

Application of organic petrology and geochemistry to coal waste studies

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ARTICLE INFO

Article history:

Received 30 March 2011

Received in revised form 30 June 2011

Accepted 3 July 2011

Available online 23 July 2011

Keywords:

Coal wastes

Macerals

Self heating

Organic biomarkers

Geochemical indices

Thermal alteration

ABSTRACT

Coal wastes produced during mining activities are commonly deposited in nearby dumps. These wastes mostly composed of minerals and variable amounts (usually 20–30%) of organic matter start to weather immediately after deposition. Oxidation of the organic matter can lead to self heating and self combustion as a result of organic and mineral matter transformations. The degree of alteration depends on the properties of the wastes, i.e., the maceral and microlithotype composition of the organic matter and its rank.

Alteration of wastes also depends on the heating history, i.e., the rate of heating, final heating temperature, duration of heating, and the degree of air access. Although air is probably necessary to initiate and drive the heating processes, these usually take place under relatively oxygen depleted conditions. With slow heating, color of organic matter particles changes, irregular cracks and oxidation rims develop around edges and cracks, and bitumen is expelled. As a result, massive and detrital isotropic and strongly altered organic matter forms. On the other hand, higher heating rates cause the formation of devolatilization pores, oxidation rims around these pores and along cracks, vitrinite-bands-mantling particles, and bitumen expulsions.

Organic compounds generated from the wastes include *n*-alkanes, iso-alkanes, alkylcyclohexanes, acyclic isoprenoids, mainly pristane, phytane and, in some cases, farnesane, sesquiterpanes, tri- and tetracyclic diterpanes, tri- and pentacyclic triterpanes, and steranes, polycyclic aromatic hydrocarbons (mostly with two- to five rings, rarely six rings), and phenols. The compounds formed change during the heating history. The fact that phenols are found in dumps where heating has not yet been completed, but are absent in those where heating ceased previously suggests the presence of water washing. The organic compounds formed may migrate within the dumps. However, when they migrate out of the dumps, they become a hazard to environment.

This paper is a review on transformations of organic matter (both maceral composition and reflectance and chemical composition) in coal wastes deposited in coal waste dumps. Immediately after deposition the wastes are exposed to weathering conditions and sometimes undergo self heating processes.

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Contents

1. Introduction	2
1.1. Internal factors	3
1.2. External factors	3
2. Sampling of coal wastes and gaseous products of self heating	3
2.1. Sampling of coal wastes	3
2.2. Sampling of gaseous products of self heating	4
3. Methods of investigation of coal wastes	4
3.1. Petrographic analyses of coal wastes	6
3.2. Gas chromatography of gases and VOCs	6
3.3. Analyses of liquid- and semi-liquid products of self heating of coal wastes	6
4. Data obtained from organic petrology and geochemistry and their application in coal waste studies	6
4.1. Organic petrology of coal wastes	6
4.2. Organic geochemistry of coal wastes	10
4.2.1. Geochemical characteristics of coal wastes unaltered by self heating	10
4.2.2. Products of self heating formed within a dump	12

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4.2.3.	Gases produced in self heating and self combustion	12
4.2.4.	Pyrolytic products of self heating	12
4.2.5.	Main groups of organic compounds in coal wastes	12
4.2.6.	Distributions of particular organic compounds groups	13
5.	Discussion	18
5.1.	Migration of pyrolysates within coal-waste dumps	19
5.2.	Effects of leaching (water-washing) on the composition of the bituminous fraction in coal wastes	19
5.3.	Assessment of temperature ranges in a self heating zone	20
5.4.	Correlations of geochemical parameters with reflectance	20
6.	Conclusions	20
	Acknowledgments	21
	References	21

1. Introduction

Coal wastes are generated during the preparation of coal seams for exploitation (mining wastes) and as slurry wastes. The origin of mining wastes is connected with preparatory mining works and coal seam exploitation. Individual fragments of these wastes are up to 500 mm. Slurry wastes are generated during coal separation. They are commonly divided into (a) coarse grained (10–250 mm) wastes produced from suspension plants, (b) fine-grained (0.5–30 mm) wastes produced from sedimentation processes, and (c) very fine-grained (<1 mm) slurries (tailings) resulting from flotation processes (Skarżyńska, 1995).

Constituent elements of wastes vary in size and composition. Mineral matter, the main component, typically occurs as fragments of sandstone, shale, mudstone and, less often, conglomerate and carbonate (Skarżyńska, 1995). Organic matter, usually comprising 3–30% of the waste material (Skarżyńska, 1995), occurs as laminae and lenses of variable length and width, and as dispersed organic matter. When they come in contact with oxygen, these wastes start to oxidize and may generate fires.

In general, two types of fires occur in coal-waste dumps. Exogenic fires are caused by some external source of heat, such as dumped hot slag and badly protected welding works (Urbański, 1983). Endogenic fires are uncontrollable and occur as the end result of self heating

processes (Itay et al., 1989; Krishnaswamy et al., 1996a,b; Lu et al., 2004; Sensogut and Cinar, 2000; Shi et al., 2005; Singh et al., 2007; Urbański, 1983; Walker, 1999). In this paper, endogenic fires and their origins will be discussed. Although much research (Beamish, 2005; Beamish et al., 2001; Brooks et al., 1988; Clemens and Matheson, 1996; Kaymakçi and Didari, 2002; Krishnaswamy et al., 1996a,b; Liu and Zhou, 2010; Walker, 1999) has been conducted, the origin of endogenic fires is not understood completely. However, it is clear that these fires occur in coal wastes that contain organic matter of various rank, such as bituminous coals (Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a) and anthracites (Ribeiro et al., 2010a,b,c).

Immediately after deposition in coal-waste dumps that are usually sited close to the source mines, the coal wastes undergo a process of oxidation that, in some cases, can lead to self heating and self combustion (Fig. 1). For self combustion to take place, three key conditions are required to co-exist at the same time. These conditions are the presence of organic components and pyrite that easily react with air, easy access for air into the interior of the dump, and the conditions for heat to accumulate (Barosz, 2002, 2003; Brooks et al., 1988; Kaymakçi and Didari, 2002; Pone et al., 2007; Szafer et al., 1994; Tabor, 1999, 2002; Urbański, 1983).

Two critical stages are involved in self heating. During the first stage no change in temperature is observed (Sawicki, 2004; Walker,

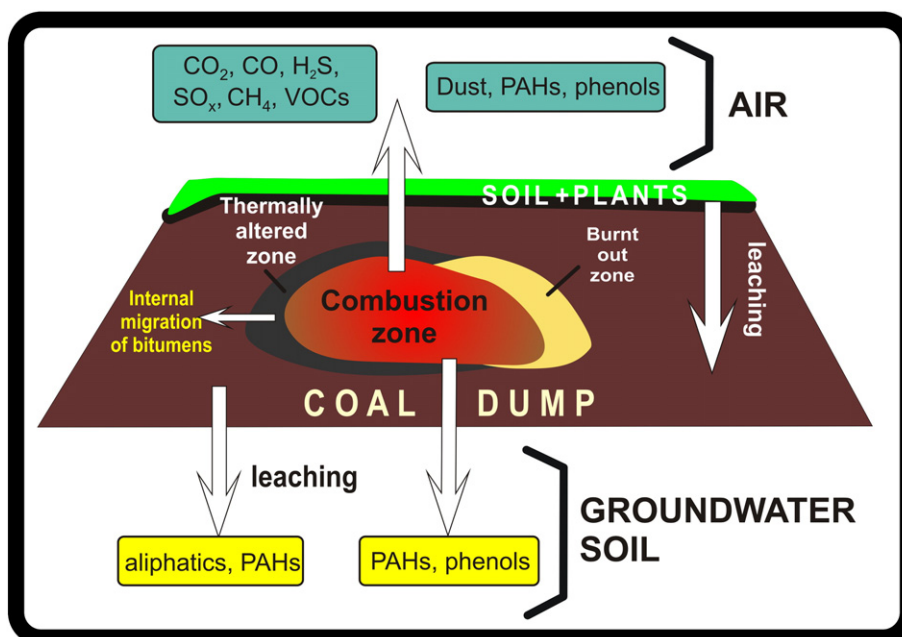


Fig. 1. The main processes that occur in a coal-waste dump.

1999). The alterations of both organic and mineral matter happen at low temperatures. Low-temperature oxidation of organic matter is believed to be the precursor of self heating (van Krevelen, 1993). The initial oxidation stage is followed by self heating of the coal wastes during which the temperature rises continuously (Sawicki, 2004; Walker, 1999). The critical temperature is 60–80 °C (Pone et al., 2007; Sawicki, 2004; Sokol, 2005); above this value, the temperature rises rapidly, also described as thermal runaway, until it reaches the self-ignition stage. The temperature of self-ignition of coal is strongly rank dependent and is ~150 °C for subbituminous coal, ~200 °C for bituminous coal, ~250 °C for coke and ~300 °C for anthracite (Sawicki, 2004; Sokol, 2005). The burning of wastes can result in a temperature of as high as 1300 °C (Heffern and Coates, 2004; Sawicki, 2004; Sokol, 2005; Querol et al., 2008; Ribeiro et al., 2010a,c).

Self heating and self combustion processes occurring in coal waste dumps are very dynamic. The temperatures fluctuate and the heating centers, which usually are located at a depth of 1.5–2.5 m beneath the dump surface, migrate (Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan and Tabor, 2011; Misz-Kennan et al., 2011b; Tabor, 2002–2009). In some cases, the burning waste is visible on the surface (Ciesielczuk, accepted for publication). As organic material is progressively burnt, the centers of heating migrate deeper into the waste dump (Szafer et al., 1994; Urbański, 1983).

Many factors influence self heating within coal waste dumps that may be classified as internal and external factors (Urbański, 1983). Internal factors are those intrinsic to the coal wastes, especially their mineral composition, the maceral composition of the organic matter present, and its rank, and moisture content (Kaymakçi and Didari, 2002; Rosiek and Urbański, 1990; Urbański, 1983; Walker, 1999). External factors are those that influence the filtration properties of dumps and their heat balance. These factors include the shape and height of the dump, the atmospheric conditions, and particle size and distribution (Kaymakçi and Didari, 2002; Krishnaswamy et al., 1996a,b; Urbański, 1983; Walker, 1999).

1.1. Internal factors

The organic matter in coal wastes is represented by all three groups of macerals, i.e., huminite/vitrinite, liptinite, and inertinite (ICCP, 1998, 2001; Sýkorová et al., 2005; Taylor et al., 1998). Macerals of the vitrinite group are, of all three maceral groups, the most prone to oxidation and self heating (Machnikowska et al., 2003; Strumiński and Rosiek, 1990; Taylor et al., 1998). Liptinite macerals also show a propensity to spontaneous combustion (Mastalerz et al., 2010; Misra and Singh, 1994). However, Beamish et al. (2001) have shown that resinite is not prone to these processes. Macerals of the vitrinite and liptinite groups are the more susceptible to spontaneous combustion because they are intrinsically the most reactive macerals; in a heating situation, their temperature increases more sharply and the ignition time is shorter (Mastalerz et al., 2010). Inertinite macerals are widely considered to be the least reactive group of macerals (ICCP, 2001; Taylor et al., 1998) although some believe that fusinite can be the cause of endogenic fires because of its high specific area (Strumiński and Rosiek, 1990).

Individual macerals respond differently to heating when the particles are composed entirely of a single maceral rather than when a particle comprises an association of macerals belonging to various groups (microlithotypes) and/or when organic matter occurs together with minerals as carbominerites (Suárez-Ruiz and Crelling, 2008; Taylor et al., 1998). The fact that vitrite undergoes oxidation before durite is especially marked during the earliest stages of oxidation (Machnikowska et al., 2003; Taylor et al., 1998).

The other important internal factor influencing self heating of coal wastes is organic-matter rank. Coals and coal wastes of every rank undergo self heating — from lignites through bituminous coals (Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan et al., 2011b; Misz-

Kennan and Fabiańska, 2010) to anthracites (Ribeiro et al., 2010a,b). However, in general, the tendency of coal wastes to spontaneous combustion decreases with increasing rank (Beamish et al., 2001; Mastalerz et al., 2010; Rosiek and Urbański, 1990; Walker, 1999). Of all coals, the most prone to spontaneous combustion is bituminous coal (Beamish, 2005; Beamish et al., 2001) which, as it is commonly inferred, reflects the fact that lower-rank coals contain greater amounts of reactive macerals (Mastalerz et al., 2010).

In coal wastes, water is always present in varying amounts. It is a component of some minerals (e.g., clay minerals) and also derives from atmospheric precipitation and from the decomposition of organic and mineral compounds during heating. Moisture participating in chemical reactions enhances self heating. At moisture content greater than 6%, coals are more prone to self heating (Rosiek and Urbański, 1990). However, too much water inhibits the process (Rosiek and Urbański, 1990; Sawicki, 2004; Smith and Glasser, 2005).

1.2. External factors

The shape and size of a dump are important factors that influence water filtration and heat accumulation. Self heating commonly occurs on the steep, windward slopes of cone-shaped dumps (Misz-Kennan and Tabor, 2011; Moghtaderi et al., 2000; Urbański, 1983).

Coal-waste dumps are a source of numerous gaseous and liquid pollutants that are emitted to the atmosphere and leached to surface and ground waters (Carras et al., 2009; Finkelman, 2004; Grossman et al., 1994; Hower et al., 2009; Nelson and Chen, 2007; O'Keefe et al., 2010; Pone et al., 2007; Querol et al., 2008; Skrzęta et al., 2010; Stracher and Taylor, 2004; Zhao et al., 2008). It has been estimated that the combustion of 1 ton of mine wastes can generate 99.7 kg CO, 0.61 kg H₂S, 0.03 kg NO_x, 0.84 kg SO₂, and 0.45 kg smoke (Liu et al., 1998). The gaseous pollutants have a strong smell of hydrocarbons and they can be suffocating.

Much research has focused on self heating and self combustion in coal seams (Beamish et al., 2001; Brooks et al., 1988; Carras et al., 2009; Clemens and Matheson, 1996; Hower et al., 2009; Jones, 2000; Liu and Zhou, 2010; Misra and Singh, 1994; Pone et al., 2007; Stracher and Taylor, 2004; Urbański, 1983; Walker, 1999). However, it is only relatively recently that similar attention has been paid to the changes of organic matter caused by these processes in coal wastes. Coal seams and coal wastes differ mainly with regard to amount of organic matter (Liu and Zhou, 2010).

Until relatively recently, efforts concentrated on attempts to explain the mechanisms of self heating, the influencing factors, and on methods for preventing and fighting coal-waste fires (Brooks et al., 1988; Jones, 2000; Kaymakçi and Didari, 2002; Krishnaswamy et al., 1996a,b; Mahadevan and Ramulu, 1985; Querol et al., 2011; Singh et al., 2007). Growing knowledge of the types of gases produced during self heating and self combustion, and their potential polluting influence on air, water, and soils prompted increased attention.

2. Sampling of coal wastes and gaseous products of self heating

2.1. Sampling of coal wastes

In order to examine coal wastes, samples of at least 1–2 kg should be collected from about 20 cm beneath the dump surface. Typically, sampling sites are places differing macroscopically in color, hardness, compactness or from places differing in temperature. The most abundant lithologies present in a coal wastes, i.e., coal, sandstone, clay, quartzite, cleat minerals and sulfide minerals, need to be sampled (Querol et al., 2008). Additionally, samples of soils covering the dump may also be collected (Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010) for investigation of bitumen migration outside the dump.

In the laboratory, each sample should be cleaned to remove surface contamination, should be quartered, dried at room temperature and crushed to a grain size of <1 mm for petrographic analyses. For geochemical analyses, samples should be crushed to a grain size of <0.2 mm (Fabiańska, 2006; Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a; Querol et al., 2008). Since semi-liquid bitumen present in self-heated coal wastes easily absorbs contaminants, only aluminum foil or glass containers should be used for sample storage to maintain inertness (Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a).

2.2. Sampling of gaseous products of self heating

Volatile organic compounds (VOCs) and other gases emitted during self heating of coal wastes can be investigated in situ or, as it is more often the case, sampled in a vacuumed container and taken to a laboratory for more detailed analyses. In situ methods give more detailed information about the spatial and temporal distributions of emissions due to heating and combustion. Laboratory analyses applying gas chromatography (GC) or gas chromatography–mass spectrometry (GC–MS) enable the general compositions and constituents of a wider range of compounds to be investigated.

Concentrations of CO₂ and CO in a combustion gas from burning coal seams or coal dumps can be assessed in situ using detection tubes (O'Keefe et al., 2010; Tabor, 2002, 2002–2009). Litschke (2005) analyzed the composition of gas emissions using a landfill gas analyzer which detected CH₄ and CO₂ via infrared absorption at 3.41 μm and 4.29 μm wavelengths, respectively, and used a galvanic cell to measure O₂ concentrations. The same author measured CO and H₂S using electrochemical cells. To assess the in-situ emission rates of gases in vents forming above dump-fire zones, the application of a S-type Pitot tube attached to a flow meter measuring gas velocity has been proposed (Litschke, 2005; O'Keefe et al., 2010).

The gaseous products of self heating may also be sampled in situ using a syringe, a gas steel probe or a hand-operated pump and pumped into an inert and impermeable container for storage and

transport (Litschke, 2005; Pone et al., 2007). Stainless steel containers (Pone et al., 2007), gas washing flasks with a rubber septum (Litschke, 2005) or Teflon bags (Ribeiro et al., 2010a) are suitable impermeable containers for this purpose. All materials involved must be resistant to heat and the corrosive influence of gases.

3. Methods of investigation of coal wastes

In recent years, self heating of coal wastes, its causes, and its detrimental effects on environment have been the focus of much research. The detection of the initial stage of self heating in coal-waste dumps, the emission of greenhouse gases, volatile organic compounds (VOCs) and trace elements to the atmosphere have been investigated. In addition, leaching of inorganic compounds, particularly heavy metals, and soluble organic compounds to soils and groundwater and resultant changes in water quality around coal wastes as well as evaluations of associated environmental dangers have been studied (Bell et al., 2001; Querol et al., 2008; Ribeiro et al., 2010a; Skręć et al., 2010). However, majority of data for these investigations came from laboratory simulations due to measuring difficulties caused by the large scale of the dumps (Kim, 2007; Kok et al., 1989; Skręć et al., 2010; Smith and Glasser, 2005; Sujanti and Zhang, 1999). Apart from environmental studies, mechanisms of coal oxidation, the geochemistry of self heated organic matter, the petrology of organic matter, the formation of new minerals and their properties have been investigated, often with possible reuse of coal wastes or self heating prevention in mind. Due to the great complexity of the waste material, and the variety of the research objectives, many advanced analytical methods are applied both in the laboratory and in the field. In the following review of methods, only those related to the organic petrology and geochemistry of self-heated coal wastes are described. The methods applied are summarized in Tables 1 and 2.

The self heating and self combustion conditions of some dumps are systematically monitored to provide information on the initiation of heating and on the dynamic behavior of the heating processes within the dumps. The monitoring includes monthly measurements of temperature on the surface and within the dump (at the depth of

Table 1
Overview of commonly-used analytical methods in coal-waste investigation.

Objects	Analytical methods applied	Short description	References
Coal waste mineralogy	X-ray diffraction (XRD) Scanning Electron Microscopy (SEM)		Dokoupilova et al., 2007; Masalehdani et al., 2009; Pone et al., 2007; Misz-Kennan et al., 2011a; Querol et al., 2008; Ribeiro et al., 2010a,b
Coal waste organic petrology	Maceral, microlithotype, and carbominerite composition Reflectance measurements, oil immersion	With accordance to International Standards ISO 7404-3 and ISO 7404-4 With accordance to International Standard ISO 7404-5	Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a; Ribeiro et al., 2010a
Trace elements in coal wastes and leachates	Inductively-Coupled Plasma Atomic-Emission Spectrometry (ICP-AES) Inductively-Coupled Plasma Mass Spectrometry (ICP-MS)		Querol et al., 2008; Ribeiro et al., 2010a
Leaching potential	Batch leaching Column leaching	A single or multiple leaching, time: 24 h with stirring, deionized water as leachant Deionized water as leachant, under a saturated flow regime	Querol et al., 2008; Skręć et al., 2010, Querol et al., 2008
Gases and VOCs sampling	Vacuum stainless steel canisters, or pumping to storage containers		Pone et al., 2007; Ribeiro et al., 2010a
VOCs	Cryogenic pre-concentration, gas chromatography–FID (flame ionization detector) and gas chromatography–ECD (electron capture detector), gas chromatography–mass spectrometry		Davidi et al., 1995; Pone et al., 2007; Ribeiro et al., 2010a
Gases	Gas chromatography–FID (flame ionization detector) and gas chromatography–thermal conductivity detector		Pone et al., 2007; Stracher and Taylor, 2004
Bitumen in coal wastes	Gas chromatography–mass spectrometry		Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a

Table 2

Selected indicators of biological source and environment and the degree of organic-matter maturation and alteration based on biomarkers and aromatic hydrocarbons.

