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Variations in Concentrations and Compositions of Polycyclic Aromatic Hydrocarbons (PAHs) in Coals Related to the Coal Rank and Origin

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ABSTRACT

The release of unburnt coal particles and associated polycyclic aromatic hydrocarbons (PAHs) may cause adverse impacts on the environment. This study assessed variations in the concentration and composition of PAHs in a set of fifty coal samples from eleven coal basins worldwide. The maximum PAH concentrations at high volatile bituminous rank were recorded in samples from a single basin. Considering the entire sample, the highest PAH concentrations were in fact found outside of this rank range, suggesting that the maceral composition and thus the coal's origin also influenced PAH concentrations. The examination of the PAH compositions revealed that alkylated 2-3 ring PAHs remain dominant compounds irrespective of coal rank or origin. Multivariate analysis based on PAH and maceral content, bulk and maturity parameters allowed the recognition of seven groups with different rank and origin within the coal sample set.

Capsule: The origin of coal has a strong influence on the concentration and composition of indigenous PAHs.

Keywords: coal origin, coal rank, polycyclic aromatic hydrocarbons

1. Introduction

Coal is a fossil fuel that has been mined for centuries in various parts of the world. It provided the main source of primary energy from the 18th century to the 1950s. More recently coal has been mainly used as a solid fuel for the generation of electricity and heat through combustion, and for industrial processes. It has been estimated that the worldwide hard coal production is currently approximately six billion tons per year (Thielemann et al., 2007).

The mining, transportation, and use of coal all produce a number of adverse impacts on the environment. Extensive coal combustion, for example, results in an increase in pollutants such as sulfur dioxide, nitrogen oxides, mercury, and polycyclic aromatic hydrocarbons (PAHs) in the atmosphere (e.g., Chen et al., 2004). The residues of coal processing, such as coal tar and coke, are also important sources of contaminants including phenols, heterocyclic compounds, and in particular PAHs in affected water, soils, and sediments (Khalil et al., 2006; Micić et al., 2007a). The release of unburnt coal particles into the environment as a result of either the mining and transportation of coal (Ahrens and Morrissey, 2005; French, 1998; Pies et al., 2007), or the natural erosion of coal seams (Short et al., 1999; Stout et al., 2002), is also of environmental concern. Given their occasionally high content of PAHs (e.g., Achten and Hofmann, 2009; Micić et al., 2007b; Willsch and Radke, 1995), unburnt coal particles may introduce significant quantities of these compounds into areas impacted by intensive coal production, transportation, and processing (e.g., Micić et al., 2011). Yang et al. (2008) and Pies et al. (2008) have shown this to be the case in river sediments and floodplain soils in the vicinity of a coal mining district, in which large quantities of unburnt coal particles had been identified. Such soils and sediments may therefore easily become a secondary source of pollution (Salomons and Brils, 2004) or even themselves come to be considered hazardous waste (Pies et al., 2007). In natural waters, most PAHs are generally of low concern, due to their low water solubility (deMaagd et al., 1998). However, if there is a sufficiently long contact of coal with natural waters, lower molecular weight compounds (such as naphthalenes and phenanthrenes) may be mobilized and transported by co-eluting humic-like substances derived from the coals (Orem et al., 2007).

The environmental concerns regarding coal-related pollutants are widely recognized. Stout and Emsbo-Mattingly (2008) stated that, since coal is a natural material with variable properties, more detailed investigations are required into coal-related pollutants with regard to their origin (i.e., differing structure and composition of the coal). The origin of a coal embraces its depositional environment, precursor material, formation history, and geological age.

Coal is a complex heterogeneous material composed of a number of distinct organic constituents called macerals and variable quantities of inorganic substances. Macerals - the remains of plants and degraded plant material - are divided into three main groups: (a) the vitrinite group, derived from coalified woody tissue, (b) the liptinite group, derived from the resinous and waxy parts of plants, and (c) the inertinite group, derived from charred and biochemically altered plant material (Taylor et al., 1998). The structure of coal can be simplified as a two component system, which includes a macromolecular network (an insoluble phase) and a “mobile” (soluble) phase, both of which contain PAHs (Given, 1987; Haenel, 1992). The macromolecular component consists of aromatic structural units that

enclose the “mobile” phase, which consists of relatively small molecules (including 2-6 ring PAHs). The PAHs in the “mobile” phase are of particular environmental concern since they can be more easily released into the environment than those that are interlinked with the macromolecular network (Achten and Hofmann, 2010; Haenel, 1992). PAHs in coals are usually present as complex mixtures with a range of physicochemical properties and the composition of PAHs is therefore variable. Sixteen of the “mobile” phase PAHs are particularly toxic and carcinogenic, and therefore defined by the US Environmental Protection Agency (US EPA) as priority pollutants. In addition to the 16 US EPA PAHs, toxic effects are also observed with some alkylated counterparts (IARC,2010), as well as with dibenzopyrenes (Siemiatycki et al., 2004).

