-
Cholestan-3-ol, (3α,5β) TMS	75	0.47	-	1.32	0.44	0.95	0.39	1.21	0.14	0.25	0.41	0.95	-	-	-	-	-	-	-	-
Cholesterol, TMS	75	1.58	-	3.33	0.33	2.31	1.05	1.36	0.21	0.26	0.56	1.29	-	-	-	-	-	0.05	0.19	-
Cholestan-3-ol, (3β,5α) TMS	75	2.32	-	4.60	0.89	4.07	1.11	4.13	2.53	0.26	1.16	4.07	-	-	-	-	-	-	0.20	-
Campesterol, TMS	75	1.43	-	0.51	1.25	0.45	0.38	0.45	0.29	-	0.12	0.30	-	-	-	-	-	-	-	-
5α-cholestan-3β-ol TMS	75	0.57	-	0.56	-	0.31	-	0.35	-	-	0.16	-	-	-	-	-	-	-	2.04	-
Stigmasterol TMS	75	1.24	-	0.14	-	0.30	0.50	0.28	0.32	0.18	0.11	0.60	-	-	-	-	0.09	-	-	-
β-Sitosterol TMS	75	3.51	0.40	1.05	2.38	1.97	2.07	2.66	0.56	0.15	0.89	3.01	-	-	-	-	0.09	-	-	-
Stigmastanol TMS	75	2.47	-	1.42	3.22	1.83	1.35	2.59	0.58	-	0.82	2.70	-	-	-	-	-	-	-	-
α-Amyrin TMS	75	0.33	0.25	0.16	0.19	0.39	-	0.37	-	0.07	0.12	0.46	-	-	-	-	-	-	-	-
Lupeol TMS	75	0.60	0.30	-	0.61	0.60	0.54	0.96	0.21	-	0.34	1.02	-	-	-	-	-	-	-	-
Friedelan-3-one	426	-	0.03	-	0.27	0.84	0.09	0.05	0.03	0.02	0.02	0.12	-	-	-	-	-	-	-	-
Ursolic acid 2TMS	75	0.53	-	0.59	-	0.65	-	0.53	0.11	-	2.31	0.33	-	-	-	-	-	-	-	-
α-Tocopherol	502	0.38	0.20	0.14	0.68	0.29	0.18	0.79	2.22	-	0.19	1.11	-	-	-	-	-	-	-	-
ω-Hydroxy fatty acid, C22, bis-TMS derivative	75	1.39	-	0.07	0.53	-	0.93	0.88	0.01	-	0.01	0.74	-	-	-	-	-	-	-	-
Pimaric acid TMS	374	-	-	-	0.14	-	-	-	-	-	0.01	-	-	-	-	-	-	-	-	-
Isopimaric acid TMS	374	-	-	-	0.04	-	0.02	0.02	-	-	0.01	-	-	-	-	-	-	-	-	-
Tyrosol 2TMS	75	-	-	-	0.09	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Oxalic acid TMS	147	0.65	0.09	0.31	0.05	0.22	0.02	0.06	0.07	0.10	0.05	0.10	0.07	-	0.06	0.07	0.03	-	-	-
Levulinic acid TMS	75	-	-	0.33	-	-	-	0.29	0.04	0.05	0.03	0.04	-	-	0.04	0.03	-	-	-	-
Benzeneacetic acid TMS	73	0.08	-	-	0.22	0.02	-	0.14	0.04	-	0.03	0.06	-	-	-	-	0.13	0.09	-	-
β-Hydroxybutyric acid 2TMS	73	0.03	-	-	-	-	0.02	-	-	-	-	0.01	-	-	-	-	0.05	0.11	-	-
Propanedionic acid TMS	73	-	-	0.03	-	-	-	0.02	-	-	-	0.01	-	-	-	-	0.05	0.02	-	-
Palmitoleic acid TMS	326	0.08	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Glycerol TMS	147	0.32	0.19	-	0.09	0.12	0.56	-	0.03	0.14	0.02	0.12	-	-	-	-	-	-	-	-
Benzoic acid TMS	179	0.08	0.10	0.05	0.06	0.05	0.05	0.28	0.09	0.20	0.07	0.09	-	-	0.19	0.05	1.62	0.85	0.04	-
2-Methylbenzoic acid (o-Toluic acid) TMS	119	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.04	0.09	-	-
3-Methylbenzoic acid (m-Toluic acid) TMS	119	-	0.02	-	-	0.01	0.01	0.07	-	0.02	0.01	0.02	-	-	-	-	0.09	0.24	-	-
4-Methylbenzoic acid (p-Toluic acid) TMS	119	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.05	0.11	-	-
Succinic acid TMS	147	0.07	0.11	0.14	0.05	0.02	0.02	0.12	0.05	0.02	0.02	0.04	-	-	-	-	0.05	0.02	-	-
Dehydroabietic acid TMS	372	0.04	0.06	0.01	1.11	0.02	0.02	0.16	0.10	0.01	0.07	0.07	-	-	-	0.01	0.01	-	-	-
n-Tertylbenzene	92	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 1 (*continued*)