Short formula or parameter symbol	Total formula of parameter	Geochemical meaning and application	References
$\Sigma (n-C_{12}-n-C_{22}) / \Sigma (n-C_{23}-n-C_{35})$	Sum of $C_{12}-C_{22}$ <i>n</i> -alkanes/sum of $C_{23}-C_{35}$ <i>n</i> -alkanes	Higher content of long chain <i>n</i> -alkanes is indicative of vascular plants forming organic matter	Tissot and Welte, 1984
$n-C_{23}/n-C_{31}$	Ratio of <i>n</i> - C_{23} and <i>n</i> - C_{31} alkane contents	High content of <i>n</i> - C_{21} , <i>n</i> - C_{23} and <i>n</i> - C_{25} compared to <i>n</i> - C_{29} , <i>n</i> - C_{31} and <i>n</i> - C_{33} is typical for organic matter originating from <i>Sphagnum</i>	Pancost et al., 2002
Pr/Ph	Pristane/phytane ratio	Pr/Ph > 1 – oxic environment of deposition Pr/Ph < 1 – anoxic environment of deposition, (except kerogen III)	Didyk et al., 1978; Jiamo et al., 1990
Pr/ <i>n</i> - C_{17}	Pristane/ <i>n</i> -heptadecane ratio	Various interpretations; determination of degree of alteration of organic matter and water leaching	Leythaeuser and Schwarzkopf, 1986
Ph/ <i>n</i> - C_{18}	Phytane/ <i>n</i> -octadecane ratio	Various interpretations; determination of degree of maturation/alteration of organic matter and water leaching	Leythaeuser and Schwarzkopf, 1986
CPI	$CPI = 0.5 \{ [(n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31} + n-C_{33}) / (n-C_{24} + n-C_{26} + n-C_{28} + n-C_{30} + n-C_{32})] + [(n-C_{25} + n-C_{27} + n-C_{29} + n-C_{31} + n-C_{33}) / (n-C_{26} + n-C_{28} + n-C_{30} + n-C_{32} + n-C_{34})] \}$	Value decreases to about 1.0 with the increasing maturity	Bray and Evans, 1961
$C_{31}S/(S+R)$	$C_{31}S/(S+R) = 17\alpha(H), 21\beta(H)$ -29-homohopane 22S/($17\alpha(H), 21\beta(H)$ -29-homohopane 22S + $17\alpha(H), 21\beta(H)$ -29-homohopane 22R)	Value increases with maturity from 0 to about 0.6; at $R_r = 0.7\%$ parameter validity ends (equilibrium)	Ourisson et al., 1979; Seifert and Moldowan, 1978
Ts/(Ts + Tm)	$Ts/(Ts + Tm) = 18\alpha(H)$ -22,29,30-trisnorneohopane/($18\alpha(H)$ -22,29,30-trisnorneohopane + $17\alpha(H)$ -22,29,30-trisnorhopane)	Increase of Ts relative to Tm; ratio values increase from 0.0 to about 0.80–0.85	Seifert and Moldowan, 1978
$C_{30}\beta\alpha/(\alpha\beta + \beta\alpha)$	$C_{30}\beta\alpha/(\alpha\beta + \beta\alpha) = 17\beta(H), 21\alpha(H)$ -29-hopane $C_{30}/(17\alpha(H), 21\beta(H)$ -29-hopane C_{30} + $17\beta(H), 21\alpha(H)$ -29-hopane $C_{30})$	Decreases with maturity from about 0.8 to 0.0	Seifert and Moldowan, 1980
$C_{30}\beta\beta/(\beta\beta + \alpha\beta + \beta\alpha)$	$C_{30}\beta\beta/(\beta\beta + \alpha\beta + \beta\alpha) = 17\beta(H), 21\beta(H)$ -29-hopane/($17\beta(H), 21\beta(H)$ -29-hopane + $17\beta(H), 21\alpha(H)$ -29-hopane)	Decreases with maturity from about 0.8 to 0.0	Seifert and Moldowan, 1980
MNR	MNR = 2-methylnaphthalene/1-methylnaphthalene	Increases with increasing degree of maturity; very sensitive to water leaching	Radke et al., 1994
DNR	DNR = (2,6-dimethylnaphthalene + 2,7-dimethylnaphthalene)/1,5-dimethylnaphthalene	Increases with increasing degree of maturity	Radke et al., 1982
TNR-1	TNR-1 = 2,3,6-trimethylnaphthalene/(1,3,6-trimethylnaphthalene + 1,4,6-trimethylnaphthalene + 1,3,5-trimethylnaphthalene)	Increases with increasing degree of maturity	Radke et al., 1986
TNR-2	TNR-2 = (1,3,7-trimethylnaphthalene + 2,3,6-trimethylnaphthalene)/(1,3,5-trimethylnaphthalene + 1,4,6-trimethylnaphthalene + 1,3,6-trimethylnaphthalene)	Increases with increasing degree of maturity	Radke et al., 1986
TNR-4	TNR-4 = 1,2,5-trimethylnaphthalene/(1,2,5-trimethylnaphthalene + 1,2,7-trimethylnaphthalene + 1,6,4-trimethylnaphthalene)	Increases with increasing degree of maturity	Peters et al., 2005
MPI-3	MPI-3 = (2-methylphenanthrene + 3-methylphenanthrene)/(1-methylphenanthrene + 9-methylphenanthrene)	Increases with increasing degree of maturity before decreasing	Radke and Welte, 1983
2-MP/2-MA	2-MP/2-MA = 2-methylphenanthrene/2-methylanthracene	Values depend on degree of influence of fire and self heating	Fabiańska, 2007
MB/DBF	MB/DBF = (3-metylbiphenyl + 4-metylbiphenyl)/dibenzofurane	Increases with increasing degree of alteration before decreasing	Radke, 1987

1.0 m) as well as measurements of CO, CO₂ and O₂ (Misz-Kennan and Tabor, 2011).

3.1. Petrographic analyses of coal wastes

For petrographic analyses, crushed coal wastes are embedded in epoxy resin and polished according to the procedure described in ISO 7404-2 (Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a; Ribeiro et al., 2010a,b).

The analyses include the identification of maceral groups and mineral contents, and the different forms of transformed organic matter. Identifications are carried out at 500 points on each pellet using a magnification of 500× following the procedures described in ISO 7404-3. Depending on the degree of organic-matter alteration, random reflectance is measured at 100–500 points according to ISO 7404-5:2002 (Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a; Ribeiro et al., 2010a,b).

3.2. Gas chromatography of gases and VOCs

The analytical gas-chromatography procedure used to investigate the compositions of gases and VOCs involves the cryogenic pre-concentration of a gaseous sample with liquid nitrogen (−196 °C) and its vaporization with hot water (Pone et al., 2007), or direct desorption from Tenax to a GC–MS chromatograph (Ribeiro et al., 2010a). Litschke (2005) used a gas chromatograph equipped with a thermal conductivity detector (TCD) for N₂, CO₂, H₂ and O₂/Ar and two flame ionization detectors (FID) for saturated and unsaturated hydrocarbons. Pone et al. (2007) applied the most complex analytical procedure which involved the division of a sample into three separate gas chromatographs equipped with five different detectors, namely two electron capture detectors (ECD), a mass spectrometer (MS) and two flame ionization detectors (FID). This enabled hydrocarbons, halocarbons, and halogenated compounds to be analyzed. For CO₂ analyses, a gas chromatograph equipped with a thermal conductivity detector can be used (Pone et al., 2007).

3.3. Analyses of liquid- and semi-liquid products of self heating of coal wastes

Prior to analysis, the bituminous fraction of coal wastes is extracted with pre-distilled organic solvents such as dichloromethane (DCM), or mixtures of solvents, e.g., dichloromethane:methanol=4:1, following a procedure similar to that applied in the extraction of source rocks or coals (Peters et al., 2005). Ultrasonic extraction or the Soxhlet apparatus can be used. All extracts are collected, evaporated, weighed and stored in amber glass and under freezing conditions. At the next stage, the extracts may be separated into main compound groups such as aliphatic hydrocarbons, aromatic and polar compounds, with asphaltenes precipitated *n*-pentane, *n*-hexane or *n*-heptane prior to analysis or they may be analyzed as total analytes, depending on the research aim and quantity of extract available. Methods such as liquid column chromatography and preparative layer chromatography may be applied (Fabiańska, 2006).

Gas chromatography–mass spectrometry (GC–MS) is the main technique applied in the compositional investigation of bituminous fractions of sedimentary organic matter of various origins (Peters et al., 2005). Because of its origin and general similarity to pyrolysis products from coals, e.g., Upper Silesian Coal Basin (USCB) coals (Fabiańska and Matuszewska, 1998) or hydrothermal bitumens (Simoneit, 1993), bitumen in coal wastes may be investigated by GC–MS. Capillary columns of medium polarity can be used, e.g., with 5% diphenyl-95% dimethyl polysiloxane or 35% diphenyl-65% dimethyl polysiloxane as a bonded or cross-linked coating, with a minimum length 60 m. Some differences in the distributions of particular

compounds such as *n*-alkanes can reflect column polarity. Helium is commonly applied as a carrier gas in such analyses. The total retention time of the GC analysis should be quite long (90–120 min) as many coal-waste extracts contain compounds of high molecular mass. Due to high variability in boiling temperatures of the compounds present in coal wastes extracts the temperature program should show a wide range of temperatures, at least from 50 to 300 °C. Electron Impact (EI, 70 eV) mode for a spectrometer is used to enable comparisons with other geochemical objects since such conditions are standard in organic geochemistry. Due to the great compositional variability of the analytical products, mass data should be acquired in a full-scan mode. Every GC–MS analysis should be repeated at least twice to confirm results. The detailed analytical conditions for GC–MS are given in Misz et al. (2007), Misz-Kennan and Fabiańska (2010), and Misz-Kennan et al. (2011a).

4. Data obtained from organic petrology and geochemistry and their application in coal waste studies

Oxidation, self heating and self combustion cause the transformation of coal wastes to varying degrees. In terms of their organic-matter content, four types of wastes can be distinguished in all dumps: 1 – wastes with organic matter in the form of microscopic constituents and organic compounds; 2 – wastes with organic matter as microscopic constituents but organic compounds are absent; 3 – wastes with organic compounds but lacking microscopic constituents; 4 – wastes lacking both microscopic constituents and organic compounds (Misz-Kennan, 2010; Misz-Kennan et al., 2011a).

4.1. Organic petrology of coal wastes

Organic matter present in coal wastes ranges widely from 0 to nearly 100%. It usually constitutes 20–30%. Macroscopically and microscopically, it occurs as interlayers and, microscopically, as laminae, lenses of varying length and width and as irregular particles among minerals. Microscopically-visible organic matter is absent in the most strongly altered wastes (Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a; Ribeiro et al., 2010a).

Organic matter is represented by three groups of macerals: huminite/vitrinite, liptinite, and inertinite (ICCP, 1998, 2001; Taylor et al., 1998 and references therein; Sýkorová et al., 2005). Their nomenclature can also be applied to coal wastes where all occur, on a microscopic scale, variably unaltered and altered (Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a; Ribeiro et al., 2010a,b).

Individual macerals, depending on their optical properties (color, reflectance, fluorescence, morphology) which, in turn, reflect their origin and organic-matter rank, respond differently to heating. Their response to heating also depends on the heating conditions, mostly the heating rate, the end temperature, duration of heating and the degree of access of oxygen into the hosting dump (Suárez-Ruiz and Crelling, 2008; Taylor et al., 1998 and references therein).

Vitrinite is the maceral group that responds prior to heating (Taylor et al., 1998). A low heating rate increases viscosity and reduces anisotropy in organic matter (Murchison, 2006). With increasing heating rates, vitrinites display an increasing tendency to soften and their particle edges to become rounded and, in addition, gas released from individual particles in increasing amounts leads to the formation of vacuoles. The vacuole walls of such vitrinites are thinner. Vitrinites occurring in anthracites show no evidence of softening on heating whereas those with reflectances between 1.08 and 1.55% develop mosaic structure and anisotropy. Fluidity rises to a maximum in coals containing approximately 32% volatile matter and then falls. Rising temperature and heating rate increases the apparent fluidity of organic matter irrespective of its rank. Increasing heating

rates greatly increase the number and size of vacuoles produced during devolatilization, particularly in lower rank coals (Goodarzi and Murchison, 1978).

Liptinite undergoes vitrinitization and devolatilization at temperatures above 300 °C (Cloke and Lester, 1994; Mastalerz and Mastalerz, 2000). At low heating rates, the color of liptinite macerals became paler and its reflectance increases and they gradually take on the appearance of vitrinite macerals. High heating rates result in the rapid devolatilization of liptinite macerals and formation of pores. When occurring together with vitrinite macerals in clarites, liptinites act to increase the plasticity of vitrinite (Cloke and Lester, 1994; Taylor et al., 1998).

Inertinite response to heating is strongly dependent on the properties of individual macerals in the sample. Low-reflecting, fluorescent inertinite is partially fused during carbonization and, during combustion, they form anisotropic porous chars. Non fluorescent inertinite does not fuse during carbonization and, during combustion, forms isotropic massive chars that may contain small devolatilization pores (Cloke and Lester, 1994; ICCP, 2001; Taylor et al., 1998).

The complex conditions pertaining in coal-waste dumps are reflected in the presence of a great variety of microscopic forms of

organic matter present in the wastes. Currently, there is no broadly accepted classification of these forms though some attempts to develop a classification have been undertaken. Any complete classification of the microscopic forms of organic matter in coal wastes will be complicated; the primary organic matter is heterogeneous as are the conditions within dumps. A variety of organic-matter microscopic forms can be distinguished on the basis of color, reflectance, fluorescence, morphology, and size (Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2009, 2010, 2011a; Ribeiro et al., 2010a).

In coal wastes, unaltered organic matter is represented by unaltered macerals belonging to all three groups. These have the optical properties of unaltered macerals (Fig. 2A). Moderately-altered particles that underwent slow heating typically have a paler color (Goodarzi and Murchison, 1978; Murchison, 2006). These are not only paler in color but have a higher reflectance and weaker fluorescence than the primary particles. This is particularly so for macerals of the vitrinite group (Fig. 2B). Liptinite macerals rarely show paler colors (Fig. 2C).

Cracks commonly occur within particles (Fig. 2D–F) and/or on their edges (Fig. 2E–F). These cracks are usually short and, if occurring within a particle, irregular. Where they occur at the edges, they are set

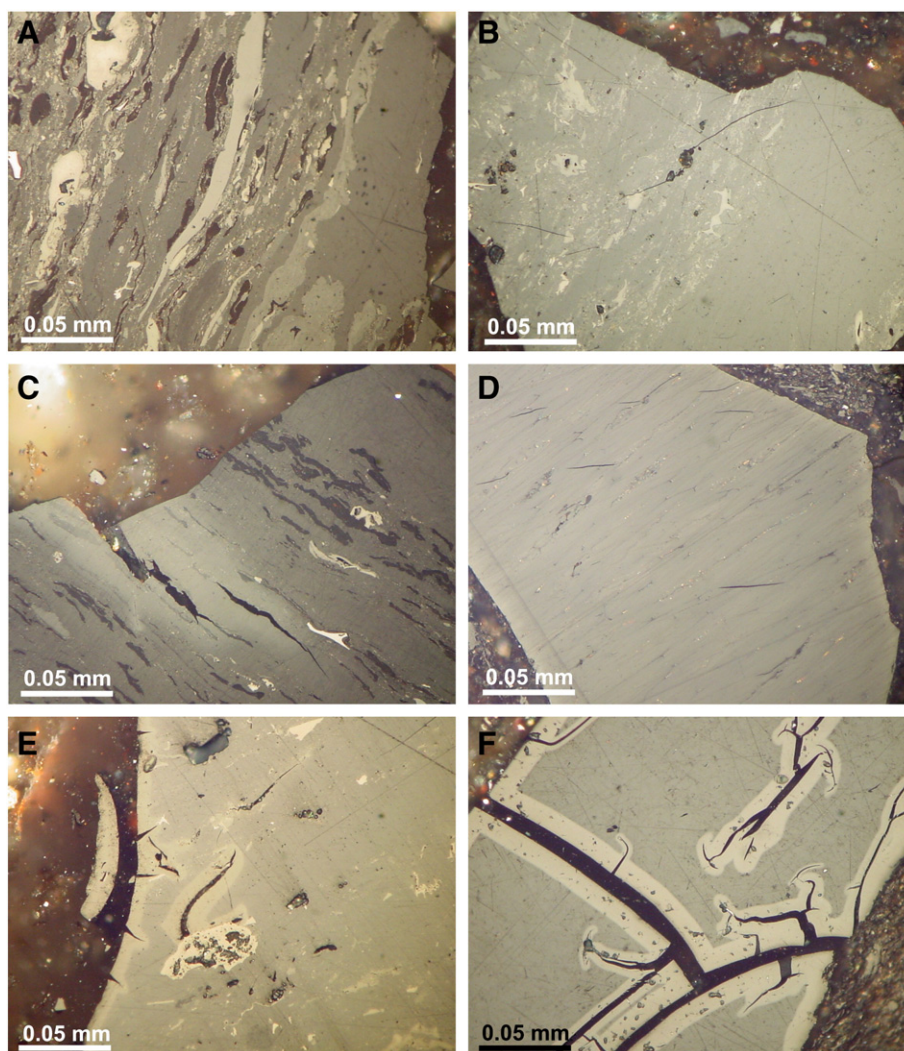


Fig. 2. Organic- and mineral matter in coal wastes from the USC (immersion oil, white light). A – macerals in trimacerite (upper part of the Starzykowiec dump). B – paler-colored vitrinite co-occurring with inertinite (upper part of the Starzykowiec dump). C – partially-oxidized trimacerite with paler-colored spores (lower part of the Starzykowiec dump). D – paler-colored vitrinite with oxidation rim and irregular cracks (Siemianowice Śląskie dump). E – paler-colored vitrinite particle associated with inertinite with irregular cracks inside and perpendicular to its edges, and paler-colored oxidation rims (lower part of the Starzykowiec dump). F – paler-colored oxidation rims around edges of vitrinite particle with irregular cracks (Rymer Cones dump).

perpendicular to them. Cracks occur typically only in moderately altered particles (Misz-Kennan et al., 2009; Misz-Kennan and Fabiańska, 2010). However, they also occur within and on the edges of strongly thermally altered organic matter particles.