Radke et al. (1980) were among the first to study the composition of PAHs in the “mobile” phase of coals, reporting that trends in PAH concentration and composition are not monotonic with variations in coal rank. In fact, PAH concentrations reach their maximum at bituminous coal rank, and then decrease as coalification progresses further. Several other studies investigated PAHs in coals, from either a single basin or a limited number of coal basins (e.g., Krüge, 2000; Püttmann and Schaefer, 1990; Stout and Emsbo-Mattingly, 2008; van Kooten et al., 2002; Willsch and Radke, 1995; Zhao et al., 2000). They mainly emphasized the influence of coal rank on the PAH concentration and composition. The influence of coal origin has not been systematically studied to date. Furthermore, a lack of uniformity in the analytical methods employed or the number of targeted PAHs in previous studies hinders any direct comparison between the existing data sets.

The aim of our study is therefore (1) to evaluate variations in the molecular signature of coal pyrolyzates in relation to coal rank and origin, and (2) to assess the differences in concentrations and compositions of PAHs from the “mobile” phase in coals of different rank, elemental composition, and origin. This was achieved by investigating a broad range of PAHs (including alkylated compounds) and applying principal component analysis to a set of fifty coal samples from eleven coal basins around the world.

2. Material and methods

2.1 Sample descriptions

The coal samples used in this study originated from eleven different coal regions, these being the Ruhr Basin (including Aachen and Ibbenbüren) and the Saar Basin in Germany (GER), the Upper Silesian Basin in Poland (POL), the Donets Basin in the Ukraine (UKR), the Sydney and Bowen basins in Australia (AUS), the Karoo Basin in South Africa (SAF), three basins in the USA, and the South Sumatra Basin in Indonesia (IND) (Figure 1). Samples were provided by scientific institutions and originate from different sections of the respective coal seams as described in e.g., Vorres et al. (1990) and Sachsenhofer et al. (2003).

Although some important coal basins could not have been embraced, to our knowledge this is the most comprehensive world-wide set of coal samples for which the results of a broad suite of bulk and molecular analyses are reported.

Most of the samples investigated were Carboniferous and Permian bituminous coals. Carboniferous sub-bituminous coal (Sample US2, Table 1) and anthracite (GR10, GR11), as well as Paleogene (US1) and Neogene (IS1-4) sub-bituminous coals were also investigated. Neogene samples from the Suban coal seam in Indonesia (IS5-IS8) warranted special

attention as they had been thermally metamorphosed, and even coked at the contact of an andesitic igneous intrusion (Amijaya et al., 2006).

Coal rank was determined on the basis of vitrinite reflectance, R_o (Table 1) and was additionally validated using Rock Eval T_{max} , the methylphenanthrene based maturity indices, and the mean reflectance calculated after Radke and Welte (1981), and Kruge (2000) (Figure S1, Supplementary data).

<Fig. 1>

Figure 1. Map showing the main coal deposits of the world, including the origin and age of the coals studied (after van Krevelen, 1993).

<Table 1>

Table 1. Investigated coal samples, location of the mines or coal seams, temperature of maximum hydrocarbon generation (T_{max}), and coal rank expressed as vitrinite reflectance (R_o). Samples are arranged by increasing R_o within their geographic groups.

2.2 Bulk analysis

The Rock Eval pyrolysis, used to determine the temperature of maximum hydrocarbon generation (T_{max}), was performed in the laboratories of the Department of Applied Geological Sciences and Geophysics (University of Leoben, Austria) and the Institute des Sciences de la Terre d'Orléans (University of Orléans, France). The elemental composition of the coals was determined using an Elementar Vario MACRO CHNS analyzer with a reproducibility of $\pm 0.5\%$ (C), $\pm 0.5\%$ (H), $\pm 1.3\%$ (N), $\pm 4.1\%$ (S), and $\pm 1.7\%$ (O). Moisture content was determined gravimetrically following the standard procedure (DIN 51718). Total organic carbon (TOC) content was determined with a LECO R612 Carbon Analyzer after Micić et al. (2010) with a reproducibility of $\pm 1.5\%$.

2.3 Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS)

Py-GC/MS was performed using a CDS 2000 Pyroprobe coupled to a Thermo Finnigan Focus DSQ GC/MS equipped with a DB-1MS column (30 m, 0.25 mm i.d., film thickness 0.25 μm , from J&W Scientific). The GC oven temperature was programmed from 50°C to 300°C at 5°C min^{-1} , with an initial hold of 5 minutes at 50°C and a final hold of 5 minutes at 300°C. Pyrolysis was performed for 20 seconds at 610°C. The MS was operated in full scan mode (m/z 50-500 Da, 1.08 scans/s). Measured aliquots (0.1 to 2.0 mg) of dry, homogenized coal were pyrolyzed directly, without derivatization. Fifteen coal samples, representative of the whole sample set (indicated by an asterisk in Table 1) were selected for Py-GC/MS analysis.