Identified compounds	m/z	River sediments		River sediments borehole samples		River sediments							Fresh coal wastes		Self-heated coal wastes					
		AN_M46	AN_M62	DR2_1	DR2_2	AN_M3	AN_M6	AN_M7	AN_M8	AN_M9	AN_M11_2	AN_M12	SZ_F_12	SZ_F_13	AN8	AN9	WE2	WE5	CZ7	RC7
n-Pentylbenzene	92	-	-	0.01	-	0.01	-	0.01	-	-	0.01	0.01	-	-	-	-	-	-	-	-
n-Hexylbenzene	92	-	-	0.01	-	0.01	-	0.02	-	-	0.01	0.01	0.44	0.11	-	-	-	-	-	-
n-Heptylbenzene	92	-	-	0.01	-	0.01	-	0.02	0.01	-	0.01	0.01	0.55	0.31	0.19	0.22	-	-	-	-
n-Octylbenzene	92	-	-	0.01	-	0.01	-	0.03	0.01	0.03	0.01	0.02	0.53	0.61	0.41	0.37	-	-	-	-
n-Nonylbenzene	92	-	-	0.01	-	0.02	-	0.04	0.01	0.10	0.02	0.03	0.50	0.84	0.49	0.40	-	-	-	-
n-Decylbenzene	92	-	-	0.01	-	0.02	-	0.04	0.01	0.18	0.02	0.04	0.43	0.69	0.49	0.32	-	-	-	-
n-Undecylbenzene	92	-	-	0.01	-	0.02	-	0.03	0.01	0.18	0.02	0.03	0.31	0.35	0.40	0.22	-	-	0.38	-
n-Dodecylbenzene	92	-	-	0.01	-	0.02	-	0.03	0.01	0.12	0.02	0.03	0.25	0.19	0.33	0.14	0.09	-	0.42	-
n-Tridecylbenzene	92	-	-	-	-	0.02	-	0.03	0.01	0.11	0.02	0.02	0.22	0.10	0.21	0.08	0.21	-	0.36	-
n-Tetradecylbenzene	92	-	-	-	-	0.03	-	0.03	0.01	0.10	0.02	0.03	0.19	0.11	0.11	0.04	0.36	-	0.32	-
n-Pentadecylbenzene	92	-	-	-	-	0.02	-	0.03	0.01	0.12	0.02	0.03	0.21	0.09	0.06	0.03	0.43	-	0.19	-
n-Hexadecylbenzene	92	-	-	-	-	0.03	-	0.03	0.01	0.13	0.02	0.03	0.15	0.08	0.03	0.02	0.47	-	0.10	-
n-Heptadecylbenzene	92	-	-	-	-	0.02	-	0.03	0.01	0.11	0.02	0.03	0.14	0.08	0.02	0.02	0.49	-	0.05	-
n-Octadecylbenzene	92	-	-	-	-	0.03	-	0.03	0.01	0.11	0.02	0.04	0.12	0.07	0.02	0.01	0.55	-	0.03	-
n-Nonadecylbenzene	92	-	-	-	-	0.03	-	0.03	0.02	0.09	0.02	0.04	0.14	0.08	0.02	0.02	0.45	-	0.02	-
n-Eicosylbenzene	92	-	-	-	-	0.04	-	0.05	0.08	0.12	0.02	0.07	0.11	-	0.02	0.01	0.51	-	0.02	-
n-Heneicosylbenzene	92	-	-	-	-	-	-	-	0.02	0.11	0.02	-	0.13	-	0.02	0.02	0.34	-	-	-
n-Docosylbenzene	92	-	-	-	-	-	-	-	0.05	0.22	-	-	-	-	0.02	0.02	0.25	-	-	-
n-Tricosylbenzene	92	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.20	-	-	-
n-Tetracosylbenzene	92	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Phthalimide TMS	204	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1,2-Benzenedicarboxylic acid TMS (phthalic acid)	147	-	0.23	0.11	0.03	-	-	0.09	0.09	-	-	-	-	-	-	-	7.39	13.30	-	-
1H-Isoindole-1,3(2H)-dione (phthalimide)	147	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.14	0.05	-	-
Phosphoric acid triTMS	314	-	0.02	0.11	-	-	0.03	0.01	-	-	-	-	-	-	-	-	0.15	0.57	-	-
4-Hydroxybenzaldehyde TMS	194	-	-	-	-	0.04	0.03	-	-	-	0.04	0.08	-	-	0.56	0.42	0.06	0.51	-	-
Vanillin TMS	194	0.04	0.02	-	0.06	0.03	-	0.21	0.08	0.05	0.05	0.12	-	-	0.42	-	0.13	0.17	-	-
Acetophenone TMS	208	-	-	-	-	-	-	-	-	0.05	-	-	0.29	2.60	6.39	3.53	0.06	0.47	0.04	-
Chromone	146	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.06	0.15	-	-
Coumarin	118	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.07	0.10	-	-
Phenol TMS	166	-	-	-	-	-	-	0.01	-	0.02	-	-	0.08	0.02	0.05	1.25	0.01	0.01	0.02	0.19
o-Cresol-TMS	165	0.01	0.01	0.01	0.01	0.01	-	0.01	-	0.02	-	0.01	0.26	0.08	0.38	2.86	0.01	0.01	0.02	0.84
m-Cresol-TMS	165	0.02	0.02	0.01	0.03	0.02	-	0.04	0.01	0.15	0.01	0.04	0.36	0.87	3.77	10.89	0.02	0.05	0.08	2.30
p-Cresol-TMS	165	0.02	0.01	-	0.02	0.02	-	0.33	0.02	0.11	0.03	0.03	0.31	0.59	2.07	9.34	0.01	0.07	0.10	2.96
Dimethylphenols TMS	179	0.08	0.07	-	0.05	0.10	0.05	0.23	0.03	0.52	0.06	0.11	1.99	7.39	19.90	24.58	0.13	0.31	0.25	32.31
m-Hydroxyacetophenone TMS	208	-	-	-	-	0.03	-	-	-	0.05	-	0.01	0.27	1.40	5.63	1.38	0.04	0.41	0.02	7.39
2-Ethoxyphenol TMS	151	0.08	0.03	-	0.04	0.03	0.03	0.10	0.04	0.11	0.04	-	0.36	0.11	-	-	-	-	0.32	-
2-Isopropylphenol TMS	222	-	-	-	-	-	-	-	-	-	-	-	-	-	0.75	-	-	-	-	-
Thymol TMS	222	-	-	-	-	-	-	-	-	-	-	-	-	-	0.16	0.05	-	0.14	-	-
Propiophenone TMS	222	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.17	-	-	-	-
Pyrocatechol TMS	73	-	0.12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Note: '-' indicates that the compound was absent or occurred in very small amounts.
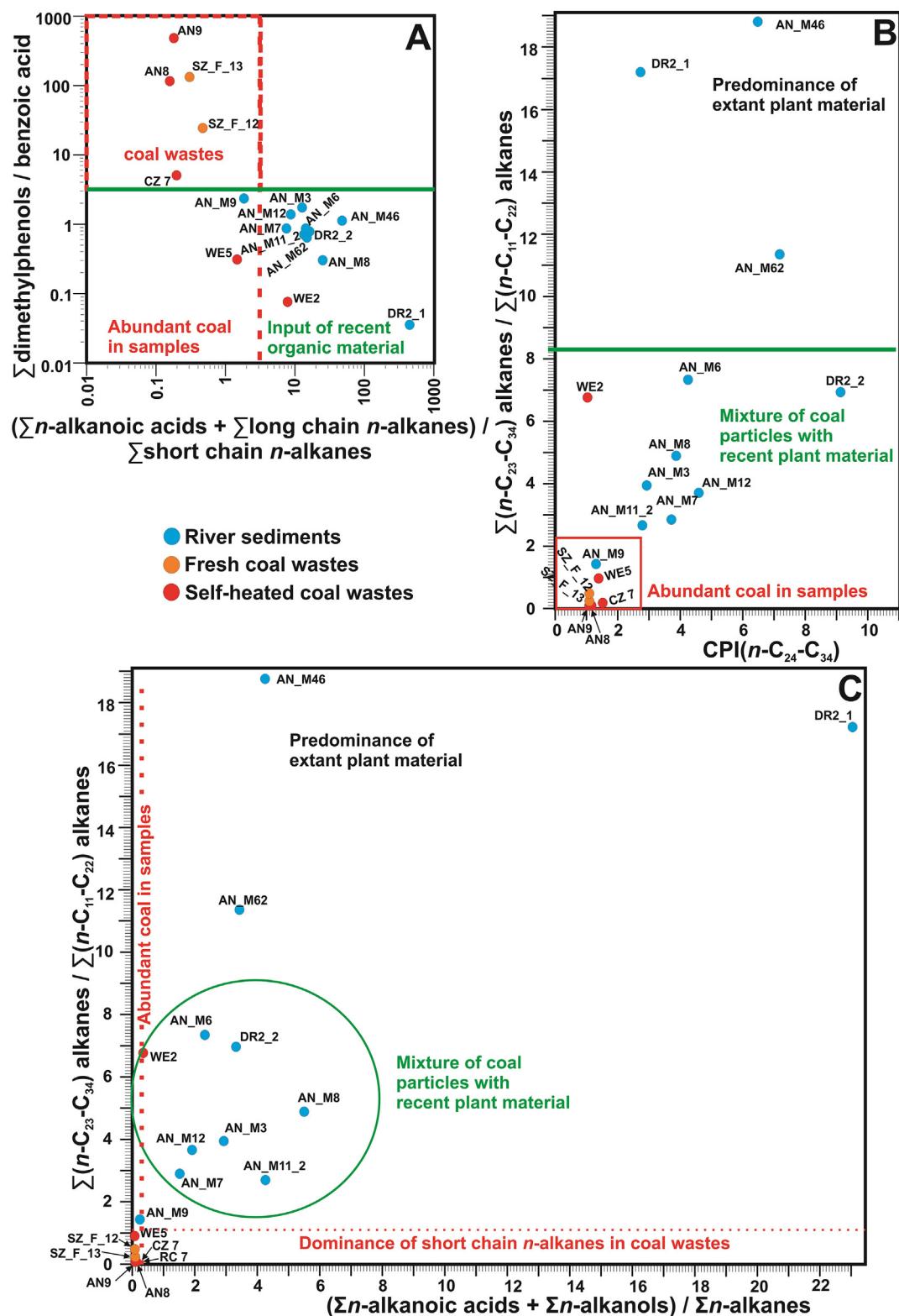
Fig. 2. Diagrams indicating input of recent organic-matter in the samples. Values were calculated on the basis of selected ion chromatograms (see Table 1).