Oxidation rims occur around particle edges (Fig. 2F) and/or around pores or irregular cracks (Fig. 2F). They can be paler in color (Calemma et al., 1995; Chandra, 1962; Misz et al., 2007; Misz-Kennan, 2010; Ndaji and Thomas, 1995; Stach et al., 1982) or darker in color (Bend

and Kosloski, 1993; Ingram and Rimstidt, 1984; Nelson, 1989). Oxidation rims that are paler in color have higher reflectance resulting from higher aromaticity (Chandra, 1962; Stach et al., 1982). They are probably formed at temperatures of 200 °C (Calemma et al., 1995; Ndaji and Thomas, 1995). They are typical for vitrinite particles from bituminous coals (Misz-Kennan, 2010; Misz-Kennan et al., 2011a). Darker oxidation rims probably form during oxidation in the presence of moisture and are linked to the formation of humic acids (Bend and

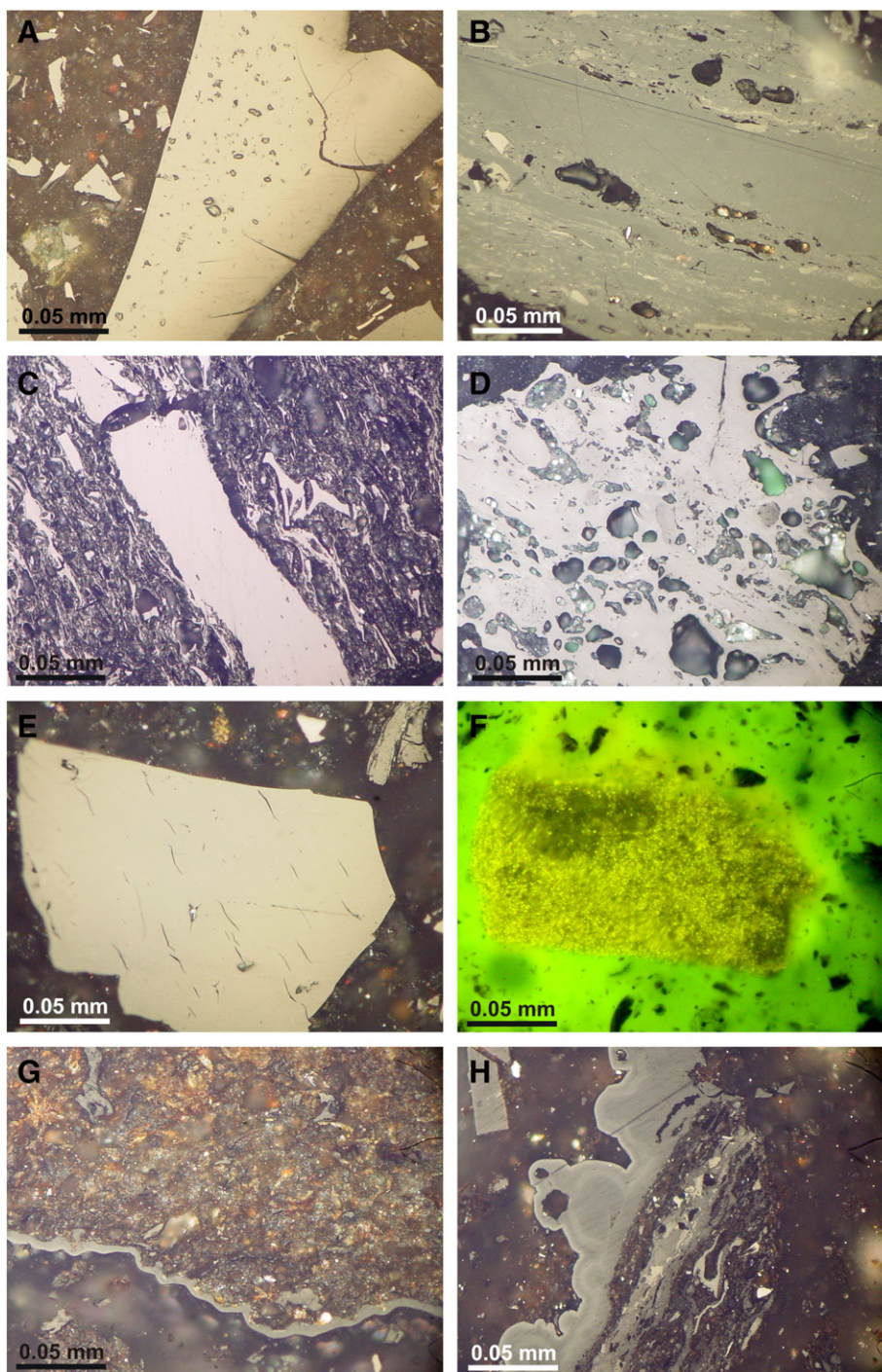


Fig. 3. Organic- and mineral matter in coal wastes from the USCBA (immersion oil). A – darker-colored oxidation rim on strongly thermally altered organic matter particle (upper part of the Starzykowice dump, white light). B – devolatilization pores in vitrinite particle (Siemianowice Śląskie dump, white light). C – strongly thermally altered organic matter in the form of massive layer and detritus occurring together with transformed minerals (Siemianowice Śląskie dump, white light). D – porous strongly thermally altered organic matter (upper part of the Starzykowice dump, white light). E – cracks in massive strongly thermally altered organic matter particle (upper part of the Starzykowice dump, white light). F – bitumen droplets (Siemianowice Śląskie dump, fluorescence). G – thin vitrinitic band surrounding mineral particle (Siemianowice Śląskie dump, white light). H – thick complex vitrinitic band on carbominerite particle (Siemianowice Śląskie dump, white light).

Kosloski, 1993). Their reflectance is also lower than that of the parent vitrinite. They have been observed in strongly altered wastes of high rank (Ribeiro et al., 2010a,b,c) and also on edges of strongly thermally altered organic matter (Fig. 3A). In some conditions, zoned oxidation rims can form that likely reflect heating stages interrupted by a drop in temperature (Ćmiel and Misz, 2005).

Porous forms are formed during faster heating that causes the organic matter to go through a plastic stage (Fig. 3B). Mostly vitrinite macerals have circular or oval pores that, in some instances, are surrounded by pale oxidation rims. It is rare for pores to occur in liptinite macerals.

Strongly thermally altered organic matter is the product of long and slow heating of organic matter, mostly of vitrinite type within the dump (Goodarzi and Murchison, 1978; Murchison, 2006). As a result, it does not give out any extractable chemical compounds. This term is used in this paper in the meaning of organic matter that was altered by temperature in self heating processes and not as a degree of thermal evolution as applied in organic geochemistry in the case of natural geochemical products. Strongly thermally altered organic matter commonly occurs with transformed clay minerals as layers of widths ranging from a few to several tens of μm , as lenses and as small irregular particles (Fig. 3C–E). Some wastes also contain porous strongly thermally altered organic matter formed during rapid heating (Fig. 3D). In general, strongly thermally altered organic matter is characterized by a white or yellowish color and high reflectance. Usually, it does not show any signs of anisotropy (Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2009). It is commonly the only form of altered organic matter remaining in heavily-altered wastes.

Bitumen expulsions are present in some wastes, e.g., in the Rymer Cones- and the Siemianowice Śląskie dumps in the Upper Silesian Coal Basin (Ćmiel and Misz, 2005; Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010). They are present in the form of droplets a few μm in size (Fig. 3F) or have irregular shapes. Their fluorescence is always very strong and yellowish. They were mostly generated from liptinite macerals in heated coal wastes.

Pyrolytic carbon is occasionally present in coal wastes. If present, it has a ribbon-like shape and is strongly anisotropic. Under laboratory conditions, it is obtained at temperatures of about 500 °C (Taylor et al., 1998). It forms in the cooler parts of dumps as a product of the thermal cracking of volatiles.

Vitrinite bands occur only in Siemianowice Śląskie dump in Upper Silesia, Poland (Misz et al., 2007). The bands, a few to several μm wide, comprise vitrinite that became plastic and now surround trimacerite-, carbominerite-, and mineral particles (Fig. 3G–H).

The random reflectance (R_r) of organic matter present in the wastes gives information about the degree of their alteration. The reflectance of unaltered organic matter in coal-waste dumps located in Poland is 0.60–0.76% (Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a). In Portugal, the reflectance is 4.82% and 4.97% R_r for wastes from the Lomba dump and 4.25 and 4.05% for wastes from S. Pedro da Cova (Ribeiro et al., 2010a; Table 3). Higher reflectance values are typical of wastes from dumps in the Upper Silesian Coal Basin (Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a). With increasing temperature, reflectance increases in bituminous coals and, commonly decreases in metaanthracites. Strongly-weathered metaanthracite wastes can have considerably lower reflectance (3.76% R_r). In wastes from burning zones, reflectance is commonly lower and in the range 4.46–5.00% for the Lomba dump and 4.18–4.75% for S. Pedro da Cova (Ribeiro et al., 2010a). The reflectance of organic matter in moderately-altered wastes from USCB dumps is approximately 0.70–1.50% (Table 3). In the most strongly altered wastes, it can reach values as high as 6.57% (Misz et al., 2007). Reflectograms of unaltered organic matter are usually narrow (Fig. 4A), commonly wider for moderately-altered

wastes (Fig. 4B–D) and widest of all for the most strongly-altered material (Fig. 4E–F). Reflectance may reveal the presence of material of different degrees of alteration in wastes; in such cases, reflectograms are wide and contain more than one maximum (Fig. 4C–D).

There is little information about the contents of individual altered forms of organic matter in wastes; publications usually give description of these forms and reflectance (e.g., Ribeiro et al., 2010a, b,c) but do not give quantitative data about contents of these forms (Table 3). Attempts at such have been made in the USCB dumps (Ćmiel and Misz, 2005; Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a). The type of organic matter is strongly dependent on the maceral composition and the level of transformation of the wastes and varies greatly (Table 3). In microscopically-unaltered wastes of low reflectance, unaltered macerals dominate. With increasing transformation and reflectance, vitrinite with cracks, pale-colored vitrinite, and vitrinite with oxidation rims dominate. Strongly thermally altered organic matter is commonly the component of strongly-altered wastes. Organic matter is microscopically absent in the most severely-altered material (Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a).

The various organic forms give information about the maceral composition and rank of unaltered organic matter, the heating rate, and presence of air within a dump. Darker-colored oxidation rims are typical of organic matter that was originally of high rank, as in Portuguese wastes (Ribeiro et al., 2010a). The forms in this type of wastes also typically contain cracks and fissures, devolatilization vacuoles, and partially-burnt particles. The reflectance of altered anthracite particles is lower than that of unaltered particles (Ribeiro et al., 2010a,b).

Wastes containing organic matter of lower rank contain a great variety of forms. These wastes are unaltered and altered to varying degrees. The heating rate seems to play a crucial role in the formation of variously altered forms. Where the temperature rose slowly (as in some dumps in the Rybnik area, Upper Silesian Coal Basin), the organic forms show no signs of plasticity (Fig. 2). The particles of organic matter have the same features as unaltered organic matter though, where more strongly altered, their color is paler gray to white and yellowish. Cracks and, in some cases, oxidation rims are also typical for moderately altered samples (Fig. 2C–F). The presence of bitumen (Fig. 3F) is characteristic for some samples. The bitumen, expelled from organic matter under conditions of slow heating and oxygen depletion occur as droplets, in irregular forms, fill gaps between minerals (e.g., clay minerals), and probably migrated into vitrinite micropores (Taylor et al., 1998). Organic matter is absent, as always, in the most strongly-altered material.

Different conditions existed in other dumps, e.g. Siemianowice Śląskie, Upper Silesian Coal Basin. Here flames were seen above the dump surface. Organic matter in the dump is mostly terrestrial. A heating rate that was much higher than in the dumps in the Rybnik area is reflected in a greater variety of forms (Fig. 3B, F, G, H). Except for unaltered wastes, organic matter is altered to varying degrees including strongly altered in this dump. Commonly, particles have pale oxidation rims around their edges and/or along cracks (Fig. 2D). Plasticized vitrinite forms bands of various widths around trimacerite, carbominerite, and mineral particles (Fig. 3G–H). Zoned oxidation rims indicating periods of heating interrupted by periods of lower temperature (Ćmiel and Misz, 2005) are, to-date, unique to this dump. Higher heating levels are reflected in the usual devolatilization pores surrounded, in some cases, by pale oxidation rims. Bands formed of plasticized vitrinite occur, as above, enclosing particles of various types. Expulsions of hydrocarbons as droplets are observed in heated sapropel material that releases a strong hydrocarbon smell and stains blotting paper on contact for a few minutes (Ćmiel and Misz, 2005; Misz et al., 2007).

Table 3
Content of various forms of organic matter and its rank in coal wastes.

Locality	Unaltered vitrinite (vol.%)	Vitrinite with cracks (vol.%)	Paler colored vitrinite (vol.%)	Plasticized vitrinite (vol.%)	Vitrinite with oxidation rims (vol.%)	Vitrinite surrounding other particles (vol.%)	Liptinite (vol.%)	Inertinite (vol.%)	Pyrolytic carbon (vol.%)	Strongly thermally altered organic matter (vol.%)	Minerals (vol.%)	R _t (%)	Reference
Rymer Cones	Min. 0.0 Max. 74.4 Aver. 14.0	0.0 9.0 1.4	0.0 33.0 2.1	0.0 0.0 0.0	- - -	- - -	0.0 10.8 1.5	0.0 13.0 3.6	0.0 0.2 0.0	0.0 5.8 0.9	17.6 100.0 76.8	0.53 1.59 0.72	Misz-Kennan, 2010
Rymer Cones	Min. 0.0 Max. 39.0 Aver. 7.6	0.0 10.8 2.0	0.0 16.8 2.4	0.0 0.0 0.0	- - -	- - -	0.0 7.6 1.2	0.0 33.8 3.0	- - -	0.0 87.0 33.1	0.0 100.0 45.5	0.65 1.32 0.83	Misz-Kennan and Fabiańska, 2010
Starzykowiec (lower part)	Min. 0.0 Max. 61.4 Aver. 14.9	0.0 6.2 0.6	0.0 11.0 0.7	0.0 0.0 0.0	- - -	- - -	0.0 5.2 1.1	0.0 12.0 2.8	0.0 0.0 0.0	0.0 2.8 0.3	21.2 98.8 79.6	0.50 1.79 0.70	Misz-Kennan, 2010
Starzykowiec (upper part)	Min. 0.0 Max. 77.8 Aver. 13.9	- - -	0.0 68.2 3.2	- - -	- - -	- - -	0.0 6.2 0.7	0.0 23 2.7	- - -	0.0 72.8 28.1	4.0 95.8 51.6	0.57 5.42 2.76	Misz-Kennan et al., 2011a
Marcel Coal Mine dump	Min. 0.0 Max. 19.4 Aver. 3.3	0.0 17.2 0.8	0.0 55.0 6.0	0.0 0.8 0.0	- - -	- - -	0.0 8.4 0.6	0.0 26.4 3.0	0.0 2.8 0.1	0.0 65.0 4.7	14.8 100.0 81.6	0.72 5.83 2.28	Misz-Kennan, 2010
Siemianowice Śląskie dump	Min. 0.0 Max. 32.2 Aver. 10.3	0.0 2 0.3	0.0 32.4 3.5	0.0 7.6 1.6	0.0 6.8 1.1	0.0 2.2 0.3	0.0 17.2 4.8	0.2 25.4 6.3	- - -	0.4 57.8 25.2	0.4 98.4 46.9	0.58 6.47 2.51	Misz et al., 2007
Douro Coalfield	Min. - Max. - Aver. -	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -	50.6 ^a 98.1 ^a 79.9 ^a	3.76 5.00 4.76	Ribeiro et al., 2010a,b

- No data;

^a ash (air dry basis; wt.%).

4.2. Organic geochemistry of coal wastes

The chemical composition of coal-waste extracts reflects the biogenic origins of their constituent organic matter, the evolution of its thermal maturity in a deposit and secondary post-depositional processes such as weathering, water-washing, and self heating (Killops and Killops, 2004; Peters et al., 2005; Tissot and Welte, 1984). As a result of many influencing factors, sometimes leading to contradictory effects, organic matter in coal wastes is very variable in character and complex in composition. However, self heating is the most important factor in dumps, profoundly altering coal-waste organic matter (Fig. 1). As outlined above, conditions such as temperature range, heating time, presence or absence of humidity and oxygen access, together with coal-waste properties such as particle sizes, rank, and inherent inorganic matter, particularly pyrite content, decree the types of products formed (Kaymakçi and Didari, 2002; Küçük et al., 2003; Lyman and Volkmer, 2001; Wanatabe and Zhang, 2001; Wang et al., 2003). Thus, from a geochemical point of view, coal waste samples should be divided into two major groups: these which underwent self heating episodes during their storage in a dump and those that did not.

4.2.1. Geochemical characteristics of coal wastes unaltered by self heating

In coal wastes not subjected to self heating, sedimentary organic matter usually shows two different geochemical characteristics. Most contain type III kerogen formed predominantly from remains of terrestrial plants subjected to bacterial activity in a swamp (Tissot and Welte, 1984). Its geochemical features are similar to those of bituminous coal excavated with the wastes both with regard to the biogenic origins of the organic matter, its chemical composition and its thermal maturity. The organic geochemistry of associated coals, when known, can be used as a reference for coal waste compositions altered by self heating and water washing in a dump. As, in many cases, it is not possible to know the detailed history of a dump or the source(s) of material in it, knowledge of the geochemistry of the parent coals can be invaluable. The organic geochemistry of bituminous coals in the Upper Silesian Coal Basin, investigated by many (Fabiańska et al., 2003; Kotarba et al., 2002; Kotarba and Clayton, 2003), underpins the understanding of the organic geochemistry of coal wastes stored in the same region (Misz et al., 2007; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2010, 2011a).

The USCB bituminous coals were formed as a part of the Upper Carboniferous coal-bearing sequence more than 8000 m thick infilling a flexural foreland basin. Its lower part (Namurian A) is of paralic type and comprises deposits of marine, shore, deltaic and fluvial sediments, whereas the upper part (Namurian B to Westphalian D) consists of non-marine deposits laid down in various fluvial systems (Kotas, 1990). The rank of coals in the USCB ranges from subbituminous to high-volatile bituminous coals. Maceral composition is more uniform; humic coals rich in vitrinites dominate here with rare sapropelic coals. The ranks and maceral-group compositions of the USCB coals have been investigated by many authors (Gabzdyl and Probiez, 1987; Knafel, 1983; Kotarba et al., 2002; Kruszevska, 1983).

In the last decade, the organic geochemistry of these bituminous coals has been investigated (Fabiańska and Matuszewska, 1998; Fabiańska et al., 2003; Kotarba and Clayton, 2003; Kotarba et al., 2002). A wide range of biomarker types and their distributions, among them *n*-alkanes, steranes, cyclic and acyclic isoprenoids, has been delineated. This work has shown that the organic matter contained in them was derived predominantly from higher-plant (terrestrial) precursors.

In some dumps, there are wastes, mostly coal shales and mudstones, in which organic matter occurs in a dispersed form without any visible coaly aggregations (Misz-Kennan et al., 2011a). This type of organic matter shows a much more pronounced

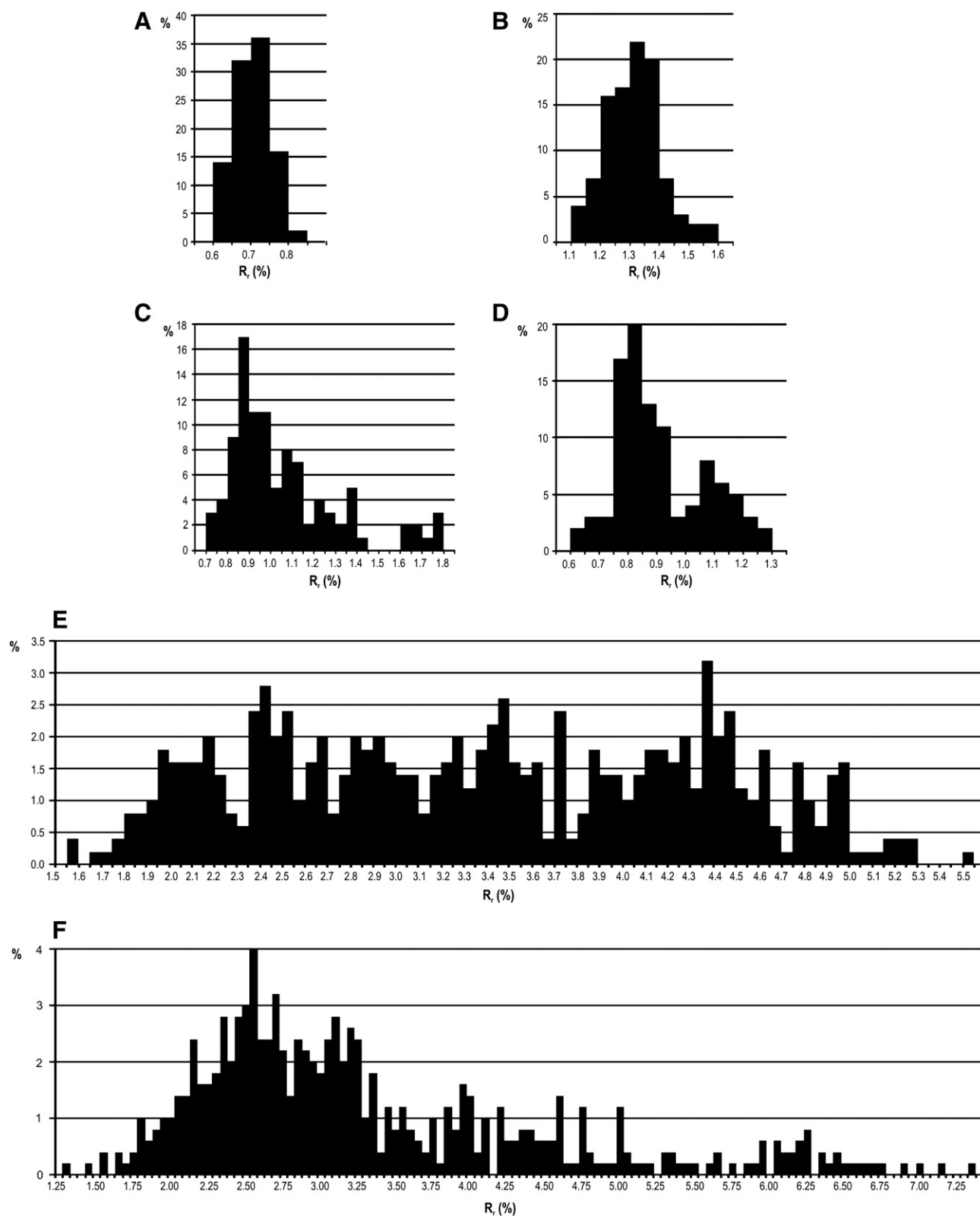


Fig. 4. Reflectograms of vitrinite-type organic matter in coal wastes from the USCB. A – reflectogram of unaltered wastes (Rymer Cones dump). B – reflectogram of moderately-altered wastes (Marcel dump). C – reflectogram of moderately-altered wastes (Rymer Cones dump). D – reflectogram of moderately-altered wastes (Rymer Cones dump). E, F – reflectograms of strongly-altered wastes (upper part of the Starzykowice dump).

sapropelic geochemical character than do coaly-type wastes. The bacterial input is much more prominent here together with some algal input whereas vascular-plant material was more degraded

before deposition. For example, geochemical investigation of USCB carbonaceous shales has shown that depositional conditions and sources of organic matter changed sharply between deposition of the

coals and the shales; the transition was not solely a continuum in relative proportions of organic-carbon- and mineral-matter input (Kotarba and Clayton, 2003).

4.2.2. Products of self heating formed within a dump

It is generally accepted that self heating causes coal oxidation, comprising such processes as chemisorption of oxygen with the formation of intermediate oxygenated complexes, the formation of unstable oxygenated complexes, the decomposition of unstable oxygenated intermediates to gaseous products and stable complexes, the degradation of stable complexes and the generation of new active sites and the decomposition of stable complexes (Wang et al., 2002a). Phenolic, carboxylic, and ketone groups increase their contents in aromatic and aliphatic structures (Garcia et al., 1999; Singh et al., 2007; Wang et al., 2002a,b). With temperature increase, the thermal destruction of organic matter macromolecules (pyrolysis) begins to dominate. It is the most important process participating in changes caused by self heating since it leads to the formation of gaseous, liquid and solid products (Stracher and Taylor, 2004). Gases comprise carbon and sulfur monoxides and dioxides, methane and volatile organic compounds (VOCs), liquid and semi-liquid products are complex mixtures of bituminous substances of pyrolytic origin and solid products are strongly thermally altered organic matter and completely burnt-out wastes (Carras et al., 2009; Pone et al., 2007; Misz-Kennan et al., 2011a; Misz et al., 2007; see Fig. 1).

4.2.3. Gases produced in self heating and self combustion

The gaseous products of self heating are of particular interest due to their toxicity, carcinogenicity and greenhouse effects (Finkelman, 2004; Finkelman et al., 2002; Kim, 2007; Stracher, 2004; Stracher and Taylor, 2004; Younger, 2004). Self heating coal-waste dumps are often situated in highly-populated industrial regions such as Upper Silesia. Such dumps should be considered a major environmental and health hazard. The odor of bitumens expelled from coal waste dumps when there is an oxygen deficiency leads to complaints from nearby residents. The most harmful compounds, however, are often odorless (e.g., carbon monoxide, monoaromatic hydrocarbons). In addition, ammonia, sulfur oxides, nitrogen oxides, hydrochloride, hydrofluoride, hydrosulphide, *n*-alkanes, *n*-alkenes, sugars, alcohols, PAHs, and heavy metals (Hg, As, Pb, and Se) are found in volatilized products (O'Keefe et al., 2010; Pone et al., 2007; Querol et al., 2011; Simoneit et al., 2007; Stracher, 2004; Stracher and Taylor, 2004).

Carbon dioxide is the main product of the self heating process, accompanied by carbon monoxide and lighter organic compounds, partially from gaseous compounds trapped in the pores of organic matter and partly from pyrolysis, depending on the temperature range, fixed carbon concentration and oxygen availability (Davidi et al., 1995; Kim, 2007; Querol et al., 2008; Younger, 2004). However, emissions of carbon dioxide and methane, the main greenhouse gases from coal and coal waste self heating, are extremely difficult to estimate because of measurement problems such as representative sampling, emission variability in time, the diffuse nature of the emissions, the large scale of measurement sites, and influence of weather conditions. For example, Carras et al. (2009) investigating emission fluxes of CO₂ and CH₄ from spoil piles and coal waste dumps at 11 mines in Australia found great variability, e.g., CO₂ emission from 1 m² ranged from about 12 kg CO₂ per year to 8200 kg CO₂ per year. According to Kim (2007), methane desorption from coal increases with temperature by about 0.001% per 1 °C.

VOCs emitted during coal- or coal-waste self combustion comprise aromatic and aliphatic hydrocarbons, and halocarbons. Benzene, toluene, ethylbenzene, xylenes, ethyltoluene, and trimethylbenzene are the main aromatic compounds present, with benzene contributing 53.7%, and toluene 42.9% of the VOCs emitted. Aliphatic hydrocarbons, present in lesser amounts than aromatic hydrocarbons, include ethane, ethylene, followed by propane, propene and butane; ethane

occurs in the highest concentrations. Small amounts of higher *n*-alkanes up to *n*-dodecane were found in emissions from burning coal wastes by Ribeiro et al. (2010a). Halogenated hydrocarbons, such as bromomethane, iodomethane, and trichloromethane, occur in the lowest concentrations of all VOCs (Davidi et al., 1995; Pone et al., 2007). Heterocyclic oxygen compounds such as furane derivatives, sulfur (thiophene derivatives) and nitrogen heterocyclics (e.g., pyridine and pyrazine) have also been identified (Ribeiro et al., 2010a).

Most of these compounds show toxic, carcinogenic and mutagenic properties (Finkelman et al., 2002; Yan et al., 2003). Because they are emitted at relatively low temperatures (Davidi et al., 1995), some of these light compounds, e.g., ethylene, can be used for early detection of spontaneous combustion of coals or coal wastes as has been proposed by Xie et al. (2011).

4.2.4. Pyrolytic products of self heating

Research on the chemical composition of coal-waste extracts should give particular attention to biomarkers (molecular fossils), organic compounds with a molecular structure showing a direct and unambiguous relationship to their precursors synthesized by living organisms (Peters et al., 2005; Tissot and Welte, 1984). After the death of an organism, biomarker precursors deposited in sediments undergo a complete evolution together with the rest of the biogenic material. Since the main chemical changes in their molecular structure are defunctionalization and saturation of double bonds, a general carbon atom skeleton of a molecule becomes preserved. Biomarker occurrences and distributions are commonly applied in research to assess thermal maturity of organic matter (rank), input of organisms participating in biogenic organic-matter formation and the sedimentary environment of the organic matter. Since coal wastes contain significant amounts of sedimentary organic matter, biomarkers can also be used to estimate the influence of water-washing, self heating and weathering.

4.2.5. Main groups of organic compounds in coal wastes

It is worth noting that, up to now, the bituminous products of self heating have been investigated in most detail in the coal wastes stored in the USCB (Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010). Thus, unfortunately, it is not possible to compare these results with others on coal wastes of lower or higher ranks from other self heating sites elsewhere.

The main groups of biomarkers commonly found in extracts from USCB coal wastes unchanged by self heating correspond to those found in bituminous coals. They comprise *n*-alkanes (*m/z* = 71), iso-alkanes (*m/z* = 71), alkylcyclohexanes (*m/z* = 83), acyclic isoprenoids, mainly pristane, phytane and, in some cases, farnesane (*m/z* = 71, 183), sesquiterpanes, tri- and tetracyclic diterpanes (*m/z* = 123, 254), tri- and pentacyclic triterpanes (*m/z* = 191), and steranes (*m/z* = 217). Steranes are, in some cases, and as in USCB coals, not present in USCB coal wastes, or occur only in low concentrations despite their obviously terrestrial origin (Fabiańska et al., 2003). When present, they show a predominance of C₂₉ sterane diastereomers, typical for coals and type III kerogens (Huang and Meinschein, 1979).

Apart from these aliphatic compounds, aromatic hydrocarbons are also abundant. Extracts of coal wastes can contain alkylbenzenes, partially aromatized compounds such as monoaromatic steranes and triaromatic steranes, and polycyclic aromatic hydrocarbons (PAHs). The last group comprises compounds with two to five condensed rings, and only rarely six rings. They include naphthalene (*m/z* = 128), fluorene (*m/z* = 166), phenanthrene and anthracene (*m/z* = 178), fluorantene and pyrene (*m/z* = 202), benzo[*a*]anthracene and chrysene (*m/z* = 228), benzo[*a*]fluoranthene, benzo[*a*]pyrene, benzo[*e*]pyrene and perylene (*m/z* = 252). In some coal wastes, benzohopanes have also been found.

Unsubstituted PAHs are accompanied by their C₁–C₅ alkyl derivatives. The most common are alkylnaphthalenes ($m/z=142$, 156, 170, 184, and 198) and alkylphenanthrenes ($m/z=192$, 206, 220, and 234) but methylpyrenes ($m/z=216$) and methylchrysenes ($m/z=232$) are also found.

All of the above compounds come from organic matter unaffected by heating within a dump. They can be preserved in coal wastes subjected to self heating as well, despite the relatively high temperatures reached. Apart from these biomarkers, such wastes can contain large amounts of products formed by the thermal destruction of organic-matter macromolecules. As a result, the extracts show the geochemical features of coal pyrolysates.

Coal wastes affected by self heating usually contain phenol and its alkyl derivatives, most commonly in the range from C₁ to C₂ ($m/z=94+14$). In some cases, even higher substituted compounds up to C₅ phenols are found ($m/z=134$, 150, 164). In addition, C₃ phenols such as *p*-propylphenol, *p*-vinylguaiacol, 2-ethyl-6-methylphenol and 3-ethyl-5-methylphenol are quite common in relatively freshly-heated coal wastes (Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010).

Despite the high contents of elementary sulfur in most extracts of the USCB coal wastes, benzothiophenes and dibenzothiophenes have not been found in amounts significant enough to allow their application in geochemical interpretation.

4.2.6. Distributions of particular organic compounds groups

4.2.6.1. *n*-Alkanes. Aliphatic hydrocarbons are dominated by *n*-alkanes. In some USCB coal waste extracts, *n*-alkenes ($m/z=69$) are also found. Generally, four types of *n*-alkane distributions can be distinguished (Fig. 5):

- 1) Bimodal distributions with variable contents of short-chain (*n*-C₁₃–*n*-C₂₂) and long-chain (*n*-C₂₃–*n*-C₃₆) compounds, similar to distributions found in the bituminous coals of the region (Fig. 5A),
- 2) Monomodal wide distributions characteristic of organic matter in coal muds and coal shales with almost the same concentrations in the range of *n*-C₁₈–*n*-C₂₆ (Fig. 5B);
- 3) Monomodal Gaussian distribution with *n*-alkane peaks indicating pyrolysis (Fig. 5C–F). Though *n*-alkanes can occur in variable ranges and numbers of compounds, generally these types of *n*-alkane distributions are similar to those of low-temperature tars recovered from USCB coals (Fabiańska and Matuszewska, 1998). The *n*-alkane distribution maximum moves in response to increasing self heating temperatures.
- 4) Distributions of mixed type, with a partial input of pyrolytic-type (3) and coal-type *n*-alkanes (3). These distributions result from pyrolysate migration within a dump and mixing migrating pyrolysates and coaly bitumen present in situ.

The widest distributions contain compounds in the range from *n*-C₁₃ to *n*-C₃₅ *n*-alkanes, whereas the narrowest ranges comprise only a few compounds. Many USCB coal-waste extracts of types (1) and (2) show a slight predominance of odd-over-even carbon atom number

n-alkanes – a feature characteristic of thermally unchanged coal wastes which is numerically reflected by values of the Carbon Preference Index (CPI) > 1.0 (Tables 2 and 4).

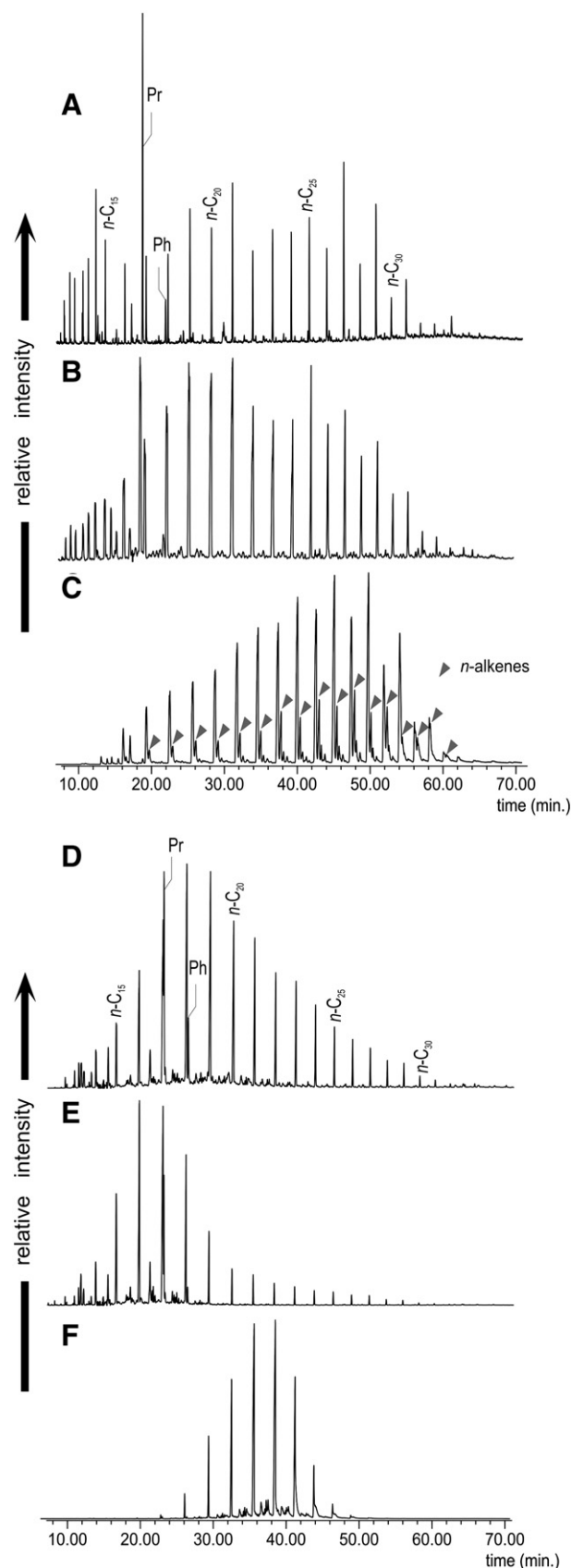


Fig. 5. Distributions of *n*-alkanes ($m/z=71$) in coal-wastes extracts from the Upper Silesian Coal Basin. A – Terrestrial type of *n*-alkane distribution unchanged by self heating, kerogen type III (Starzykowice dump). Pr – pristane, Ph – phytane. GC separation performed on a DB-17 column. B – *n*-Alkanes in coaly-mud extract, kerogen type II/III (Starzykowice dump). GC separation performed on a DB-17 column. C – *n*-Alkane- and *n*-alkene distributions in coal wastes highly altered by self heating (Starzykowice dump). GC separation performed on a DB-17 column. D – Wide *n*-alkane distribution reflecting a wide range of heating temperatures affecting coal wastes (Marcel dump). GC separation performed on a HP5 column. E – A narrow distribution of short-chain *n*-alkanes with *n*-C₁₅–*n*-C₁₉ predominance reflecting processes of pyrolysates migration and precipitation within a dump (Marcel dump). GC separation performed on a HP5 column. F – Narrow distribution of longer-chain *n*-alkanes with *n*-C₂₂–*n*-C₂₅ predominance reflecting processes of pyrolysate migration and precipitation within a dump (Marcel dump). GC separation performed on a HP5 column.

Table 4

Ranges of values for extract yields and common biomarker parameters in coal wastes from the Upper Silesia Coal Basin (Misz et al., 2007; Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a); biomarker-parameter formulae are shown in Table 2.

Parameter	Range of values	Biomarker parameter	Range of values
Extract yield (% wt.)	Max. 11.29 Min. 0.0001 Aver. 2.40	Pr/n-C ₁₇	Max. 11.29 Min. 0.18 Aver. 2.40
CPI	Max. 2.89 (7.30 ^a) Min. 0.71 ^b Aver. 1.47	Ph/n-C ₁₈	Max. 1.58 Min. 0.06 Aver. 0.51
Σ2/Σ1	Max. 30.26 Min. 0.03 Aver. 4.55	Ts/(Ts + Tm)	Max. 0.91 Min. 0.37 Aver. 0.76
23/31	Max. 82.3 Min. 0.02 Aver. 6.24	C ₃₀ βα/(αβ + βα)	Max. 0.48 Min. 0.07 Aver. 0.36
Pr/Ph	Max. 10.89 Min. 0.55 Aver. 4.21	C ₃₀ ββ/(ββ + αβ + βα)	Max. 0.26 Min. 0.01 Aver. 0.13
C ₃₁ S/(S + R)	Max. 0.62 Min. 0.32 Aver. 0.51	TNR-4	Max. 0.79 Min. 0.13 Aver. 0.57
MNR	Max. 2.30 Min. 0.38 Aver. 1.13	2-MP/2-MA	Max. 10.28 Min. 0.61 Aver. 48.50
DNR	Max. 3.75 Min. 0.70 Aver. 1.49	MPI-3	Max. 2.15 Min. 0.51 Aver. 1.04
TNR-1	Max. 7.31 Min. 0.34 Aver. 1.06	MB/DBF	Max. 0.69 Min. 0.07 Aver. 0.42
TNR-2	Max. 0.47 Min. 1.75 Aver. 0.81		

^a Coal wastes contaminated by recent soil material.

^b Some pyrolysates show CPI values below 1.0

The common feature of coal-wastes self heated to relatively low temperatures is a predominance of short-to-long chain *n*-alkanes. In some USCB (Rymer Cones) wastes, this predominance is extremely high; contents of long-chain *n*-alkanes are very low. These differences in distribution are reflected in values of S1/S2 ratio (Table 2). The ratio of *n*-C₂₃/*n*-C₃₁, normally considered a source parameter (Pancost et al., 2002), may also be used to estimate a range of thermal alterations; lowest values are found in completely-altered wastes and the highest (14.83) in moderately-altered material (Table 4).

n-Alkenes in waste extracts can have two sources – soils covering many dumps (recent organic matter) and pyrolysates. However, it is not difficult to distinguish between the two sources as their distribution types differ markedly. Soil *n*-alkenes show high odd-over-even predominance with CPI values in the range 5–7 (the range similar to soil *n*-alkanes) whereas pyrolysate *n*-alkenes have a smoothly-outlined chromatogram with a general outline of *n*-alkene peaks following the *n*-alkane distribution. *n*-Alkenes in pyrolysates mainly come from liptinite macerals with only some short chain *n*-alkenes possibly related to vitrinite (Fig. 5F).