sample contained mostly tyrosol, as well as pimaric and isopimaric acids (Table 1). Pimaric, isopimaric, and dehydroabietic acids are natural resin acid constituents, of which the last-named occurs most abundantly (Råbergh et al., 1999). Additional compounds included oxalic, succinic, and benzeneacetic acids, along with methylbenzoic acids, vanillin, and β-hydroxybutyric and levulinic acids occurring in river sediments and in those coal waste samples contaminated by initial

soil formation, e.g. CZ7, WE2, and WE5. These compounds were not identified in fresh coal wastes (Table 1). Therefore, in the samples, they originated recently from vegetation. Benzeneacetic acid is widely present in vascular and non-vascular plants (Kim and Chung, 2000; Sugawara et al., 2015). Oxalic and succinic acids and vanillin have also been identified in resin components, leaves, roots, stems, fruits and seeds, prairie grassland soils, and in pyrolysis/oxidation products of

Table 2

Calculated relative percentages of identified compounds from the TIC (total ion chromatogram) based on their peak areas. Only representative, non-overlapping compounds were selected. Dibenzofuran, phenanthrene, and retene, commonly present in coal and coal wastes, were chosen solely in order to compare their distributions with others.

Identified compounds	River sediments		River sediments borehole samples		River sediments							Fresh coal wastes		Self-heated coal wastes					
	AN_M46	AN_M62	DR2_1	DR2_2	AN_M3	AN_M6	AN_M7	AN_M8	AN_M9	AN_M11_2	AN_M12	SZ_F_12	SZ_F_13	AN8	AN9	WE2	WE5	C27	RC7
n-Dodecane	–	–	–	–	–	–	–	–	–	–	–	0.94	0.05	–	–	–	–	–	–
n-Tridecane	–	–	–	–	–	–	–	–	–	–	–	1.93	0.23	0.66	0.83	–	–	–	–
n-Tetradecane	–	–	–	–	0.01	–	0.07	–	–	–	–	3.11	1.51	3.47	4.34	–	–	–	–
n-Pentadecane	–	–	–	–	–	–	0.04	–	–	0.05	0.16	5.17	3.58	5.70	5.16	–	–	–	–
n-Hexadecane	0.02	–	–	–	–	0.05	–	–	–	0.15	0.41	5.87	8.08	9.46	9.96	–	–	2.55	–
n-Heptadecane	–	0.40	–	–	0.38	0.09	0.42	–	–	0.45	0.37	7.19	11.22	10.60	8.71	–	1.49	4.47	–
Pristane	–	–	–	–	–	–	0.93	0.09	2.70	0.25	0.69	5.25	6.63	6.19	3.72	–	1.14	6.07	–
n-Octadecane	–	–	–	–	–	0.14	0.19	0.26	5.60	0.55	–	0.90	16.29	5.14	8.22	–	–	9.11	–
Phytane	–	–	–	–	–	–	–	–	–	–	–	1.01	1.23	–	0.55	–	–	3.99	–
n-Nonadecane	0.08	0.23	–	–	0.32	0.22	0.64	0.22	2.82	0.40	0.39	5.93	7.80	11.52	6.58	0.71	4.09	14.52	–
n-Eicosane	–	–	–	–	0.43	0.33	0.51	0.25	3.23	0.38	0.45	4.20	4.40	8.25	5.28	1.71	6.20	21.43	–
n-Heneicosane	0.13	0.34	0.07	0.57	0.35	0.52	0.77	0.32	3.33	0.43	0.61	4.87	3.05	5.67	3.65	2.09	9.58	12.23	–
n-Docosane	0.16	0.27	0.08	0.73	0.59	0.99	0.66	0.22	3.74	0.41	0.55	5.13	3.17	3.06	1.84	3.47	11.85	8.18	–
n-Tricosane	0.46	0.35	0.13	0.60	0.45	1.08	0.81	0.33	2.57	0.46	0.66	4.67	3.06	2.02	1.43	5.18	11.75	6.02	–
n-Tetracosane	0.35	0.30	0.17	0.12	0.39	1.08	0.85	0.40	3.22	0.52	0.61	2.85	2.22	1.46	0.90	5.46	9.50	3.59	–
n-Pentacosane	0.67	0.20	0.10	1.24	0.51	0.79	0.09	1.17	3.27	1.54	2.18	4.70	3.24	1.34	1.08	11.09	7.79	3.19	–
n-Hexacosane	0.39	0.52	0.18	0.17	0.68	2.36	0.72	0.40	4.22	0.51	0.64	3.19	2.41	1.17	0.88	7.53	4.30	1.72	–
n-Heptacosane	1.59	1.00	0.16	0.83	1.36	0.79	2.40	1.22	3.78	1.10	2.69	3.03	2.20	1.04	1.11	7.20	2.63	0.96	–