4.2.6.2. Acyclic isoprenoids. Pristane (Pr) and phytane (Ph) seen on the *m/z* = 71 and 183 ion chromatograms are common in the USCB wastes but there are significant differences in their concentrations and ratios depending on the self heating temperature and on increasing pyrolytical changes in organic matter (Fig. 5). Generally, coaly wastes influenced to a low degree by self heating show high values of Pr/Ph and Pr/n-C₁₇ (ca 5.0–10.0; Table 4) similar to those typical of bituminous coals (Didyk et al., 1978; Goossens et al., 1984; Mastalerz et al., 1997). With increase in heating, values of both ratios tend to decrease significantly. The most severely altered samples from the Rymer Cones have the lowest values of Pr/Ph (ca 0.70) (Misz-Kennan

and Fabiańska, 2010). These same samples are also characterized by low Pr/n-C₁₇ and the highest Ph/n-C₁₈ values. Such changes are commonly found in pyrolysates of bituminous coals of this region (Fabiańska and Matuszewska, 1998; Razvigorova et al., 1995). It is worth mention that values of Pr/Ph, Pr/n-C₁₇ and Ph/n-C₁₈ are affected by many factors such as organic-matter rank and water-washing (Leythaeuser and Schwarzkopf, 1986).

Pristenes, compounds commonly found in laboratory pyrolysates of organic matter formed under various conditions (Goossens et al., 1988a,b) are not present in the USCB coal wastes affected by self heating.

4.2.6.3. Diterpanes. Diterpanes (*m/z* = 123) are mainly present in the USCB wastes unaltered or relatively weakly altered by heating within a dump. Small amounts of 16α(H)-phylocladane (*m/z* = 259 and 274) have been found in a few Rymer Cones samples. Since these compounds derive from biochemical precursors present in conifer resins, they are commonly found in coals, including bituminous coals of the Upper Silesian Coal Basin and other European coal basins (Fabiańska et al., 2003; Kotarba and Clayton, 2003; Schultze and Michealis, 1990). The presence of tetracyclic diterpanes, including 16α(H)-phylocladane, in the Pennsylvanian coals is explained by assuming that their biochemical precursors were synthesized by conifer ancestors since conifers had not evolved at that time (Michealis et al., 1990; Schultze and Michealis, 1990).

4.2.6.4. Pentacyclic triterpanes. Distributions of pentacyclic triterpane (hopanes and moretanes) are very similar in all USCB coal-waste extracts in which these compounds occur (Fig. 6A–C). This group of biomarkers comprises compounds from C₂₇ to C₃₃ including a series of 22R and 22S diastereomers from 17α(H),21β(H)-29-homohopane

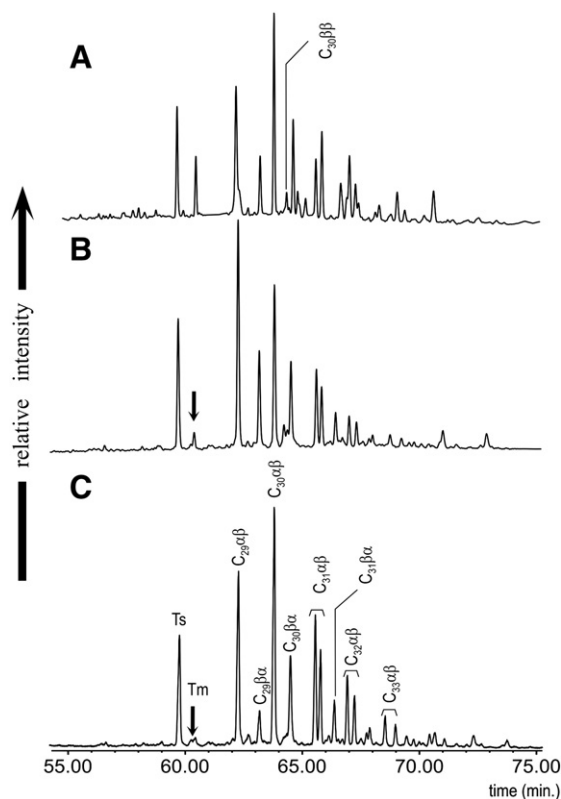


Fig. 6. Examples of pentacyclic triterpenoid distributions in USCB coal wastes (*m/z* = 191). A – Coal wastes from the upper part of the Starzykowice dump unaffected by self heating. B – Coal wastes from the Rymer Cones dump that underwent a recent episode of self heating. C – Coal wastes from the Marcel dump coal strongly affected by self-heating.

(C₃₁) to 17 α (H),21 β (H)-29-trishomohopane (C₃₃). In all samples, 17 α (H),21 β (H)-30-norhopane (abbrev: C₂₉ $\alpha\beta$ hopane) or 17 α (H),21 β (H)-29-hopane (abbrev: C₃₀ $\alpha\beta$ hopane) occurs in the greatest amounts. Such a short distribution, typical for kerogen III hopanes, is sometimes used to differentiate between marine- and terrestrial organic matter, for example in smoke or atmospheric precipitation (Oros and Simoneit, 2000; Peters et al., 2005). Despite the temperature, moretanes are present in relatively high quantities even in coal wastes affected by self heating, but the concentrations of 17 α (H),21 β (H) hopane diastereomers (abbrev: $\alpha\beta$) are much higher than those of (17 β (H),21 α (H) moretane diastereomers (abbrev: $\beta\alpha$). Values of the moretanes/hopanes ratio are to be seen on Fig. 6B–C and Table 4. That a comparable pattern of hopane distribution has been noted in humic-coal pyrolysates after heating for 1000 h (Lu and Kaplan, 1992) indicates their relatively high resistance to thermal degradation.

Despite the relatively high rank of the primary organic matter, (R_r 0.65%–1.32%) 17 β (H),21 β (H) hopane diastereomers (abbrev: $\beta\beta$) occur in some self heated USCB coal wastes, but always in the lowest concentrations (see Fig. 6A). This is reflected by ratios of 17 β (H),21 β (H)-29-hopane C₃₀ to the sum of all C₃₀ hopanes (abbrev: C₃₀ $\beta\beta$ /($\beta\beta$ + $\alpha\beta$ + $\beta\alpha$) in the range 0.01–0.26 (Table 4). A lack of pentacyclic triterpanes in some USCB coal wastes reflects the fact that their extracts are low-temperature pyrolysates prone to migrate; these compounds require high temperatures to evaporate.

Hopane parameters are of variable use in the assessment of degrees of self heating. Vitrinite reflectance values in thermally unaffected wastes are about 0.8%. At this point, the ratio of 17 α (H),21 β (H)-29-homohopane 22S/(17 α (H),21 β (H)-29-homohopane 22S + 17 α (H),21 β (H)-29-homohopane 22R) (abbrev: C₃₁ S/(S + R)) reaches its validity range also with its most common values being about 0.52–0.60 (Table 4). The ratio 18 α (H)-22,29,30-trisnorhopane/(18 α (H)-22,29,30-trisnorhopane + 17 α (H)-22,29,30-trisnorhopane) (abbrev: Ts/(Ts + Tm)) seems much more useful. The arrow in Fig. 6 shows a decrease in Tm relative concentration with heating. Values of Ts/(Ts + Tm) range from 0.37 to 0.91, though the most common lie in the range 0.75–0.90. Such high values are obviously caused by self heating since they are, as noted above, not consistent with the presence of hopane $\beta\beta$ diastereomers indicating low thermal maturity. Values of the moretane to $\alpha\beta$ hopane ratio also seem to be quite sensitive to self heating; this ratio ranges from 0.08 in high-temperature pyrolysates to 0.48 in coal wastes unaffected by heating.

4.2.6.5. Steranes. Steranes occur in some thermally-unchanged USCB coal wastes. Their concentrations are, however, so low that biomarker parameters based on them are unreliable. All distributions are dominated by stigmastane diastereomers (C₂₉ steranes) as shown in Fig. 7. This feature is common in coals since their primary organic matter predominantly comes from vascular plants in the tissues of which sitosterol and other C₂₉ steranes prevail (Huang and Meinschein, 1979; Peters et al., 2005).

4.2.6.6. Aromatic hydrocarbons

4.2.6.6.1. Polycyclic aromatic hydrocarbons (PAHs). Most coal-waste extracts contain unsubstituted polyaromatic hydrocarbons in variable contents and distributions, depending on types of coal wastes stored and the self heating history of the hosting dump. Naphthalene and biphenyl are common two-ring PAHs. Three-ring PAHs include phenanthrene, anthracene, and, sometimes, phenyl-naphthalenes. Four-ring PAHs are represented by fluoranthene, pyrene, benzo[ghi]fluoranthene, benzo[a]anthracene and chrysene. Five-ring PAHs, e.g., benzo[b+k]fluoranthene, benzo[a]fluoranthene, benzo[e]pyrene, benzo[a]pyrene and perylene are common in very low concentrations.

These compounds can come from coal-waste organic matter unaffected by self heating or be formed by incomplete combustion/

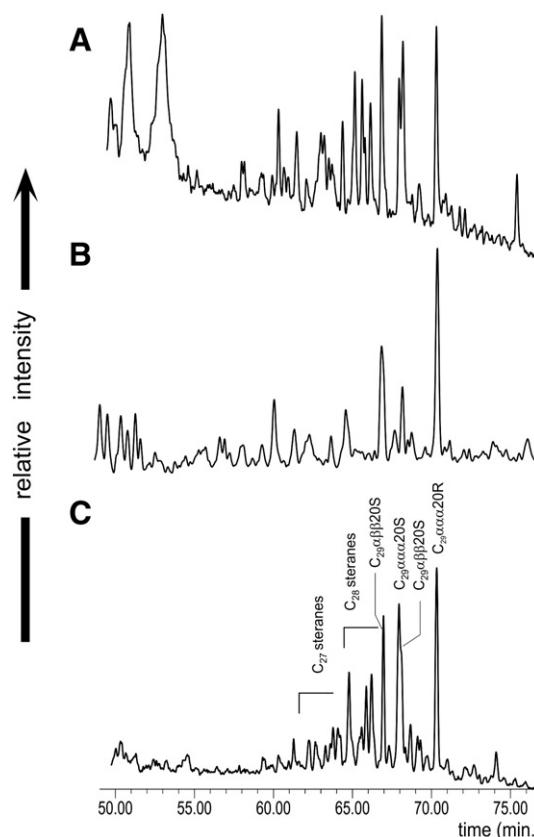


Fig. 7. Examples of sterane distributions ($m/z = 217$) in USCB coal wastes. A – Marcel dump. B – Upper part of the Starzykowice dump. C – Lower part of the Starzykowice dump.

self heating (Simoneit, 1998). In USCB wastes, PAHs are mainly represented by two- to five-ring compounds (Fig. 8). PAHs with more than five rings were generally absent despite their wide occurrence in the products of incomplete combustion of fossil fuels and coal pyrolysates (e.g., Radke, 1987; Simoneit, 1998). Only in a few coal waste extracts do six-ring PAHs such as benzo[ghi]perylene occur (Fig. 8A). This may reflect their origin in the primary organic matter of the coal wastes rather than during self heating; the most common PAHs in fossil fuels are compounds with up to five aromatic rings (Peters et al., 2005).

Two important factors influence PAHs distribution. The first is the self heating temperature range. In particular, this strongly affects the composition of wastes also subjected to a chain of subsequent processes, e.g., heating, coal-waste pyrolysis, pyrolysate evaporation migration of pyrolysates and eventual precipitation in colder zones of a dump (Fig. 1). As a result, pyrolysate fractionation occurs with a heavier fraction being left closer to a heating zone and a lighter fraction precipitated distally. Thus, in many coal waste dumps, PAHs' distributions reflect ranges of self heating temperatures of heating and precipitation. PAHs' distributions changed in this way are commonly found in pyrolysed coal wastes also showing a Gaussian n -alkane distribution (Fig. 8B, C; e.g., Casal et al., 2008; van Niekerk et al., 2008).

The second factor affecting PAHs' distribution is coal wastes is weathering and leaching by atmospheric precipitation (Fig. 1). Due to longevity of PAHs' residence in a dump, they can be dissolved in water or oxygenated. The first to be removed is naphthalene due to its relatively high solubility in water. Phenanthrene and anthracene, less soluble in water, are affected to the lesser degree, but can be removed in older dumps (Misz-Kennan, 2010; Misz-Kennan et al., 2011a).

Generally, two- and three-ring PAHs predominate in thermally-unaltered, unweathered- and moderately-altered wastes. Biological

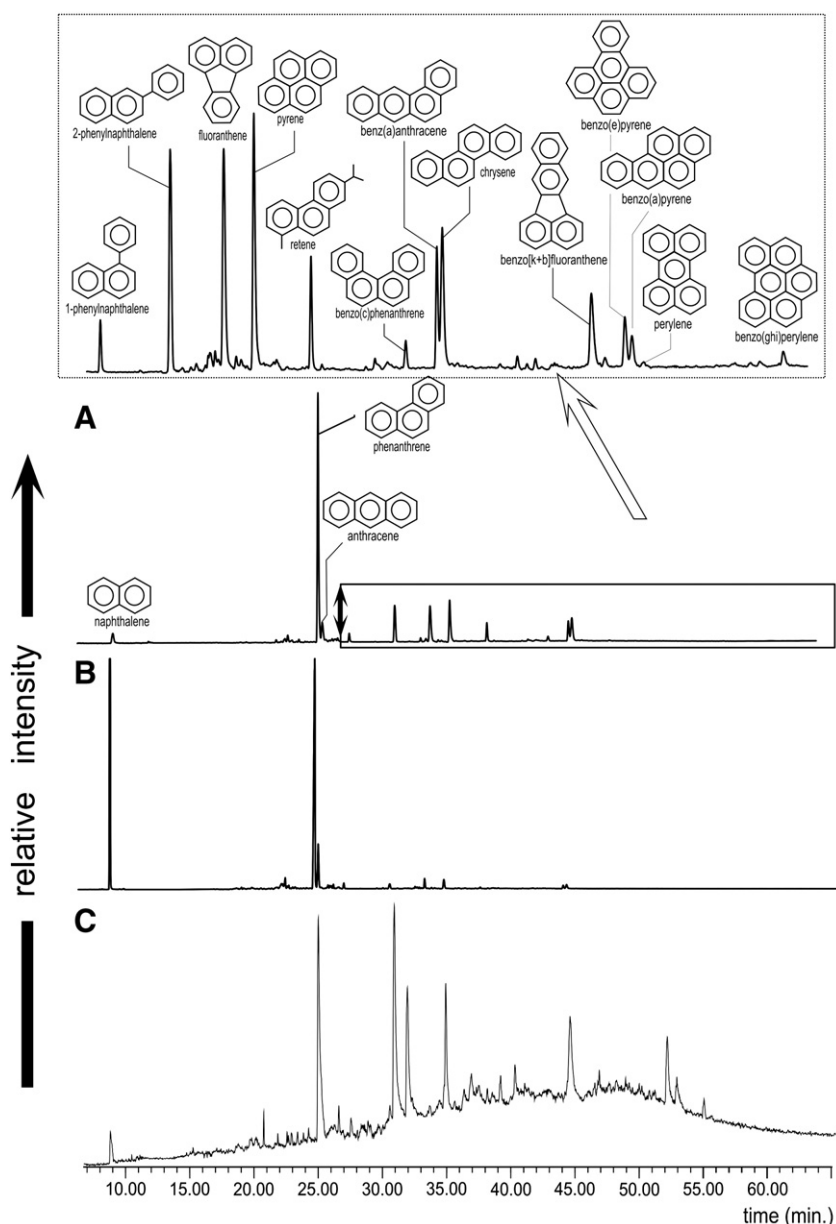


Fig. 8. Variability of polycyclic hydrocarbon (PAHs) distribution in USCB coal wastes shown on combined ion chromatograms $m/z = 128 + 178 + 202 + 204 + 228 + 252 + 276$. A – Siemianowice Śląskie dump. B – Marcel dump. C – Upper part of the Starzykowice dump.

precursors of phenanthrene such as diterpanes, or abietic acid and its derivatives, are so common in the biosphere (particularly in vascular plants) that it is often the most abundant polyaromatic hydrocarbon (Alexander et al., 1986; Killops and Killops, 2004; Simoneit, 1977). Anthracene usually occurs in much lower concentrations though, in inertinite-rich wastes, it can reach about 40% rel. (Misz-Kennan, 2010). Such distributions, similar to those found in the coals of the Silesian region and in other bituminous coals all over the world (Casal et al., 2008; Fabiańska et al., 2003; Mastalerz et al., 1997; Stout and Emsbo-Mattingly, 2008), indicate low influence by self heating. Very high naphthalene quantities, found in freshly-heated coal wastes, result from pyrolysate fractionation as described above. Such pyrolysates usually also contain high quantities of lighter n -alkanes in the range n -C₁₀– n -C₂₂ and abundant phenol derivatives. Only in coal wastes severely altered by self heating do four-ring PAHs dominate over those with two- and three-rings. Five-ring PAHs occur always in low amounts, usually less than 15% of all PAHs, with contents in coal-shale extracts being particularly low (Misz-Kennan et al., 2011a).

4.2.6.6.2. Alkyl naphthalenes and alkyl phenanthrenes. Various thermal parameters based on aromatic hydrocarbons give additional insight into the alteration of organic matter in wastes. Methyl naphthalenes, dimethyl naphthalenes and various other aromatic compounds are generated during the pyrolysis of vitrinite and sporinite (Horsfield, 1989). Contents of aromatic compounds relative to n -alkanes increase with temperature and, at 400 °C, they are dominant in pyrolysates (Pan et al., 2009, 2010). It has also been noted that amounts of aromatic hydrocarbons markedly increase with reflectance (Radke et al., 1986). As a result, alkyl naphthalenes and alkyl phenanthrenes-based parameters are among the most important in interpretation of coal-waste geochemistry.

In USCB coal wastes, the highest concentrations are usually shown by lighter aromatic hydrocarbons, i.e., C₀–C₄ alkyl naphthalenes and C₀–C₄ alkyl phenanthrenes (Figs. 9 and 10). This is particularly evident in those coal wastes that were not severely leached or weathered (Misz-Kennan et al., 2010; Skręt et al., 2010). Except for cadalene and isocadalene ($m/z = 198$) which usually show high contents, amounts

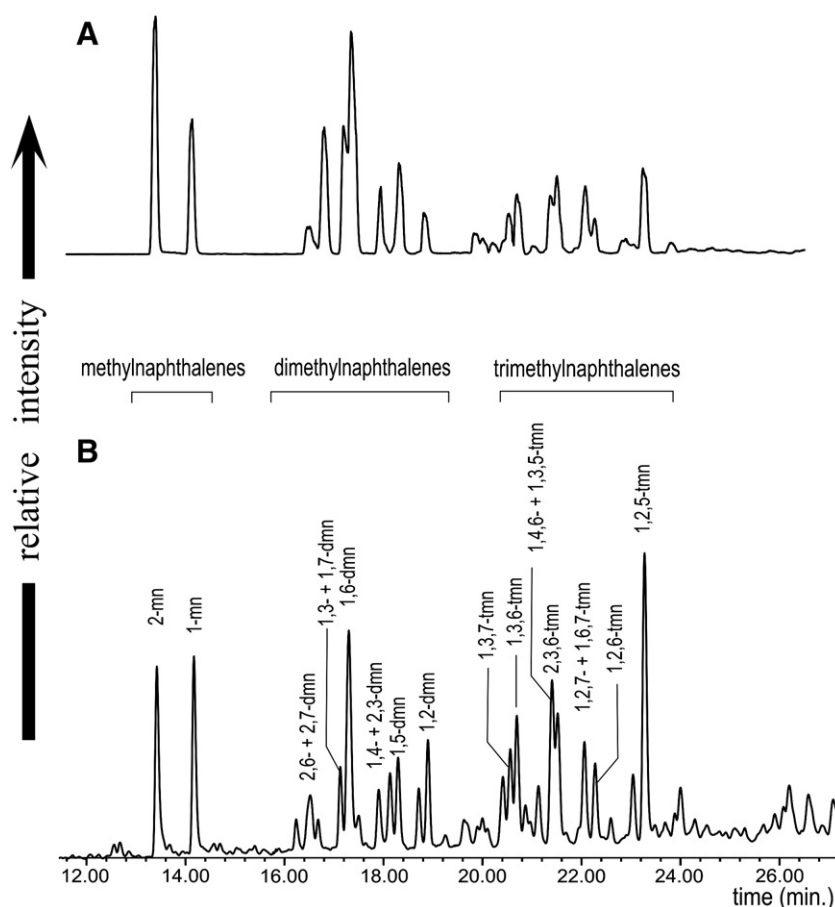


Fig. 9. Distributions of alkylnaphthalenes in USCB coal wastes shown on combined ion chromatograms $m/z = 142 + 156 + 170$. A – lower part of the Starzykowice dump. B – upper part of the Starzykowice dump.