n-Octacosane	0.24	0.28	0.08	0.12	0.53	4.03	0.56	0.37	2.75	0.39	0.48	2.23	1.30	0.66	0.63	5.81	1.24	–	–
n-Nonacosane	2.82	2.59	0.42	0.90	1.66	0.64	2.31	1.63	4.32	1.22	2.35	1.46	1.06	0.60	0.59	5.16	1.14	–	–
n-Tricontane	0.26	0.39	0.13	–	0.38	2.67	0.54	0.31	1.69	0.36	–	1.79	1.16	0.56	0.51	2.80	0.40	–	–
n-Hentriacontane	1.68	4.83	0.38	–	–	–	1.46	1.59	1.62	–	–	1.27	0.85	0.40	0.36	2.16	0.60	–	–
n-Dotriacontane	–	–	–	–	–	–	–	–	–	–	–	0.66	–	0.29	0.24	1.50	–	–	–
n-Octanoic acid TMS	0.05	0.03	0.04	0.01	0.04	0.02	0.10	0.03	0.07	0.27	0.05	–	–	0.21	–	0.07	0.12	0.04	–
n-Nonanoic acid TMS	0.09	0.06	0.06	0.02	0.05	0.07	0.16	0.06	0.10	0.10	0.06	–	–	–	–	0.13	0.28	0.03	–
n-Decanoic acid TMS	0.07	0.04	0.03	0.02	0.06	0.06	0.14	0.07	0.03	0.54	0.07	–	–	–	–	0.18	0.52	–	–
n-Dodecanoic acid TMS	0.17	0.17	0.29	0.03	0.18	0.18	0.29	0.16	–	5.04	0.24	–	–	–	–	0.34	–	–	–
n-Tetradecanoic acid TMS	0.50	0.22	1.16	0.06	0.27	0.39	0.87	0.31	0.39	4.16	0.46	–	–	–	0.14	0.48	0.52	–	–
n-Eicosanoic acid TMS	0.79	0.55	1.12	0.27	0.72	0.70	1.66	0.95	0.90	0.47	0.95	–	–	–	–	2.42	0.38	–	–
n-Docosanoic acid TMS	2.70	0.90	1.07	1.15	1.43	2.12	3.07	3.49	0.61	0.78	2.71	–	–	–	–	3.36	0.47	–	–
n-Tetracosanoic acid TMS	6.53	–	1.25	1.98	6.07	5.45	4.22	7.82	1.17	1.62	4.87	–	–	–	–	2.46	0.41	–	–
n-Hexadecanoic acid TMS	3.30	0.73	17.46	0.46	2.05	2.98	5.66	1.80	2.08	16.86	3.52	0.63	0.62	0.83	0.38	4.09	2.00	–	16.48
n-Heptadecanoic acid TMS	0.10	–	0.73	0.05	–	0.08	0.37	0.16	0.37	0.57	–	–	–	0.20	2.56	2.52	1.59	–	4.52
Oleic acid TMS	2.17	–	3.79	–	1.50	0.42	2.04	0.51	0.59	23.35	1.97	–	–	–	–	–	–	–	–
n-Octadecanoic acid TMS	1.89	–	15.33	–	1.98	2.07	4.30	0.84	–	12.67	2.98	–	–	0.25	0.84	3.54	1.58	–	4.74
n-Nonadecanoic acid TMS	0.13	–	0.16	–	0.14	0.18	0.37	0.24	0.41	0.16	0.30	–	–	0.34	0.62	1.22	0.71	–	12.49
n-Eicosanoic acid TMS	0.79	–	1.25	0.29	0.67	0.88	1.55	0.89	0.63	0.47	1.05	–	–	–	0.31	2.71	0.60	–	–
n-Heneicosanoic acid TMS	0.23	–	0.12	–	0.25	0.33	0.67	0.57	1.49	0.20	0.52	–	–	–	0.26	1.21	0.38	–	–
n-Docosanoic acid TMS	3.01	0.93	1.08	1.35	1.51	2.14	3.17	3.47	0.42	0.16	2.74	–	–	–	–	3.41	0.58	–	–
n-Tricosanoic acid TMS	1.40	0.53	0.33	0.19	0.93	1.62	1.14	2.00	0.73	0.38	1.17	–	–	–	0.07	1.89	0.30	–	–
n-Tetracosanoic acid TMS	6.30	5.22	1.32	2.05	5.90	5.81	4.45	7.82	0.76	1.77	5.14	–	–	–	0.03	2.40	0.56	–	–
n-Pentacosanoic acid TMS	1.22	0.50	0.17	–	1.15	2.03	0.60	1.65	1.04	0.33	0.75	–	–	–	–	0.70	0.34	–	–
n-Hexacosanoic TMS	3.63	3.87	0.70	1.01	3.82	4.21	2.00	7.88	1.12	0.65	3.04	–	–	–	–	1.07	0.45	0.21	–
n-Heptacosanoic acid TMS	0.64	0.45	–	0.38	0.98	1.19	0.76	1.62	0.51	–	0.51	–	–	–	–	–	0.20	–	–
n-Octacosanoic acid TMS	3.66	2.26	–	1.28	4.07	3.38	2.06	7.45	1.08	0.45	2.28	–	–	–	–	0.56	0.26	–	–
n-Nonacosanoic acid TMS	0.55	0.57	–	0.46	0.81	–	–	1.77	–	–	–	–	–	–	–	–	–	–	–
n-Triacontanoic acid TMS	1.70	3.52	–	1.49	2.36	1.87	1.47	5.29	0.86	0.22	1.35	–	–	–	–	1.03	–	–	–
n-Hentriacontanoic acid TMS	1.13	0.32	–	0.42	0.80	–	–	0.90	0.18	–	–	–	–	–	–	–	–	–	–
n-Dotriacontanoic acid TMS	0.65	0.91	–	0.76	–	–	0.23	2.94	–	–	0.42	–	–	–	–	–	–	–	–
n-Hexadecanol TMS	0.21	–	0.16	–	0.30	0.15	0.41	0.34	–	0.13	0.31	–	–	–	–	–	–	0.23	–
n-Octadecanol TMS	0.25	0.14	0.28	0.04	0.32	0.23	0.36	0.12	–	0.19	0.54	–	–	–	–	–	–	–	–

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Table 2 (*continued*)