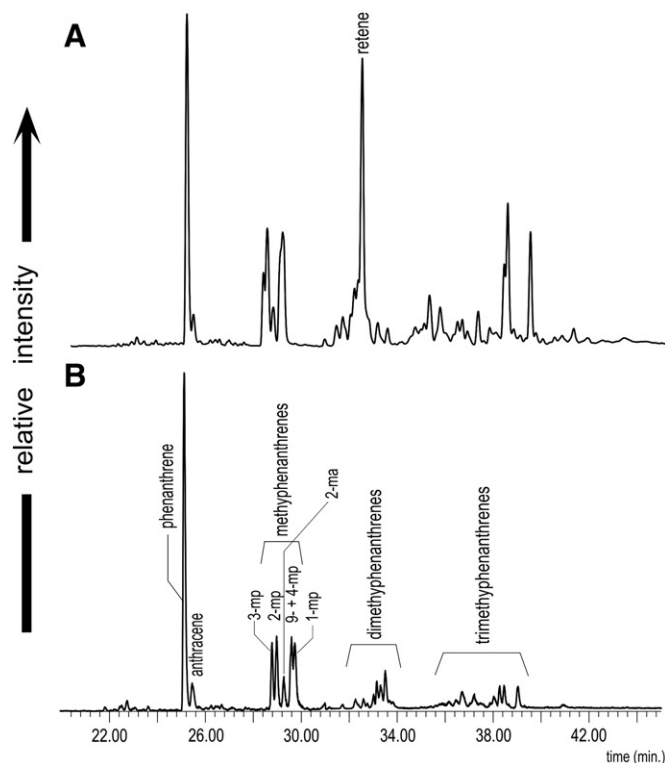


Fig. 10. Distributions of alkyphenanthrenes in USCB coal wastes shown on combined ion chromatograms $m/z = 192 + 202 + 220$. A – Rymer Cones dump. B – Lower part of the Starzykowice dump.

of C_4 and C_5 alkylnaphthalenes are so low that it is difficult to identify particular compounds or to calculate parameters (Fig. 9).

Alkylphenanthrenes in most USCB wastes are essentially limited to methyl-, ethyl- and dimethylphenanthrenes (Fig. 10), though C_3 and C_4 alkyphenanthrenes are occasionally found. Usually, only methylphenanthrenes amounts are sufficiently high to calculate geochemical parameters. Only a few extracts contain C_3 to C_5 alkyphenanthrenes. Retene and isoretene ($m/z = 234$) are an exception to this rule; they are found in most extracts.

Alkylnaphthalene- and alkyphenanthrene parameters of thermal maturity can be used to assess the influence of self heating on coal wastes (Table 2; Radke, 1987; Radke et al., 1986, 1994). However, in the case of the Methylphenanthrene Ratio (MNR), it is difficult to find any significant trends as it is easily influenced by leaching due to the relatively high solubility of these compounds in water. Values of the dimethylnaphthalene- (DNR) and trimethylnaphthalene ratios (TNR-1, TNR-2 and TNR-4; see Table 2) seem to show much better trends related to self heating. Maximal-, minimal- and average values of these ratios are given in Table 4. The methylphenanthrene ratio (MPI-3, see Table 2) seems to be one of the best aromatic-hydrocarbon parameters since its validity range falls in the range of coal wastes both affected and unaffected by self heating, methylphenanthrenes occur commonly in coal-waste extracts and, compared to alkylnaphthalenes, they are not so easily leached with water.

4.2.6.7. Phenol derivatives and other oxygen compounds. Alkyl derivatives of phenol are one of the most important functional compounds in USCB coal-waste extracts (Fig. 11). They comprise phenol ($m/z = 94$), *o*-, *m*- and *p*-cresols ($m/z = 108$), ethylphenol and dimethylphenol isomers with 2,4- and 3,5- dimethylphenol most

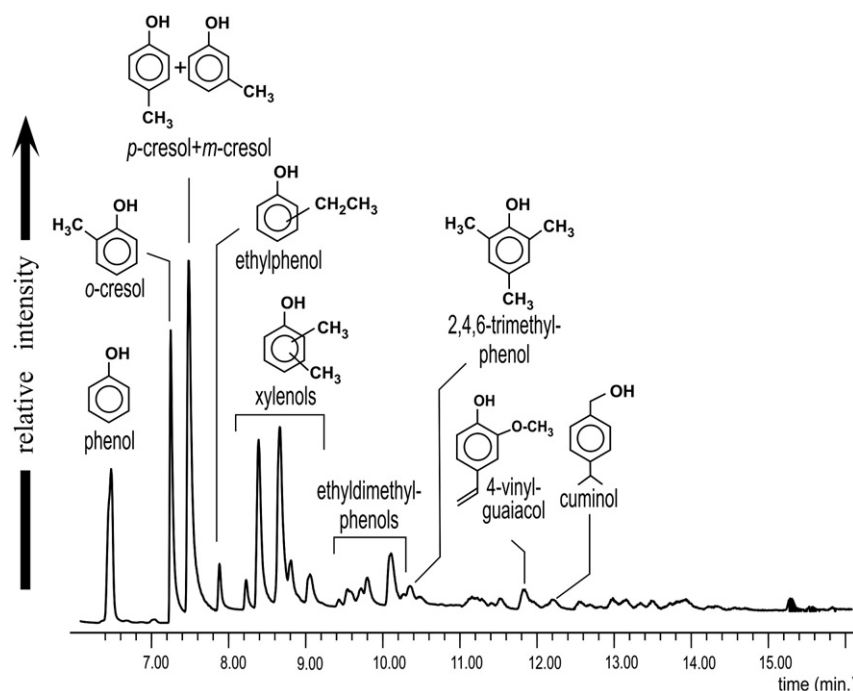


Fig. 11. Distribution of phenol derivatives in the USCIB coal wastes shown on combined chromatograms $m/z = 94 + 108 + 122 + 134 + 150$ (Marcel dump).

commonly identified ($m/z = 122$) and more highly substituted compounds up to C_5 phenols ($m/z = 134, 150, 164$). Usually, there are a few C_3 phenols present with various functional and aliphatic groups substituted in an aromatic ring, for example *p*-propylphenol, *p*-vinylguaiacol, 2-ethyl-6-methylphenol and 3-ethyl-5-methylphenol. The group of C_4 phenols comprises several compounds with 4-vinyl-2-methoxyphenol and methylpropylphenols the most abundant. C_5 phenols, if present, occur in the lowest amounts. Distributions are very similar with phenol or cresols showing the highest contents and decreasing concentrations for more highly substituted phenols. This uniformity of phenol distributions results from the similar humic characteristics of the organic matter (kerogen III) present in the wastes. These compounds derive from vitrinite macerals from which thermal destruction released units formerly components of the lignin macromolecule (Hatcher and Clifford, 1997; Hatcher et al., 1992). They are commonly found in pyrolysates or thermochemolysis products of terrestrial organic matter recovered under laboratory conditions (Casal et al., 2008; Greenwood et al., 2000; Iglesias et al., 2000; McKinnley and Hatcher, 1996; Standley and Kaplan, 1998; van Niekerk et al., 2008).

High concentrations of phenols correlate with high concentrations of heterocyclic oxygen compounds such as benzofurane, dibenzofurane, alkylbenzofuranes and alkylidibenzofuranes. As it is assumed that the source of furanes is cellulose in sedimentary organic matter which contains pentacyclic furanose units, their abundance in the extracts is related to thermal destruction of the organic matter macromolecule (Iglesias et al., 2002; Radke et al., 1990, 2000).

The exact distribution of phenols can be influenced by many factors, e.g., organic-matter origin and its rank (Hatcher et al., 1992). Post-depositional processes such as the leaching of organic compounds related to atmospheric precipitation are also influential (Skřet et al., 2010).

5. Discussion

Petrographic- and geochemical data from coal-waste dumps are mutually complementary. The experience gained investigating dumps located in the USCIB suggests that all dumps are different. This is not

surprising considering their history and the varied properties of the material dumped in them.

In the literature, the term “coal waste fires” is found. The studies carried out on four dumps in the USCIB have shown that the term does not always reflect the nature of the processes taking place within dumps. Pyrolysis or smoldering would seem to be more appropriate terms (Hadden and Rein, 2009) as the processes take place under oxygen-depleted conditions and commonly without flames. Flames were seen only in Siemianowice Śląskie dump. Oxygen present in the dumps originates from atmospheric precipitation (rain fall and melting snow) and/or decomposition of organic compounds (Berkowitz, 1985; Clemens et al., 1991; Sokol, 2005; Wang et al., 2002a). With regard to the presence of water, the term hydrous pyrolysis can be applied (Misz-Kennan, 2010). Water present in dumps also acts as a solvent and probably promotes the migration of organic compounds through them. Chemical reaction leads to the incorporation of water-derived hydrogen in organic matter (Leif and Simoneit, 2000; Lewan, 1992).

The presence of air seems to be important for the initiation of self heating. Later reactions take place under oxygen-depleted conditions. Two types of chemical reactions, cracking and condensation, are important in this context.

Chemical compounds generated from organic matter migrate within dumps (Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a). This migration is multidirectional and driven by evaporation and leaching processes. Migration is generally from spots of higher temperature to parts of the dumps with lower temperatures. That explains the presence of organic compounds in the range of 50–400 Da in wastes totally altered thermally in which no organic matter is visible under the microscope. Organic compounds are typically absent in wastes containing strongly thermally altered organic matter (Misz-Kennan, 2010; Misz-Kennan et al., 2011a).

One of the best examples of a place where the processes described above have occurred is the upper part of the Starzykowice dump (Misz-Kennan et al., 2011a). Self heating took place there over several tens of years and the wastes show varying degrees of alteration. Coal muds in the top part of the dump usually contain unaltered organic

matter of reflectance 0.6–0.7% and the highest contents of unaltered macerals. In other parts of the dump, moderately thermally-altered wastes of reflectance 0.6–1.6% contain considerable amounts of oxidized vitrinite and strongly-altered wastes with strongly thermally altered organic matter of reflectance 1.86–5.42%. Though organic compounds are typically absent in strongly thermally altered wastes, they are to be found nearby in adjacent, completely altered wastes; the organic compounds apparently migrated into and precipitated in the completely burnt-out wastes. These wastes elsewhere generally contain very low amounts of extractable organic matter.

5.1. Migration of pyrolysates within coal-waste dumps

Surprisingly, some burnt-out wastes, rich in mineral matter, contain considerable amounts of extractable bitumen fraction (Misz-Kennan et al., 2011a). This indicates that significant migration of pyrolysates occurred from deeper, self heating zones. This process occurs in the following stages (Fig. 1):

- 1) Pyrolysis of coal wastes under oxygen-deficient conditions with the formation of pyrolysates;
- 2) Partial evaporation of pyrolysate causing fractionation; lighter compounds concentrate in vapors whereas heavier compounds stay in the pyrolysate residue close to the heating zone;
- 3) Migration of lighter fractions outwards from the heating zone;
- 4) Precipitation of organic compounds in colder dump environments.

If self heating occurred several times in the history of a dump, migrating bitumen can be found even in totally burnt-out coal wastes formed during earlier heating events. Moreover, such burnt-out wastes are highly adsorptive for pyrolysates.

Additionally, in this way the migrating lighter fractions of coal-waste pyrolysate can mix with bitumen present in situ, derived from

two sources, i.e., primary unaltered coaly wastes and thermally-changed organic material (Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a). This adds to the general compositional complexity of the coal-waste bituminous fraction. While in-situ bitumens occur within coal waste fragments or in their pores, migrated bitumens are usually on grain surfaces and not bound to the organic-matter macromolecule.

5.2. Effects of leaching (water-washing) on the composition of the bituminous fraction in coal wastes

Apart from the leaching of heavy metals from burnt-out wastes described by, e.g., Wang et al. (2001) and Querol et al. (2008), organic compounds are susceptible to dissolution in water and removal from the dump. It may be assumed that at an initial stage of water-washing, phenol is leached as it is relatively highly soluble in water as comparison of parts A and C in Fig. 12 shows. Phenol is followed by other alkyl phenol derivatives which may lead to a partial or total removal of this compound group. Since aromatic hydrocarbons are less water soluble than phenol derivatives, their distributions are affected to the lesser extent. Among aromatic hydrocarbons, naphthalene and distributions of its derivatives are affected to the greatest extent; again the reason is their relatively high solubility in water, starting from methylnaphthalenes, next dimethylnaphthalenes and, finally, more highly-substituted compounds (Fig. 12 – compare parts A and B). Although alkylphenanthrene distributions are affected much less than those of alkylnaphthalenes, in some extracts they also are removed. Removal of phenols and aromatic hydrocarbons leads to pyrolysate enrichment in aliphatic hydrocarbons, particularly *n*-alkanes. In some cases, i.e., coal wastes stored for tens of years as in the Starzykowiec dump, even distributions of *n*-alkanes are affected by this process; in the extracts, lighter *n*-alkanes are removed and the

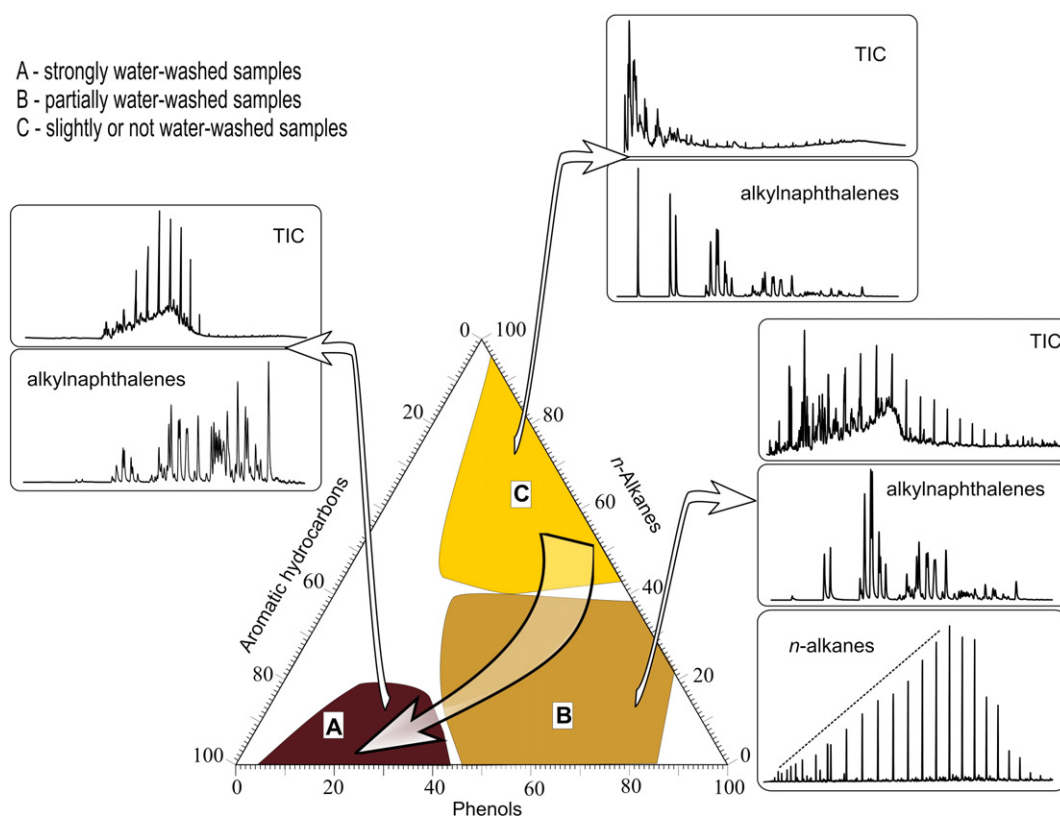


Fig. 12. Changes in the group composition of the bituminous fraction in self heated coal wastes caused by leaching. Chromatograms present generalized typical features of coal-waste bitumen composition after three degrees of leaching. Arrow shows main trend of composition change.

distributions show a characteristic “cut out” outline of peaks (Fig. 12 – part B).

Organic compound leaching must be considered a serious hazard to the environment, as is heavy-metal leaching. However, to-date, this has not been sufficiently recognized. Phenol and its derivatives can become concentrated in the lower parts of a dump (Misz-Kennan, 2010). Skręt et al. (2010), in a laboratory simulation of leaching, showed that phenols form 70–95% of the organic phases removed from thermally-changed coal wastes. Minor components leached were alkyl derivatives of aromatic hydrocarbons and oxygen compounds such as dibenzofuranes, anthracenones, xanthone, and phenylacetophenon. Methyl-naphthalenes, biphenyls and dimethyl-naphthalenes were usually the most abundant of the aromatic hydrocarbons in the leachates – as they are in the dump wastes. Several nitrogen compounds such as alkylquinolines (methylquinolines mainly), phenylpyridines and alkylanilines such as dimethyl-N, N-benzamine were more concentrated in the experimental leachates than in the coal-waste extracts. These compounds could be easily transferred to groundwater or soils, particularly from older coal-waste dumps not sealed from below.

5.3. Assessment of temperature ranges in a self heating zone

It is possible to assess roughly the temperature range in a self heating zone within a dump by reference to the distribution of compounds such as *n*-alkanes or PAHs and their boiling temperatures. During the formation of pyrolysates found in completely burnt-out wastes, these compounds are expelled from a macromolecule, evaporated and precipitated in cooler parts of a dump. Thus, their distribution ranges should be directly related to the temperature range of self heating.

Distributions of alkyl-naphthalenes and alkylphenanthrenes are also affected by fire. As shown in Fig. 9, alkyl-naphthalenes are all removed relatively early in the heating process; alkyl-naphthalenes are absent in samples with $R_r > 2.36\%$. As boiling points for methyl-naphthalenes and dimethyl-naphthalenes are 245 °C and 262 °C, respectively, these particular samples must have been heated to temperatures far exceeding 270 °C. In the case of sample 8 ($R_r = 0.90\%$), distributions of alkyl-naphthalenes are, except for the methyl-naphthalenes, unsuitable for interpretation (Fig. 10). In this case, the temperature range was <200 °C. In general, parameters based on alkyl derivatives of aromatic hydrocarbons such as MNR, MPI-3, (3 MB + 4 MB)/DBF and Σ DMB/ Σ MDBF seem to reflect the thermal influence of fire better than those based on aliphatic biomarkers.

5.4. Correlations of geochemical parameters with reflectance

Correlations of geochemical parameters of thermal alteration with increasing transformation of organic matter are generally poor (Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a). This is likely a reflection of the complex conditions within dumps (temperature fluctuations, compound migration, adsorption on organic and mineral matter), and, to a lesser extent, the complex nature of the organic matter itself (Misz-Kennan, 2010). A typical feature of the wastes is the reversal in values of individual geochemical parameters with increasing organic-matter transformation as expressed by random reflectance (R_r). The reversal always occurs at ca 1.0% R_r (Misz-Kennan, 2010; Misz-Kennan and Fabiańska, 2010; Misz-Kennan et al., 2011a). This is particularly well seen in the wastes in the upper part of the Starzykowice dump which show different degrees of alteration and reflectance values in the range 0.57–5.42% (Table 2; Misz-Kennan et al., 2011a). It is the best seen for parameters such as $Ts/(Ts + Tm)$, $C_{30}\beta\alpha/(\alpha\beta + \beta\alpha)$, TNR-2, MPI-3, relative contents of $\beta\alpha$ hopanes, phenanthrene, and five-ring PAHs. In wastes that random reflectance was <0.9%, the correlation coefficients

for these parameters were from 0.42 to 0.64 for positive correlations and –0.80 for the negative one. The correlation coefficients for these parameters in wastes having a random reflectance of >0.9%, were from –0.45 to –0.57 for negative correlations and 0.62 for positive ones. Relative contents of two- and three-ring PAHs increase and four-ring PAHs decrease with increasing reflectance up to 0.9% R_r , whereas, above that value, there is no clear trend.