Identified compounds	River sediments		River sediments borehole samples		River sediments							Fresh coal wastes		Self-heated coal wastes					
	AN_M46	AN_M62	DR2_1	DR2_2	AN_M3	AN_M6	AN_M7	AN_M8	AN_M9	AN_M11_2	AN_M12	SZ_F_12	SZ_F_13	AN8	AN9	WE2	WE5	CZ7	RC7
n-Eicosanol TMS	0.28	0.13	0.08	-	0.22	0.32	0.31	0.25	-	0.15	0.42	-	-	-	-	-	-	-	-
n-Docosanol TMS	3.57	2.95	0.63	2.81	5.20	3.22	3.46	1.62	0.37	0.86	6.20	-	-	-	-	-	-	-	-
n-Tetracosanol TMS	3.71	2.56	0.16	3.74	3.51	3.68	1.28	1.79	0.25	0.47	1.88	-	-	-	-	-	-	-	-
n-Hexacosanol TMS	9.83	34.35	0.27	2.16	5.88	10.06	2.09	14.34	0.46	1.28	4.28	-	-	-	-	0.16	0.23	-	-
n-Octacosanol TMS	5.93	10.77	-	2.20	4.08	5.57	1.58	4.14	-	1.19	2.80	-	-	-	-	0.26	-	0.15	-
n-Nonacosanol TMS	0.94	1.94	-	0.57	1.22	2.18	0.42	1.11	-	0.24	1.27	-	-	-	-	-	-	-	-
n-Triacontanol TMS	2.64	9.77	-	0.93	3.16	3.71	1.13	2.34	-	1.01	2.06	-	-	-	-	-	-	-	-
n-Hentriacontanol TMS	0.16	0.41	-	0.17	0.18	0.38	0.14	0.29	-	0.11	0.19	-	-	-	-	-	-	-	-
Cholesterol, TMS	1.52	-	30.64	0.82	11.40	3.39	11.26	0.80	1.47	3.81	7.61	-	-	-	-	-	-	-	-
Cholestan-3-ol, (3β,5β) TMS	0.53	-	-	0.30	1.28	0.72	1.43	-	-	0.58	1.81	-	-	-	-	-	-	-	-
Cholestan-3-ol, (3α,5β) TMS	4.58	0.45	9.14	0.52	5.51	2.91	4.28	0.45	1.37	1.92	3.64	-	-	-	-	-	0.17	0.69	-
Cholestan-3-ol, (3β,5α) TMS	2.84	-	5.58	0.36	4.25	1.46	4.76	-	-	1.92	4.73	-	-	-	-	-	-	0.27	-
β-Sitosterol TMS	9.21	0.85	2.96	2.64	5.28	6.06	6.82	1.42	1.07	3.05	9.40	-	-	-	-	-	-	-	-
Glycerol TMS	0.27	0.20	-	0.01	0.08	0.44	-	0.03	0.14	0.02	0.09	-	-	-	-	0.05	0.06	-	-
Benzeneacetic acid TMS	0.03	-	0.02	0.02	0.01	0.01	0.05	0.02	-	0.02	0.03	-	-	-	-	0.08	0.60	-	-
4-Hydroxybenzaldehyde TMS	-	-	-	-	0.03	-	0.08	0.06	-	0.04	0.07	-	-	0.83	-	-	-	-	-
Benzoic acid TMS	0.04	0.05	0.02	0.01	0.03	0.02	0.12	0.04	0.10	0.03	0.04	-	0.05	0.24	0.05	0.89	0.60	0.03	-
Levulinic acid TMS	-	-	0.10	-	-	-	0.13	0.08	0.06	0.01	0.05	-	-	0.06	0.04	-	-	-	-
Oxalic acid TMS	0.04	0.04	0.08	0.01	0.01	-	0.04	0.04	0.04	0.03	0.03	-	-	0.10	0.09	0.03	-	-	-
β-hydroxybutyric acid 2TMS	0.02	-	-	-	-	0.02	-	-	-	-	-	-	-	-	-	-	-	-	-
Pimaric acid TMS	-	-	-	0.69	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Isopimaric acid TMS	-	-	0.10	0.50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Phenol TMS	-	-	-	-	-	-	-	-	0.01	-	-	0.20	0.03	0.15	3.02	0.01	-	0.02	7.23
o-Cresol TMS	-	-	-	-	-	-	-	-	-	-	-	-	0.10	0.55	4.08	-	-	-	9.66
m-Cresol TMS	-	-	-	-	-	-	-	-	-	-	-	-	0.39	2.66	9.34	-	-	0.05	18.71
p-Cresol TMS	-	-	-	-	-	-	-	-	0.04	-	-	-	0.26	1.49	7.84	0.03	-	0.06	26.18
2-Ethoxyphenol TMS	0.04	0.03	-	0.01	0.02	-	0.06	0.02	0.04	0.02	0.02	0.16	0.03	-	-	-	-	0.21	-
Dibenzofuran	-	0.08	-	-	0.20	-	0.91	0.05	14.69	0.43	0.28	4.25	3.36	4.40	3.06	0.11	-	-	-
Phenanthrene	1.13	1.81	0.41	-	1.72	0.49	3.32	0.94	13.51	1.78	1.60	15.50	9.78	8.21	-	1.00	12.14	-	-
Retene	-	-	-	62.48	0.33	0.52	0.24	0.25	2.02	0.29	0.26	1.92	0.63	0.22	0.71	-	-	-	-

Note: '-' indicates that the compound was absent or occurred in very small amounts.
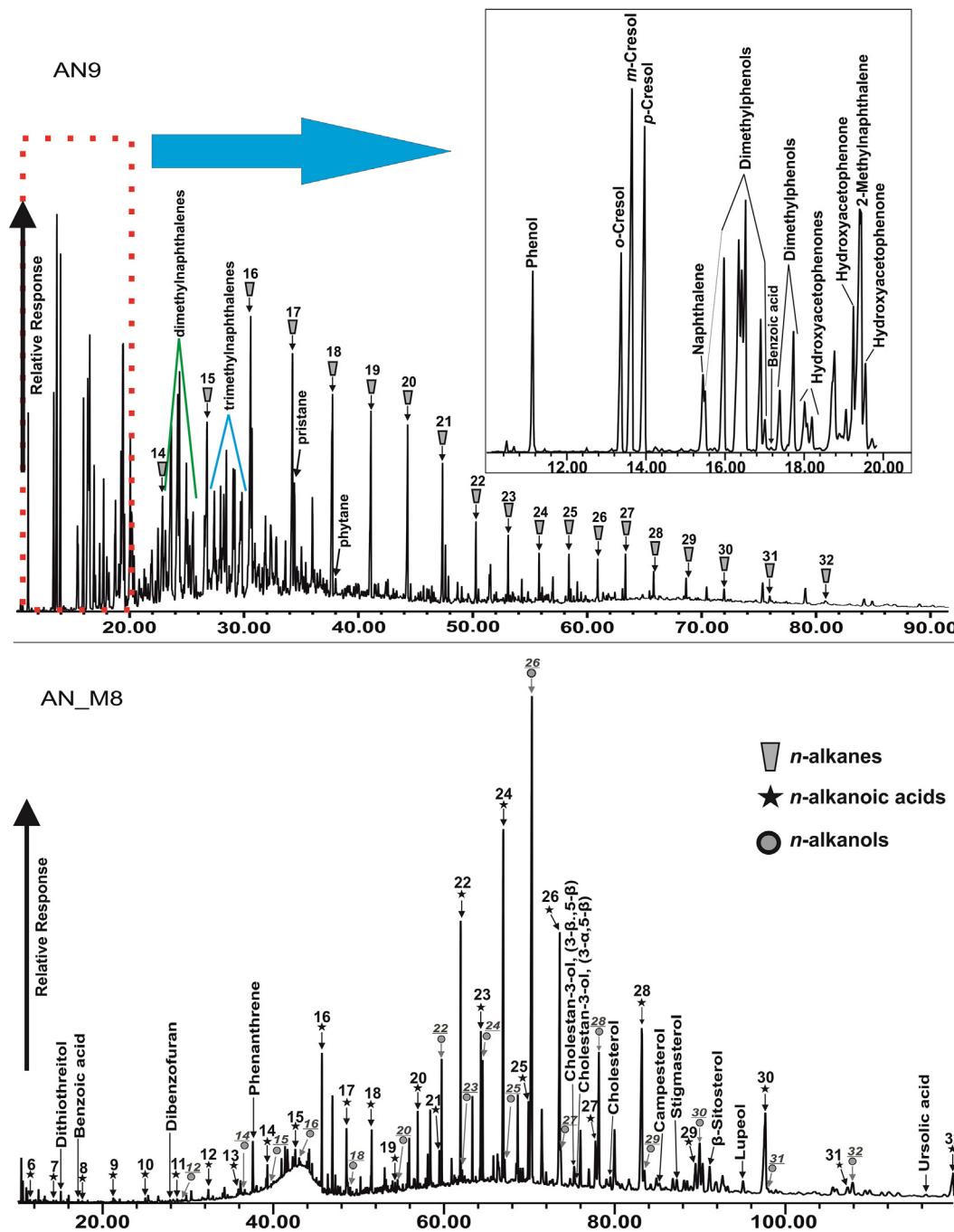
Fig. 3. Total ion chromatograms of two representative samples (self-heated coal waste and river sediment) showing differences in phenol, *n*-alkane, and *n*-alkanoic acid distributions.

low-rank coals (coal waste with self-heating) and lignites (Czechowski et al., 1996; Otto et al., 2005; Poulin and Helwig, 2012; Doskočil et al., 2014; Cheng et al., 2013; Fu et al., 2013; He et al., 2014; Khakimov et al., 2014; Prasad and Shivay, 2017). The presence of levulinic acid in river sediments can be related to the degradation of cellulose, but other sources are also plausible (Hayes et al., 2010; Kamm et al., 2010). Benzoic acid was identified in most samples, with no great differences in relative percentages. This compound may be present in coal tar, but it can occur naturally in higher plants as well (Qualley et al., 2012; Pavón et al., 2016). Therefore the ratio of *dimethylphenols/benzoic acid*, combined with that of (*Σn-alkanoic acids + Σlong chain n-alkanes)/ Σshort chain n-alkanes,* clearly distinguished between origins from coal wastes and from extant vegetation in the studied samples (Fig. 2A). One

example of a human-related inorganic pollutant was phosphoric acid, identified only in river sediments. This compound is commonly released into the environment by phosphate fertilisers used in the agricultural sector (Belboom et al., 2015). The presence of 1,2-benzenedicarboxylic (phthalic acid) in the river sediments and Wełnowiec samples is related to a human-produced organic pollutant, as this compound is widely used in e.g. plasticizers, producing polyester / alkyl – resins and insect repellents (Bang et al., 2011).

3.2.3. Ketones and alcohols

Acetophenone and *m*-hydroxyacetophenone were identified mostly in coal waste samples and, with elevated relative percentages, in self-heated samples (Table 1). As previously indicated, these compounds
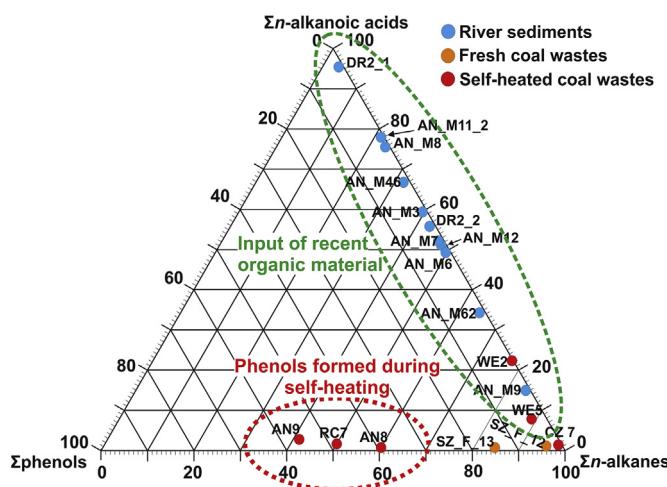
Fig. 4. Ternary diagram applied in order to distinguish the different sample groups; results were calculated using selected ion chromatograms (see Table 1). Σ(phenols) = phenols + cresols (*o-*, *m-*, and *p-*) + dimethylphenols + 2-ethoxyphenol.

can be released into the environment via petrol and residential fuel oil exhaust, coal combustion, heavy oil fractions in coal tar, waste waters from petrochemical plants, and waste incineration (Safaei-Ghomi et al., 2007; Alexieva et al., 2009; HSDB, 2010). Friedelan-3-one was identified only in river sediments as a common marker of recent vegetation input (Brassel and Eglinton, 1983; Duke, 1992; Odeh et al., 2016). In coal waste samples, cholesterol, cholestanol, stigmasterol, and sitosterol were identified with minor relative percentages as contaminants (Table 1). These compounds are usually not prominent (if present) in coals due to oxidative loss via diagenetic processes during coal deposition (Oros and Simoneit, 2000; Oros et al., 2006). Contrastingly, the river sediments were characterised by elevated percentages of sterols, such as cholesterol, β-sitosterol, campesterol, cholestanols, and cholestene, representing input from recent vegetation (Table 1; Weete, 1976; Otto and Simoneit, 2001; Killops and Killops, 2005; Oros et al., 2006). Therefore, their presence in coal waste material is secondary and indicates initial soil-formation processes or their migration with meteoric waters. Among plant triterpenoids, compounds such as α- and β-amyrin, lupeol, and ursolic acid were identified in river sediments, indicating recent input from vegetation, as they are commonly present in leaves, bark, wood resins, and roots (Bauer et al., 2004; Vázquez et al., 2012; Yasumoto et al., 2017). Alkanols with even-over-odd predominance in the number of carbon atoms occurred in river sediments (ranging from n-C_{14} to n-C_{32}) with elevated relative percentages (Tables

Table 3
The values of geochemical ratios.