6. Conclusions

Oxidation, self heating, and self combustion are the most important processes that transform both organic and mineral matter in coal wastes deposited in dumps. The scale of these processes depends on the properties of the wastes (maceral and mineral composition, rank of organic matter) and the heating history (heating time, final heating temperature, heating rate, air access). Commonly, the thermal alterations of the wastes take place under oxygen-depleted conditions. Air is necessary to start these processes and intensify them.

Forms of organic matter present in the wastes reflect the heating conditions. Microscopically unaltered organic matter is typical of wastes that did not undergo heating. Wastes heated slowly show cracks in vitrinite, oxidation rims around the external edges of particles and along cracks, and their color is paler. In such wastes exposed to slow heating for a long time, liptinite macerals disappear and organic matter became strongly thermally altered, develops a yellowish color and displays high reflectance. High heating rates cause organic matter to plasticize, reflected in devolatilization pores, bands and plasticized edges. Organic matter is lacking in coal wastes exposed to high temperature for a long time.

A variety of organic compounds are generated during self heating from organic matter in wastes. The most important groups of these are *n*-alkanes, acyclic isoprenoids, hopanes and moretanes, polycyclic aromatic hydrocarbons (PAHs) and their derivatives, and phenols. Some of these, e.g., PAHs and phenols, are significant environmental toxicants. These compounds may migrate within a dump and to the outside. Organic compounds may be completely absent in wastes containing strongly thermally altered organic matter. The presence of phenols is typical for wastes that are currently undergoing self heating and they are lacking in wastes in which heating ceased years ago. They may have been destroyed by heating or leached elsewhere.

The investigations of self heating occurring in coal waste dumps show that all dumps differ but that all have the potential to cause serious environmental problems. Apart from heavy metals, the environmental danger of coal waste dumps lies in the fact that they are a source of VOCs, gas emissions and of mobile and easily-leached organic compounds, many of which would be considered hazardous in one way or another.

Up to now, few studies on the detailed organic geochemistry of self heating coal wastes have been undertaken and those that have mostly concern coal-waste dumps in the Upper Silesian Coal Basin in Poland. They pose a challenge. The mechanisms and processes that lead to the formation of liquid- and semi-liquid pyrolytic products and their chemical composition are very complex and are easily influenced by additional external and internal factors. The latter are dump geometry, original organic-matter rank (Kaymakçi and Didari, 2002; Walker, 1999), water (Lewan, 1992) and oxygen access, self heating temperature and the presence/absence of minerals acting as catalysts in pyrolysis (Pan et al., 2009, 2010; Razvigorova et al., 2008; Seewald, 2001) to mention just a few. After the heating and combustion, weathering/oxidation and leaching can disturb the distributions of biomarkers and make definitive conclusions difficult to draw. More geochemical attention needs to be given to the active, complex physical- and chemical entities that coal-waste dumps are, and to the potential environmental- and health hazard they represent.

Acknowledgments

The authors are very grateful to two anonymous reviewers for their comments that improved the quality of the paper. We are also very grateful to Tim Horscroft and Dr. Özgen Karacan for proposing to prepare this review paper. We would like to acknowledge Dr. Pádraig S. Kennan, University College Dublin for his help with the English script.

The research was funded by grant N307 016 32/0493 from the Polish Ministry of Science and Higher Education.

References

- Alexander, R., Cumbers, K.M., Kagi, R.L., 1986. Alkylbiphenyls in ancient sediments and petroleum. *Organic Geochemistry* 10, 841–845.
- Barosz, S., 2002. Monitoring of the dismantling and reclamation of the coal waste dumps. VII Conference "Long term petrological undertakings in the Rybnik Coal Area", Rybnik, pp. 149–156 (in Polish).
- Barosz, S., 2003. Technical, economical and environmental conditions of management of coal waste dumps using the mines from the Rybnik Coal District as examples. Ph.D., Academy of Mining and Metallurgy in Cracow (unpublished). 221 pp. (in Polish).
- Beamish, B.B., 2005. Comparison of the R_{70} self-heating rate of New Zealand and Australian coals to Suggate rank parameter. *International Journal of Coal Geology* 64, 139–144.
- Beamish, B.B., Barakat, M.A., George, J.D. St., 2001. Spontaneous-combustion propensity of New Zealand coals under adiabatic conditions. *International Journal of Coal Geology* 45, 217–224.
- Bell, F.G., Bullock, S.E.T., Hällich, T.F.J., Lindsay, P., 2001. Environmental impacts associated with an abandoned mine in the Witbank Coalfield, South Africa. *International Journal of Coal Geology* 45, 195–216.
- Bend, S.L., Kosloski, D.M., 1993. A petrographic examination of coal oxidation. *International Journal of Coal Geology* 24, 233–243.
- Berkowitz, N., 1985. *The Chemistry of Coal*. Elsevier, Amsterdam-Oxford-New York-Tokyo. (513 pp.).
- Bray, E.E., Evans, E.D., 1961. Distribution of n-paraffins as a clue to recognition of source beds. *Geochimica et Cosmochimica Acta* 22 (1), 2–15.
- Brooks, K., Svanas, N., Glasser, D., 1988. Evaluating the risk of spontaneous combustion in coal stockpiles. *Fuel* 67, 651–656.
- Calemma, V., Del Piero, G., Rausa, R., Girardi, E., 1995. Changes in optical properties of coals during air oxidation at moderate temperature. *Fuel* 74, 383–388.
- Carras, J.N., Day, S.J., Saghaei, A., Williams, D.J., 2009. Greenhouse gases emissions from low-temperature oxidation and spontaneous combustion at open-cut coal mines in Australia. *International Journal of Coal Geology* 78, 161–168.
- Casal, M.D., Díez, M.A., Alvarez, R., Barriocanal, C., 2008. Primary tar of different coking coal ranks. *International Journal of Coal Geology* 76, 237–242.
- Chandra, D., 1962. Reflectivity and microstructure of weathered coals. *Fuel* 41, 185–193.
- Ciesielczuk, J., Misz-Kennan, M., Tabor, A., accepted for publication. Coal Dump Fires of Poland, in: Stracher, Glenn B., Prakash, A., Sokol, Ellina, V. (Eds.), *Coal and Peat Fires: A Global Perspective*, Volume 2, Elsevier.
- Clemens, A.H., Matheson, T.W., 1996. The role of moisture in the self-heating of low-rank coals. *Fuel* 75, 891–895.
- Clemens, A.H., Matheson, T.W., Rogers, D.E., 1991. Low temperature oxidation studies of dried New Zealand coals. *Fuel* 70, 215–221.
- Cloke, M., Lester, E., 1994. Characterization of coals for combustion using petrographic analysis: a review. *Fuel* 73, 315–320.
- Ćmiel, S., Misz, M., 2005. Petrographical changes caused by the fires of coal waste dumps. Proceedings of LXXVI Meeting of Polish Geological Institute, pp. 43–50 (In Polish).
- Davidi, S., Grossman, S.L., Cohen, H., 1995. Organic volatile emissions accompanying the low-temperature atmospheric storage of bituminous coals. *Fuel* 74, 1357–1362.
- Didyk, B.M., Simoneit, B.R.T., Brasse, S.C., Eglinton, G., 1978. Organic geochemical indicators of paleoenvironment conditions of sedimentation. *Nature* 272, 216–222.
- Dokoupilova, P., Sracek, O., Losos, Z., 2007. Geochemical behaviour and mineralogical transformations during spontaneous combustion of a coal waste pile in Oslavany, Czech Republic. *Mineralogical Magazine* 71, 443–460.
- Fabiańska, M., 2006. PLC- in a clean-up and group fractionation of geochemical samples: a review of the commonly applied techniques. In: Kowalska, T., Sherma, J. (Eds.), *Preparative Layer Chromatography*, Ch. XV, pp. 367–387.
- Fabiańska, M., 2007. *Organic Geochemistry of Brown Coals from the Selected Polish Basins*. Publisher of University of Silesia, Katowice. (319 pp. in Polish).
- Fabiańska, M., Matuszewska, A., 1998. Preliminary geochemical analysis of coal extracts and low-temperature tars of the Upper-Vistula Coal Region (Poland). *Polish Journal of Applied Chemistry* 3–4, 259–274.
- Fabiańska, M., Bzowska, G., Matuszewska, A., Racka, M., Skreń, U., 2003. Gas chromatography-mass spectrometry in appraisal of organic matter of the Grodziec Beds (Upper Carboniferous): Upper Silesian Coal Basin, Poland. *Chemie der Erde (Geochemistry)* 63, 63–91.
- Finkelman, R.B., 2004. Potential health impact of burning coal beds and waste banks. *International Journal of Coal Geology* 59, 19–24.
- Finkelman, R.B., Orem, W., Castranova, V., Tatu, C.A., Belkin, H.E., Zheng, B., Lerch, H.E., Marharaj, S.V., Bates, A.L., 2002. Health impacts of coal and coal use: possible solutions. *International Journal of Coal Geology* 50, 435–443.
- Gabzdyl, W., Probiez, K., 1987. The occurrence of anthracites in an area characterized by lower rank coals in the Upper Silesian Coal Basin of Poland. *International Journal of Coal Geology* 7, 209–225.
- Garcia, P., Hall, P.J., Mondragon, F., 1999. The use of differential scanning calorimetry to identify coal susceptible to spontaneous combustion. *Thermochimica Acta* 336, 41–46.
- Goodarzi, F., Murchison, D.G., 1978. Influence of heating-rate on the anisotropy of carbonized vitrinites. *Fuel* 57, 273–284.
- Goossens, H., de Leeuw, J.W., Schenck, P.A., Brassell, S.C., 1984. Tocopherols as likely precursors of pristane in ancient sediments and crude oils. *Nature* 312, 440–442.
- Goossens, H., Due, A., de Leeuw, J.W., van de Graaf, B., Schenck, P.A., 1988a. The Pristane Formation Index, a new molecular maturity parameter. A simple method to assess maturity by pyrolysis/evaporation-gas chromatography of unextracted samples. *Geochimica et Cosmochimica Acta* 52 (5), 1189–1193.
- Goossens, H., de Lange, F., de Leeuw, J.W., Schenck, P.A., 1988b. The Pristane Formation Index, a molecular maturity parameter. Confirmation in samples from the Paris Basin. *Geochimica et Cosmochimica Acta* 52 (10), 2439–2444.
- Greenwood, P.F., Guthrie, E.A., Hatcher, P.G., 2000. The in situ analytical pyrolysis of two different organic components of a synthetic environmental matrix doped with [4,9-¹³C] pyrene. *Organic Geochemistry* 31, 635–643.
- Grossman, S.L., Davidi, S., Cohen, H., 1994. Emission of toxic and fire hazardous gases from open air coal stockpiles. *Fuel* 73, 1184–1188.
- Hadden, R., Rein, G., 2009. Ignition and suppression of smouldering coal fires in small-scale experiments. 6th Mediterranean Combustion Symposium, Ajaccio, Corsica, France, MCS 6 http://www.see.ed.ac.uk/~grein/rein_papers/Hadden_Suppressing_Coalfires_2009.pdf.
- Hatcher, P.G., Clifford, D.J., 1997. The organic geochemistry of coal: from plant materials to coal. *Organic Geochemistry* 27, 251–274.
- Hatcher, P.G., Faulon, J.-L., Wenzel, K.A., Cody, G.D., 1992. A structural model for lignin-derived vitrinite from high-volatile bituminous coal (coalified wood). *Energy & Fuels* 6, 813–820.
- Heffern, E.L., Coates, D.A., 2004. Geology of natural coal bed fires, Powder River Basin, USA. *International Journal of Coal Geology* 59, 25–47.
- Horsfield, B., 1989. Practical criteria for classifying kerogens: some observations from pyrolysis-gas chromatography. *Geochimica et Cosmochimica Acta* 53, 891–901.
- Hower, J.C., Henke, K., O'Keefe, J.M.K., Engle, M.A., Blake, D.R., Stracher, G.B., 2009. The Tiptop coal-mine fire, Kentucky: preliminary investigation of the measurement of mercury and other hazardous gases from coal-fire gas vents. *International Journal of Coal Geology* 80, 63–67.
- Huang, W.-Y., Meinschein, W.G., 1979. Sterols as ecological indicators. *Geochimica et Cosmochimica Acta* 43, 739–745.
- Iglesias, M.J., Jimenez, A., del Rio, J.C., Suárez-Ruiz, I., 2000. Molecular characterisation of vitrinite in relation to natural hydrogen enrichment and depositional environment. *Organic Geochemistry* 31, 1285–1299.
- Iglesias, M.J., del Rio, J.C., Laggoun-Defarge, F., Cuesta, M.J., Suárez-Ruiz, I., 2002. Control of the chemical structure of perhydropyrene coals: FTIR and Py-GC/MS investigation. *Journal of Analytical and Applied Pyrolysis* 62, 1–34.
- Ingram, G.R., Rimstidt, J.D., 1984. Natural weathering of coal. *Fuel* 63, 292–296.
- International Committee for Coal and Organic Petrology, 1998. New vitrinite classification (ICCP system 1994). *Fuel* 77, 349–358.
- International Committee for Coal and Organic Petrology, 2001. New inertinite classification (ICCP system 1994). *Fuel* 80, 459–471.
- ISO 7404-4, 1988. Methods for the Petrographic Analysis of Bituminous Coal and Anthracite - Part 4: Method of Determining Microlithotype, Carbominerite and Minerite. International Organization for Standardization, Switzerland (6pp).
- ISO 7404-2, 2009a. Methods for the Petrographic Analysis of Coals - Part 2: Methods of Preparing Coal Samples, Switzerland (12 pp).
- ISO 7404-3, 2009b. Methods for the petrographic analysis of bituminous coal and anthracite - Part 3: Method of determining maceral group composition. International Organization for Standardization, Switzerland (7 pp).
- ISO 7404-5, 2009c. Methods for the petrographic analysis of coals and - Part 5: Methods of determining microscopically the reflectance of vitrinite. International Organization for Standardization, Switzerland (14 pp).
- Itay, M., Hill, C.R., Glasser, D., 1989. A study of the low temperature oxidation of coal. *Fuel Processing Technology* 21, 81–97.
- Jiamo, F., Guoing, S., Jiayou, X., Eglinton, G., Gowar, A.P., Ronfeng, J., Shanfa, F., Pingan, P., 1990. Application of biological markers in the assessment of paleoenvironments of Chinese non-marine sediments. *Organic Geochemistry* 16 (4–6), 769–779.
- Jones, J.C., 2000. On the role of times to ignition in the thermal safety of transportation of bituminous coals. *Fuel* 79, 1561–1562.
- Kaymakci, E., Didari, V., 2002. Relations between coal properties and spontaneous combustion parameters. *Turkish Journal of Engineering and Environmental Sciences* 26, 59–64.
- Killops, S.D., Killops, V.J., 2004. *An Introduction to Organic Geochemistry*. Blackwell Publishers, Oxford. (393 pp.).
- Kim, A.G., 2007. Greenhouse gases generated in underground coal-mine fires. In: Stracher, G.B. (Ed.), *Geology of Coal Fires: Case Studies From Around the World*. Geological Society of America, USA, pp. 1–13.
- Knafel, S., 1983. Petrographic descriptions of selected coals from the Lublin and the Upper Silesian coal basins. In: Bojkowski, K., Porzyski, J. (Eds.), *Geological Problems of Coal Basins in Poland*. Geological Institute Press, Warsaw, pp. 285–333.
- Kok, A., Bolt, N., Jelgersma, J.H.N., 1989. Spontaneous heating and stockpiling losses of coal. *Kema Scientific and Technical Reports* 7, 63–89.
- Kotarba, M.J., Clayton, J.L., 2003. A stable carbon isotope and biological marker study of Polish bituminous coals and carbonaceous shales. *International Journal of Coal Geology* 55, 73–94.

- Kotarba, M.J., Clayton, J.L., Rice, D.D., Wagner, M., 2002. Assessment of hydrocarbon source rock potential of Polish bituminous coals and carbonaceous shales. *Chemical Geology* 184, 11–35.
- Kotas, A., 1990. Upper Silesian Coal Basin. In: Osika, R. (Ed.), *Geology of Poland: Vol. 6. Mineral Deposits*. Publishing House: Wydawnictwa Geologiczne, Warsaw, pp. 77–93.
- Krishnaswamy, S., Bhat, S., Gunn, R.D., Agarwal, P.K., 1996a. Low-temperature oxidation of coal. 1. Single-particle reaction–diffusion model. *Fuel* 75, 333–343.
- Krishnaswamy, S., Agarwal, P.K., Gunn, R.D., 1996b. Low-temperature oxidation of coal. 3. Modelling spontaneous combustion in coal stockpiles. *Fuel* 75, 353–362.
- Kruszewska, K., 1983. Microfacies types of coal seams in Upper Silesian Coal Basin. *Geological Quarterly* 27, 41–58.
- Küçük, A., Kadioğlu, Y., Gülaboğlu, M.S., 2003. A study of spontaneous combustion characteristics of a Turkish lignite: particle size, moisture of coal, humidity of air. *Combustion and Flame* 133, 255–261.
- Leif, R.N., Simoneit, B.R.T., 2000. The role of alkanes produced during hydrous pyrolysis of a shale. *Organic Geochemistry* 31, 1189–1208.
- Lewan, M.D., 1992. Water as a source of hydrogen and oxygen in petroleum formation by hydrous pyrolysis. *American Chemical Society, Division of Fuel Chemistry Preprints* 37, 1643–1649.
- Leythaeuser, D., Schwarzkopf, Th., 1986. The pristane/n-heptadecane ratio as an indicator for recognition of hydrocarbon migration effects. *Organic Geochemistry* 10, 191–197.
- Litschke, T., 2005. Innovative technologies for exploration, extinction and monitoring of coal fires in North China: detailed mapping of coal fire sites in combination with insitu flux measurements of combustion-gases to estimate gas flow balance and fire development (Wuda Coal Field, Inner Mongolia Autonomous Region). Unpublished PhD thesis, Dortmund, Universität Duisburg-Essen. <http://www.coalfire.caf.dlr.de/media/download/results/Diplomarbeit-Litschke.pdf> (accessed 29. 03. 2011).
- Liu, L., Zhou, F., 2010. A comprehensive hazard evaluation system for spontaneous combustion of coal in underground mining. *International Journal of Coal Geology* 82, 27–36.
- Liu, Ch., Li, S., Qiao, Q., Wang, J., Pan, Z., 1998. Management of spontaneous combustion in coal mine waste tips in China. *Water, Air, and Soil Pollution* 103, 441–444.
- Lu, S.-T., Kaplan, I.R., 1992. Diterpanes, triterpanes steranes and aromatic hydrocarbons in natural bitumens and pyrolysates from different humic coals. *Geochimica et Cosmochimica Acta* 56, 2761–2788.
- Lu, P., Liao, G.X., Sun, J.H., Li, P.D., 2004. Experimental research on index gas of the coal spontaneous at low-temperature stage. *Journal of Loss Prevention in the Process Industries* 17, 243–247.
- Lyman, R.M., Volkmer, J.E., 2001. Pyrophoricity (spontaneous combustion) of Powder River Basin coals – considerations for coalbed methane development. *Coal Report Cr 01–1*, Wyoming State Geological Survey, pp. 1–12.
- Machnikowska, H., Luczak, A., Kubacki, A., 2003. Effect of oxidation method on properties and structure of coals and lithotypes. *Karbo* 3, 157–164 (in Polish).
- Mahadevan, V., Ramli, M.A., 1985. Fire risk rating of coal mines due to spontaneous combustion. *Journal of Mines, Metals and Fuels* 357–362 (August).
- Masalehdani, M.N.-N., Mees, F., Dubois, M., Coquinot, Y., Potdevin, J.-L., Fialin, M., Blanc-Valleron, M.-M., 2009. Condensate minerals from a burning coal-waste heap in Avion, Northern France. *The Canadian Mineralogist* 47, 573–591.
- Mastalerz, M., Mastalerz, K., 2000. Volcanic and post-volcanic hydrothermal activity in the Intracretaceous Basin, SW Poland: implications for mineralization. In: Glickson, M., Mastalerz, M. (Eds.), *Organic Matter and Mineralization: Thermal Alteration, Hydrocarbon Generation and Role in Metallogenesis*. Kluwer Academic Publishers, Dordrecht, pp. 185–203.
- Mastalerz, M., Stankiewicz, A.B., Salmon, G., Kvale, E.P., Millard, L.C., 1997. Organic geochemical study of sequences overlying coal seams; example from the Anfield Formation (Lower Pennsylvanian), Indiana. *International Journal of Coal Geology* 33, 275–290.
- Mastalerz, M., Drobniak, A., Hower, J.C., O'Keefe, J.M.K., 2010. Spontaneous combustion and coal petrology. In: Stracher, G.B., Sokol, E.V., Prakash, A. (Eds.), *Coal and Peat Fires: A Global Perspective: Volume 1: Coal – Geology and Combustion*. Elsevier, pp. 47–62.
- McKinnley, D.E., Hatcher, P.G., 1996. Characterization of peatified or coalified wood by the trimethylammonium hydroxide (TMAH). *International Journal of Coal Geology* 32, 217–228.
- Michaelis, W., Richow, H.H., Jenish, A., Schultze, T., Mycke, B., 1990. Structural inferences from organic geochemical coal studies. In: Intekott, V., Kempe, S., Michaelis, W., Spitz, A. (Eds.), *Facets of Modern Biogeochemistry*. Springer-Verlag, Heidelberg, pp. 388–401.
- Misra, B.K., Singh, B.D., 1994. Susceptibility to spontaneous combustion of Indian coals and lignites: an organic petrography autopsy. *International Journal of Coal Geology* 25, 265–286.
- Misz, M., Fabiańska, M., Cmiel, S., 2007. Organic components in thermally altered coal waste: preliminary petrographic and geochemical investigations. *International Journal of Coal Geology* 71, 405–424.
- Misz-Kennan, M., 2010. Thermal alterations of organic matter in coal wastes from Upper Silesia, Poland. *Mineralogia* 3–4, 105–236.
- Misz-Kennan, M., Fabiańska, M., 2010. Thermal transformation of organic matter in coal waste from Rymer Cones (Upper Silesian Coal Basin, Poland). *International Journal of Coal Geology* 81, 343–358.
- Misz-Kennan, M., Tabor, A., 2011. The thermal history of selected coal waste dumps in the Upper Silesian Coal Basin (Poland), in: Stracher, G.B., Sokol, E.V., Prakash, A. (Eds.), *Coal and Peat Fires: A Global Perspective, Volume 3 – case studies*, Elsevier, Scheduled for publication in 2011 or (early 2012).
- Misz-Kennan, M., Kus, J., Flores, D., Avila, C., Christanis, K., Hower, J., Kalaitzidis, S., O'Keefe, J., Marques, M., Pus, S., Ribeiro, J., Suárez-Ruiz, I., Sýkorová, I., Wagner, N., Životić, D., 2009. Report of the 2009 Round Robin Exercise of the Self-heating of Coal and Coal Wastes Working Group. *ICCP News Letter* 48, 58–60.
- Misz-Kennan, M., Kus, J., Flores, D., Avila, C., Christanis, K., Hower, J., Kalaitzidis, S., O'Keefe, J., Marques, M., Pus, S., Ribeiro, J., Suárez-Ruiz, I., Sýkorová, I., Wagner, N., Životić, D., 2010. Self-heating of Coal and Coal Wastes Working Group: a new approach to classify altered and newly formed particles as result of self-heating and self-combustion processes (International Committee for Coal and Organic Petrology): Second International Conference on Coal Fire Research, p. 406 (19–21.05.2010, Berlin, Abstracts).
- Misz-Kennan, M., Fabiańska, M., Ciesielczuk, J., 2011a. Thermal transformations of the waste rocks at the Starzykowice coal waste dump, Poland, in: Stracher, G.B., Sokol, E.V., Prakash, A. (Eds.), *Coal and Peat Fires: A Global Perspective, Volume 3 – case studies*, Elsevier, Scheduled for publication in 2011 or (early 2012).
- Misz-Kennan, M., Gardocki, M., Tabor, A., 2011b. Fire Prevention in Coal Waste Dumps as Exemplified by the Rymer Cones Dump Upper Silesian Coal Basin, Poland, in: Stracher, G.B., Sokol, E.V., Prakash, A. (Eds.), *Coal and Peat Fires: A Global Perspective, Volume 3 – case studies*, Elsevier, Scheduled for publication in 2011 or (early 2012).
- Moghtaderi, B., Dlugogorski, B.Z., Kennedy, E.M., 2000. Effect of wind flow on the self-heating characteristics of coal stockpiles. *Process Safety and Environmental Protection* 78, 445–453.
- Murchison, D., 2006. The influence of heating rates on organic matter in laboratory and natural environments. *International Journal of Coal Geology* 67, 145–157.
- Ndaji, F.E., Thomas, K.M., 1995. The effect of oxidation on the macromolecular structure of coals. *Fuel* 74, 932–937.
- Nelson, C.R., 1989. *Chemistry of coal weathering*. Coal Science and Technology, 14. Elsevier, Amsterdam, Oxford, New York, Tokyo (231 pp.).
- Nelson, M.I., Chen, X.D., 2007. Survey of experimental work on the self-heating and spontaneous combustion of coal. In: Stracher, G.B. (Ed.), *Geology of Coal Fires: Studies from Around the World: Geological Society of America Reviews in Engineering Geology*, vol. XVIII, pp. 31–83.
- O'Keefe, J.M.K., Hanke, K.H., Hower, J.C., Engle, M.A., Stracher, G.B., Stucker, J.D., Drew, J.W., Staggs, W.D., Murray, T.M., Hammond III, M.L., Adkin, K.D., Mullins, B.J., Lemley, E.W., 2010. CO₂, CO, and Hg emissions from the Truman Shepherd and Ruth Mullins coal fires, eastern Kentucky, USA. *Science of the Total Environment* 408, 1628–1633.
- Oros, D.R., Simoneit, B.R.T., 2000. Identification and emission rates of molecular tracers in coal smoke particulate matter. *Fuel* 79, 515–536.
- Ourlisson, G., Albrecht, P., Rohmer, M., 1979. The hopanoids. *Paleochemistry of a group of natural products*. *Pure and Applied Chemistry* 51 (4), 709–729.
- Pan, C., Geng, A., Zhong, N., Liu, J., Yu, L., 2009. Kerogen pyrolysis in the presence and absence of water and minerals: amounts and compositions of bitumen and liquid hydrocarbons. *Fuel* 88, 909–919.
- Pan, C., Geng, A., Zhong, N., Liu, J., 2010. Kerogen pyrolysis in the presence and absence of water and minerals: steranes and triterpenoids. *Fuel* 88, 336–345.
- Pancost, R.D., Baas, M., van Geel, B., Sinnighe Damste, J.S., 2002. Biomarkers proxies for plant inputs to peats: an example from a sub-boreal ombrotrophic bog. *Organic Geochemistry* 22, 675–690.
- Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. *The biomarker guide, Biomarkers and Isotopes in Petroleum Exploration and Earth History*, 2nd ed. Cambridge University Press (1155 pp.).
- Pone, J.D.N., Hein, K.A.A., Stracher, G.B., Annegarn, H.J., Finkelman, R.B., Blake, D.R., McCormack, J.K., Schroeder, P., 2007. The spontaneous combustion of coal and its by-products in the Witbank and Sasolburg coalfields of South Africa. *International Journal of Coal Geology* 72, 124–140.
- Querol, X., Izquierdo, M., Monfort, E., Alvarez, E., Font, O., Moreno, T., Alastuey, A., Zhuang, X., Lu, W., Wang, Y., 2008. Environment characterization of burnt coal gangue banks at Yangquan, Shanxi Province, China. *International Journal of Coal Geology* 75, 93–104.
- Querol, X., Zhuang, X., Font, O., Izquierdo, M., Alastuey, A., Castro, I., van Drooge, B.L., Moreno, T., Grimalt, J.O., Elvira, J., Cabañas, M., Bartoli, R., Hower, J.C., Ayora, C., Plana, F., López-Soler, A., 2011. Influence of soil cover on reducing the environmental impact of spontaneous coal combustion in coal waste gobs: a review and new experimental data. *International Journal of Coal Geology* 85, 2–22.
- Radke, M., 1987. Organic geochemistry of aromatic hydrocarbons. *Advances in Petroleum Geochemistry*, 2. Academic Press, London, pp. 141–205.
- Radke, M., Welte, D.H., 1983. The methylphenanthrene index (MPI): a maturity parameter based on aromatic hydrocarbons. In: Bjoroy, M., Albrecht, P., Cornford, C., de Groot, K., Eglinton, G., Galimov, E., Leythaeuser, D., Pelet, R., Speers, G. (Eds.), *Advances in Organic Geochemistry 1981* (pp. 504–512). Chichester: John Wiley and Sons, Inc.
- Radke, M., Willsch, H., Leythaeuser, D., Teichmüller, M., 1982. Aromatic components of coal: relation of distribution pattern to rank. *Geochimica et Cosmochimica Acta* 46 (10), 1831–1848.
- Radke, M., Welte, D.H., Willsch, H., 1986. Maturity parameters based on aromatic hydrocarbons: influence of organic matter type. *Organic Geochemistry* 10, 51–63.
- Radke, M., Willsch, H., Teichmüller, M., 1990. Generation and distribution of aromatic hydrocarbons in coals of low rank. *Organic Geochemistry* 15, 539–663.
- Radke, M., Rullkötter, J., Vriend, S.P., 1994. Distribution of naphthalenes in crude oils from the Java Sea: source and maturation effects. *Geochimica et Cosmochimica Acta* 58, 3675–3689.
- Radke, M., Vriend, S.P., Ramanampisoa, L.R., 2000. Alkyldibenzofurans in terrestrial rocks: influence of organic facies and maturation. *Geochimica et Cosmochimica Acta* 64, 275–286.

- Razvigorova, M., Goranova, M., Minkova, V., Russyanova, N., 1995. Comparative analysis of extractables and steam pyrolysis products from high volatile bituminous coal. *Fuel* 74, 1333–1342.
- Razvigorova, M., Budinova, T., Tsytsarski, B., Petrova, B., Ekinci, E., Atakul, H., 2008. The composition of acids in bitumen and in products from saponification of kerogen: investigation of their role as connecting kerogen and mineral matrix. *International Journal of Coal Geology* 76, 243–249.
- Ribeiro, J., Ferreira da Silva, E., Li, Z., Ward, C., Flores, D., 2010a. Petrographic, mineralogical and geochemical characterization of the Serrinha coal waste pile (Douro Coalfield, Portugal) and the potential environmental impacts on soil, sediments and surface waters. *International Journal of Coal Geology* 83, 456–466.
- Ribeiro, J., Li, Z., Ward, C., Flores, D., 2010b. Organic petrology and mineralogy of burning coal wastes from Douro Coalfield, Portugal. *Proceeding of Second International Conference on Coal Fire Research*, Berlin, pp. 171–176.
- Ribeiro, J., Ferreira, da Silva E., Flores, D., 2010c. Burning of coal waste piles from Douro Coalfield (Portugal): petrological, geochemical and mineralogical characterization. *International Journal of Coal Geology* 81, 359–372.
- Rosiek, F., Urbański, J., 1990. Influence of some physical properties of coal on their self-ignition. *Scientific Publications of Mining Institute of Wrocław Technical University*, 59, pp. 27–32 (in Polish).
- Sawicki, T., 2004. Spontaneous combustion in stock piles as the cause of fire. *Karbo* 1, 56–59 (in Polish).
- Schultze, T., Michalis, W., 1990. Structure and origin of terpenoid hydrocarbons in some German coals. *Organic Geochemistry* 16, 1051–1058.
- Seewald, J.S., 2001. Aqueous geochemistry of low molecular weight hydrocarbons at elevated temperatures and pressures: Constraints from mineral buffered laboratory experiments. *Geochimica et Cosmochimica Acta* 65, 1641–1664.
- Seifert, W.K., Moldowan, J.M., 1978. Application of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. *Geochimica et Cosmochimica Acta* 42 (1), 77–95.
- Seifert, W.K., Moldowan, J.M., 1980. The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. *Physics and Chemistry of Earth* 12, 229–237.
- Sensogut, C., Cinar, I., 2000. A research on the tendency of Ermenek District coals to spontaneous combustion. *Mineral Resources Engineering* 9, 421–427.
- Shi, T., Wang, X., Deng, J., Wen, Z., 2005. The mechanism at the initial stage of room-temperature oxidation of coal. *Combustion and Flame* 140, 332–345.
- Simoneit, B.R.T., 1977. Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. *Geochimica et Cosmochimica Acta* 41, 463–476.
- Simoneit, B.R.T., 1993. Hydrothermal alteration of organic matter in marine and terrestrial systems. In: Engel, M.H., Macko, S.A. (Eds.), *Organic Geochemistry. Principles and Applications*. Plenum Press, New York, London, pp. 397–418 (Chapter 17, 861 pp.).
- Simoneit, B.R.T., 1998. Biomarker PAHs in the environment. In: Neilson, A.H. (Ed.), *The Handbook of Environmental Chemistry*, vol. 3, Part I: PAHs and Related Compounds. Springer-Verlag, Berlin, Heidelberg, pp. 176–221 (Chapter 5).
- Simoneit, B.R.D., Bi, X., Orors, D.R., Medeiros, P.M., Sheng, G., Fu, J., 2007. Phenols and hydroxy-PAHs (arylphenols) as tracer for coal smoke particulate matter: source tests and ambient aerosol assessment. *Environmental Science and Technology* 41, 7294–7302.
- Singh, A.K., Singh, R.V.K., Singh, M., Chandra, H., Shukla, N.K., 2007. Mine fire gas indices and their application to Indian underground coal mine fires. *International Journal of Coal Geology* 69, 192–204.
- Skarżyńska, K.M., 1995. Reuse of coal mining wastes in civil engineering – part 1: properties of minestone. *Waste Management* 13, 3–42.
- Skreń, U., Fabiańska, M.J., Misz-Kennan, M., 2010. Simulated water-washing of organic compounds from self-heated coal wastes of the Rymer Cones Dump (Upper Silesia Coal Region, Poland). *Organic Geochemistry* 41, 1009–1012.
- Smith, M.A., Glasser, D., 2005. Spontaneous combustion of carbonaceous stockpiles. Part II. Factors affecting the rate of the low-temperature oxidation reaction. *Fuel* 84, 1161–1170.
- Sokol, E.V., 2005. High-temperature processes of organic fuel decomposition as a thermal source for pyrometamorphic transformations. In: Lepezin, G.G. (Ed.), *Combustion metamorphism*. Publishing House of the Siberian Branch of Russian Academy of Sciences, Novosibirsk, pp. 22–31 (in Russian).
- Stach, E., Mackowsky, M.-T.h., Teichmüller, M., Taylor, G.H., Chandra, D., Teichmüller, R., 1982. *Stach's Textbook of Coal Petrology*. Gebrüder Borntraeger, Berlin. (535 pp.).
- Standley, L.J., Kaplan, L.A., 1998. Isolation and analysis of lignin-derived phenols in aquatic humic substances: improvements on the procedures. *Organic Geochemistry* 28, 689–697.
- Stout, S.A., Emsbo-Mattingly, S.D., 2008. Concentration and character of PAHs and other hydrocarbons in coals of varying rank – implications for environmental studies of soils and sediments containing particulate coal. *Organic Geochemistry* 39, 801–819.
- Stracher, G.B., 2004. Coal fires burning around the world: a global catastrophe. *International Journal of Coal Geology* 59, 1–6.
- Stracher, G.B., Taylor, T.P., 2004. Coal fires burning out of control around the world: thermodynamic recipe for environmental catastrophe. *International Journal of Coal Geology* 59, 7–17.
- Strumiński, A., Rosiek, F., 1990. The evaluation of the endogenic fire-hazards in the Lower Silesian Coal Basin in the light of the tendency for the coal to self-ignite. *Scientific Publications of Mining Institute of Wrocław Technical University* 59, 33–43 (in Polish).
- Suárez-Ruiz, I., Crelling, J. (Eds.), 2008. *Applied coal petrology. The Role of Petrology in Coal Utilization*. Elsevier, Amsterdam (388 pp.).
- Sujanti, W., Zhang, D., 1999. A laboratory study of spontaneous combustion of coal: the influence of inorganic matter and reactor size. *Fuel* 78, 549–556.
- Sýkorová, I., Pickel, W., Christanis, K., Wolf, M., Taylor, G.H., Flores, D., 2005. Classification of huminite-ICCP System 1994. *International Journal of Coal Geology* 62, 85–106.
- Szafer, M., Urbański, H., Tabor, A., 1994. Rules for The Re-cultivation of Coal Waste Dumps using Modern Techniques. *Central Mining Institute, Katowice*. (63 pp., in Polish).
- Tabor, A., 1999. Technical-ecological problems in coal waste collection. IV Conference "Conditions in the local plans for land development in towns and communes of the Rybnik Coal Area", Rybnik, pp. 195–202 (in Polish).
- Tabor, A., 2002. Monitoring of coal waste dumps, re-cultivated dumps and other collection sites of Carboniferous waste rocks in the light of many years experience. VII Conference "Long term proecological undertakings in the Rybnik Coal Area", Rybnik, pp. 131–141 (in Polish).
- Tabor, A., 2002–2009. Reports from the monitoring of coal waste dumps. Unpublished materials (in Polish).
- Taylor, G.H., Teichmüller, M., Davis, A., Diessel, C.F.K., Littke, R., Robert, R., 1998. *Organic Petrology*. Gebrüder Borntraeger, Berlin. (704 pp.).
- Tissot, B.P., Welte, D.H., 1984. *Petroleum Formation and Occurrence*. Springer-Verlag, Berlin. (699 pp.).
- Urbański, J., 1983. Technical Re-cultivation of Mine Waste Dumps with Particular Reference to Fire Protection. *Training Materials, The Association of Mining Engineers and Technicians, Katowice*. (61 pp., in Polish).
- Van Krevelen, D.W., 1993. *Coal Typology – Chemistry – Physics – Constitution*. Elsevier, Amsterdam. (979 pp.).
- Van Niekerk, D., Pugmire, R.J., Solum, M.S., Painter, P.C., Mathew, J.P., 2008. Structural characterization of vitrinite-rich and inertinite-rich Permian-aged South African bituminous coals. *International Journal of Coal Geology* 76, 290–300.
- Walker, S., 1999. Uncontrolled fires in coal and coal wastes. *IEA Coal Research, CCC/16*. (72 pp.).
- Wanatabe, W.S., Zhang, D., 2001. The effect of inherent and added inorganic matter on low-temperature oxidation reaction of coal. *Fuel Processing Technology* 74, 145–160.
- Wang, G.Q., Zhao, H.H., Wu, D.X., Liu, Y., Xie, M.X., 2001. Gangue sanitary landfill and recovering ecological environment in Huaibei and Huainan mining area. *Journal of China Coal Society* 26, 428–431 (in Chinese with English abstract).
- Wang, H., Długogorski, B.Z., Kennedy, E.M., 2002a. Thermal decomposition of solid oxygenated complexes formed by coal oxidation at low temperatures. *Fuel* 81, 1913–1923.
- Wang, H., Długogorski, B.Z., Kennedy, E.M., 2002b. Examination of CO₂, CO, and H₂O formation during low-temperature oxidation of a bituminous coal. *Energy and Fuels* 16, 586–592.
- Wang, H., Długogorski, B.Z., Kennedy, E.M., 2003. Coal oxidation at low temperatures: oxygen consumption, oxidation products, reaction mechanism and kinetic modelling. *Progress in Energy and Combustion Science* 29, 487–513.
- Xie, J., Xue, Sh., Cheng, W., Wang, G., 2011. Early detection of spontaneous combustion of coal in underground coal mines with development of an ethylene enriching system. *International Journal of Coal Geology* 85, 123–127.
- Yan, R., Zhu, H., Zheng, Ch., Xu, M., 2003. Emissions of organic hazardous air pollutants during Chinese coal combustion. *Energy* 27, 485–503.
- Younger, P.L., 2004. Environmental impacts of coal mining and associated wastes: a geochemical perspective. In: Gieré, R., Stille, P. (Eds.), *Energy, Waste and the Environment: A Geochemical Perspective*. Geological Society Special Publications, 236, pp. 169–209.
- Zhao, Y., Zhang, J., Chou, C.-L., Li, Y., Wang, Z., Ge, Y., Zheng, C., 2008. Trace element emission from spontaneous combustion of gob piles in coal mines, Shanxi, China. *International Journal of Coal Geology* 73, 52–62.