		Calculated from ion chromatograms									Calculated from TIC	
Sampe types	Sample codes	(Σn-alkanoic acid (n-C_6-C_{32}) + Σn-alkanols(n-C_{12}-C_{32})) / Σn-alkanes(n-C_{11}-C_{34})	CPI(n-C_{17}-C_{31}) alkanes	CPI(n-C_{24}-C_{34}) alkanes	CPI(n-C_{25}-C_{31}) alkanes	(Σn-alkanoic acid(n-C_6-C_{32}) + Σlong chain n-alkanes(n-C_{23}-C_{34})) / Σshort chain n-alkanes(n-C_{11}-C_{22})	n-alkanes: Σlong chain (n-C_{23}-C_{34}) / Σshort chain (n-C_{11}-C_{22})	n-alkylbenzenes: Σshort chain (n-C_{14}-C_{24}) / Σlong chain (n-C_{25}-C_{34})	n-alkanoic acids: EOP	Σdimethylphenols / benzoic acid	(Σn-alkanoic acid(n-C_6-C_{32}) + Σlong chain n-alkanes(n-C_{23}-C_{34}))/ Σshort chain n-alkanes(n-C_{11}-C_{22})	(Σn-alkanoic acid(n-C_6-C_{32}) + Σn-alkanols(n-C_{12}-C_{32})) / Σn-alkanes(n-C_{11}-C_{34})
River sediments	AN_M46	4.19	5.30	6.41	6.14	59.04	18.83	-	1.35	1.06	126.13	7.77
	AN_M62	3.20	4.44	6.86	5.85	17.58	11.36	-	10.64	0.70	38.24	7.50
	DR2_1	23.00	3.45	2.72	2.46	420.26	17.13	-	9.23	0.05	300.98	23.66
	DR2_2	3.17	7.23	9.26	8.89	17.73	6.95	-	14.08	0.96	13.65	4.99
	AN_M3	2.93	1.96	2.83	2.77	11.48	3.97	0.81	9.73	1.97	24.71	7.87
	AN_M6	2.18	2.71	4.14	3.92	15.51	7.20	-	9.64	0.98	29.67	4.15
	AN_M7	1.57	2.38	3.89	3.99	7.41	2.92	1.39	7.49	0.81	14.90	3.87
	AN_M8	5.52	2.39	3.81	3.59	24.32	4.94	0.39	8.54	0.35	52.88	9.95
	AN_M9	0.20	1.12	1.28	1.26	1.88	1.43	1.05	4.46	2.59	2.21	0.34
	AN_M11_2	4.18	1.83	2.82	2.80	15.42	2.43	1.13	8.82	0.89	21.32	6.20
	AN_M12	1.79	2.87	4.49	4.74	9.33	3.87	0.93	10.27	1.21	15.17	4.39
Coal wastes	SZ_F_12	0.01	1.01	1.08	1.07	0.52	0.51	3.40	-	27.10	0.59	0.01
	SZ_F_13	0.01	1.19	1.02	0.94	0.30	0.29	5.34	-	127.10	0.31	0.01
	AN8	0.02	0.97	1.17	1.15	0.13	0.11	12.54	-	106.76	0.18	0.02
	AN9	0.08	0.98	1.16	1.18	0.19	0.11	13.02	2.11	502.72	0.24	0.08
	WE2	0.31	0.93	1.11	1.05	9.18	6.80	0.07	4.95	0.08	11.25	0.58
	WE5	0.11	0.83	1.31	1.30	1.15	0.94	-	3.84	0.36	1.55	0.18
	CZ7	0.02	0.98	1.49	1.60	0.21	0.19	1.61	7.60	7.00	0.22	0.01
	RC7	0.04	1.97	-	-	0.06	0.02	-	-	-	-	-

CPI(n-C_{17}-C_{31}) alkanes = ((C_{17} + C_{19} + … + C_{27} + C_{29}) + (C_{19} + C_{21} + … + C_{29} + C_{31}))/(2 ∗ (C_{18} + C_{20} + … + C_{28} + C_{30})) (Kotarba et al., 1994).
CPI(n-C_{24}-C_{34})   alkanes = (((C_{25} + C_{27} + C_{29} + C_{31} + C_{33})/(C_{24} + C_{26} + C_{28} + C_{30} + C_{32})) + ((C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) + (C_{26} + C_{28} + C_{30} + C_{32} + C_{34}))) ∗ 0.5 (Bray and Evans, 1961).
CPI(n-C_{25}-C_{31}) alkanes = ((C_{25} + C_{27} + C_{29}) + (C_{27} + C_{29} + C_{31}))/(2 ∗ (C_{26} + C_{28} + C_{30})) (Kotarba et al., 1994).
Σlong chain(n-C_{23}-C_{34}) / Σshort chain(n-C_{11}-C_{22}) alkanes; m/z = 71, source indicator (Tissot and Welte, 1984).
In Σ(alkanoic acids), oleic acid is not included.
EOP (even-over-odd predominance) = (Σ(n-C_{22}-C_{30})$_{even}$ + Σ(n-C_{24}-C_{32})$_{even}$)/Σ(n-C_{23}-C_{31})$_{odd}$ alkanoic acids (Bray and Evans, 1961).
Note: '–' indicates that the compound was absent, or that the ratio resulted in very low values.

1 and 2). In several coal waste samples, only *n*-octacosanol was identified. The predominance of *n*-C$_{26}$ to *n*-C$_{30}$ alkanols in river sediments indicates an origin from vascular-plant wax (Oros and Simoneit, 2000).

3.2.4. Phenols

Generally, a wide range of alkylphenols (*o*-, *m*-, and *p*-cresols and dimethylphenols) occurred in self-heated coal wastes with elevated percentages in comparison to river sediments (Tables 1 and 2; Fig. 3), as was preliminarily indicated by Nádudvari et al. (2015). Since phenols are relatively readily soluble in water, they can be used as tracers to identify the occurrence and extent of water-washing processes. This feature thus increases their hazardous environmental potential, as they are toxic and carcinogenic to humans (Clayton and Clayton, 1994; Michałowicz and Duda, 2007). The water-washing effect can be identified, using the Σ*dimethylphenols/benzoic acid* ratio (Table 3), in the WE2 and WE5 samples as compared to SZ_F_12 and SZ_F_13 or the self-heated samples AN8 and AN9. The latter were taken following restructuring of the dump's shape into a trapezoidal form, which was done only a few months before sampling. As a result these samples exhibit less water washing, as they were taken from a deeper part of the dump. The origin of phenols in these samples can be explained as the result of thermal destruction of vitrinite and may represent relatively early stages of self-heating (Skręt et al., 2010). Phenol and alkylphenols are the most prominent products of the degradation of both lignin itself and lignin-derived macromolecules in coal (Saiz-Jimenez and de Leeuw, 1985; Hatcher et al., 1992; Iglesias et al., 2002). Fig. 5 indicates the distribution of phenols in two representative samples (one

Fig. 5. Comparison of distributions of phenols (*m/z* = 165 and 179) and benzoic acid (*m/z* = 179) in two representative samples: river sediment (AN_M7) and self-heated coal waste (AN8). The predominance of benzoic acid in the sediment sample is clearly visible.

representing river sediment, the other self-heated coal waste). However, the compatibility of the distribution of cresols and dimethylphenols from coal waste dumps and river sediments, despite water-washing, indicates that these compounds, found in Bierawka river sediments, originated from coal. Among phenols, tyrosol (a polyphenol and phenylethanoid) was identified only in DR2_2; its origin is associated with lignin degradation (Stefanova et al., 2004; Grasset et al., 2010). 2-Ethoxyphenol, which appears in most samples, was identified as one of the major compounds in immature OM from internal sediments in southern Poland (Rybicki et al., 2017) and may be another lignin-degradation product.

3.3. Aromatic compounds

A homologous series of *n*-alkylbenzenes ranging from C$_{14}$ to C$_{34}$ were found in coal waste with high relative concentrations. The predominance of short-chain *n*-alkylbenzenes was observed in self-heated coal wastes such as AN8 and AN9 due to influence of elevated temperatures during their formation (Table 3). The presence of these compounds in river sediments clearly indicates input from coal material, as *n*-alkylbenzenes have been widely reported as common constituents of coals, coal pyrolysates, and coal smoke (Gallegos, 1981; Philp, 1985; Oros and Simoneit, 2000; Killops and Killops, 2005; Bi et al., 2008). However, in WE2, WE5, and river sediments, long-chain *n*-alkylbenzenes were found to be dominant. According to Fabiańska et al. (2012), *n*-alkylbenzenes exhibit various degrees of resistance to biodegradation and water washing, similarly to e.g. *n*-alkanes. As a result of these processes, short-chain *n*-alkylbenzenes are removed from samples subjected to biodegradation and water-washing. The coal particles were previously identified in river sediments by Nádudvari and Fabiańska (2015). Therefore the identification of these compounds is well agreed with the presence of coal particles in sediments. However, the applied PAH diagnostic ratios indicate their pyrogenic origin not only due to coal wastes self-heating, but also because river sediments contained other contaminations like e.g. ash deposits (Nádudvari and Fabiańska, 2015; Nádudvari et al., 2018).

Generally, elevated relative percentages of dibenzofuran and phenanthrene differentiate coal wastes from river sediments, except in the case of AN_M9 (Nádudvari and Fabiańska, 2015). The DR2_2 sample contained elevated amounts of retene, an aromatic land plant biomarker typical of terrestrial sedimentary OM (Table 2). Ramdahl (1983) also mentioned retene as wood-combustion indicator in environment.

3.4. Compounds related to an urban rubbish dump covered with coal waste and soil growth on the Wełnowiec dump

The Wełnowiec dump is a specific case, as it served as an urban rubbish dump from 1991 to 1996, when it was covered by coal wastes which began to self-heat (Ciesielczuk et al., 2015). Phthalimide and 1H-isoindole-1,3(2H)-dione or *n*-(hydroxymethyl)phthalimide were found in two self-heated samples from Wełnowiec. Phthalimide, which has been detected previously in self-heated coal waste dumps, is a transformation product formed from the gaseous phase originating in the natural pyrolytic process (Rost, 1942; Jehlička et al., 2007; Lorz et al., 2007; Fabiańska et al., 2015). Compounds related to urban rubbish, such as triphenylbenzene or triphenylpyridine (plastic combustion tracers; Simoneit et al., 2005), had been previously identified at this dump (Nádudvari et al., 2018). The chromone and coumarin occurred only in the Wełnowiec samples, indicating that their origin was connected with the plants which cover the dump, and thus were absent from river sediments. These compounds are widely present naturally in various plants, fruits, and vegetables (Dean, 1963; Robinson, 1963; Digiovanni, 1990). The complete series of methylbenzoic acids (*o*-, *m*- and *p*-toluic acid), also found only in WE samples (Table 2), are common in some vascular plants, e.g. in their flowers (Kolosova et al.,
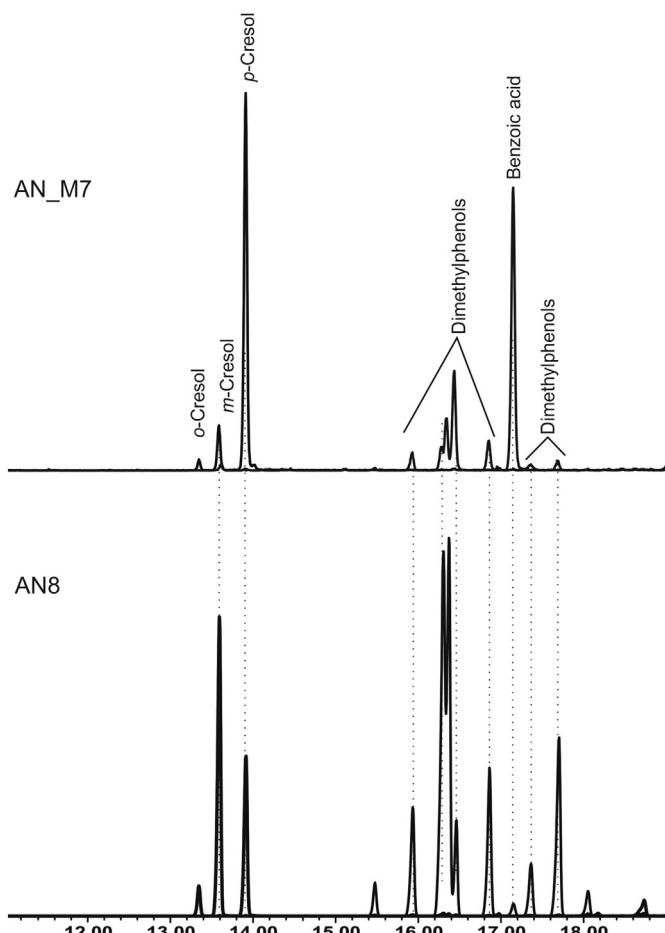
2001; Negre et al., 2003). The Wełnowiec dump features/conditions favour plant growth, e.g. an abundance of emitted CO_2, nitrates, ammonia acting as a fertiliser, and heated warm surfaces, even in winter (Doerr and Shakesby, 2013; Komnitsas et al., 2010; González-Alcaraz et al., 2011). This enables the occurrence of special and rare species (Vanderpoorten, 2001; Ciesielczuk et al., 2015). These places are seeded by pioneer species immediately after cooling of the surface. Since the seasonal vegetation cycle is disturbed, some plants may be found seeding at the same time others are blooming or fruiting (Midgley and Bond, 2013; Ciesielczuk et al., 2015).

4. Conclusions

Characteristic polar compounds from the extant OM were identified as dominant in river sediments and coal wastes exposed under air for longer time periods and contaminated by soil. These compounds included *α-* and *β*-tocopherol, sterols, stanols, glycerol, pimaric and isopimaric acids, oxalic, succinic, and ursolic acids, and friedelan-3-one. This input from recent vegetation was subsequently confirmed by the applied geochemical ratios which clearly separated young sediments from unaltered coal wastes (fresh coal wastes), e.g. *(Σn-alkanoic acids + Σn-alkanols)/Σn-alkanes, (Σn-alkanoic acid + Σlong chain n-alkanes)/Σshort chain n-alkanes*, CPI(*n*-C$_{25}$-C$_{31}$), and CPI(*n*-C$_{24}$-C$_{34}$) ratios. Among common features were the dominance of *n*-alkanes and *n*-alkylbenzenes in coal wastes, whereas alkanoic acid, alkanols, sterols, stanols, etc. occurred with elevated relative percentages or exclusively in river sediments. In several coal wastes, initial soil-formation processes had started, as indicated by the occurrence of cholestanol, sitosterol, oxalic acid, and methylbenzoic acids, and by a preponderance of odd-over-even long-chain *n*-alkanes and *n*-alkanoic acids.

Typical water washing and the initial stage of the self-heating effect was identified in coal waste samples using *Σdimethylphenols/benzoic acid* ratio. The distributions of *o-*, *m-* and *p*-cresols and dimethylphenols in river sediments was found to be similar to those in coal waste, indicating that these compounds connected with coal were derived from the same source. Other coal-related pollution compounds present in river sediments included *n*-alkylbenzenes, phenanathrene, dibenzofuran, and acetophenone. Distribution of these compounds varied due to water-washing and/or degradation processes.

Acknowledgements

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