Compounds were identified on the basis of retention behavior and mass spectra with reference to computerized mass spectral libraries (Wiley Registry 8th Edition/NIST 2008). The proportions of aliphatic (alkanes and alkenes), aromatic (PAHs, biphenyl, and their alkylated derivatives), and oxygen-containing aromatic compounds (phenol, dibenzofuran (DBF), and their alkylated derivatives) were determined using their peak areas and calculating the percentage of each group in the sum of all.

Fig. 1

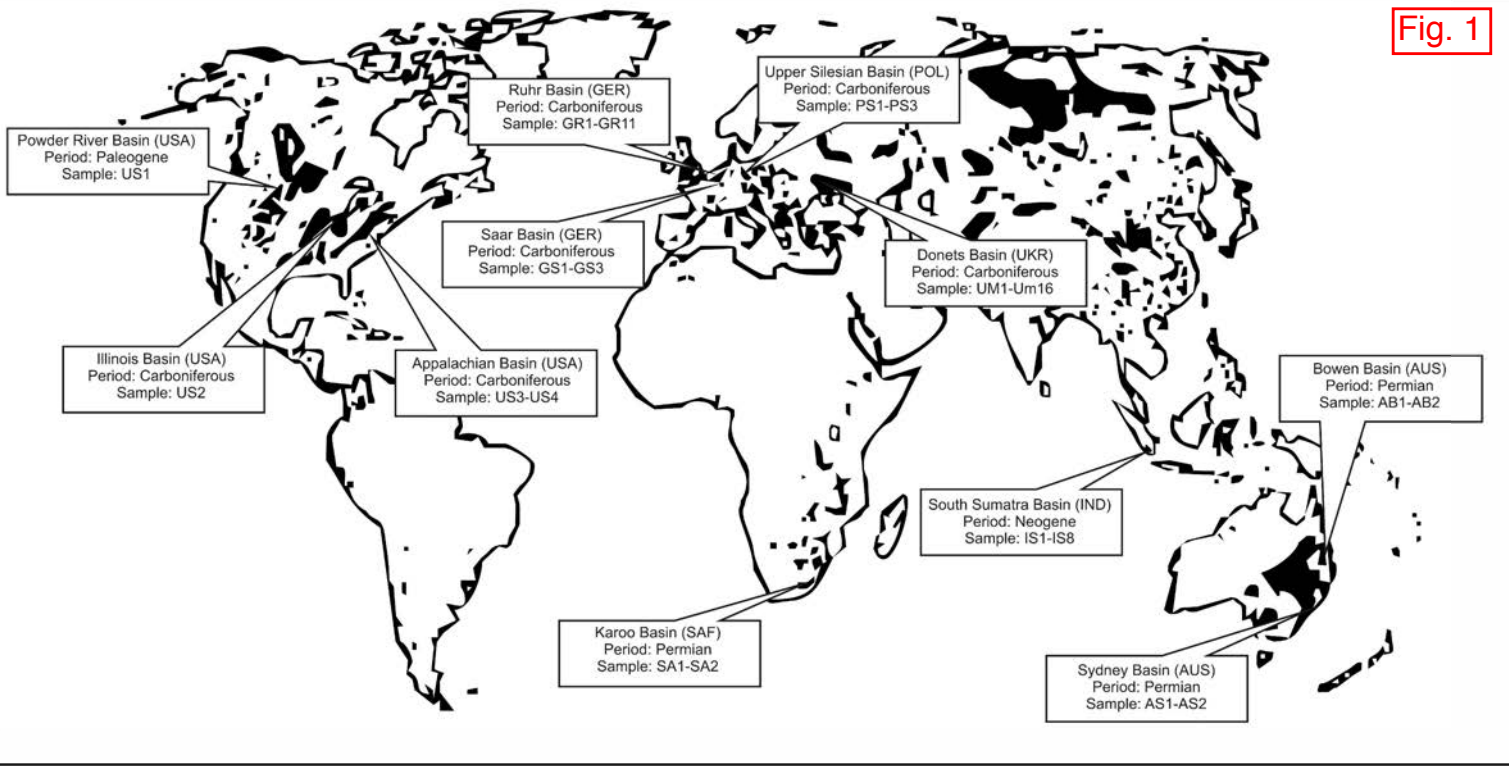


Table 1

Sample	R_o %	T_{max} °C	Coal seam / Mine location	Sample	R_o %	T_{max} °C	Coal seam / Mine location
IS1	0.52	424	Mangus	GS1	0.64	432	Ensdorf
IS2 *	0.55	424	Mangus	GS2	0.77	436	unknown
IS3	0.58	431	Mangus	GS3	0.78	443	Warndt/Luisenthal
IS4 *	0.66	437	Mangus	PS1 *	0.68	430	Brzeszcze
IS5	1.78	516	Suban	PS2	0.75	430	Brzeszcze
IS6	1.85	525	Suban	PS3 *	0.78	422	Silesia
IS7 *	5.18	n.d.	Suban	UM1	0.64	435	m2
IS8	5.18	n.d.	Suban	UM2	0.65	438	m2
AS1	0.71	474	Bulli	UM3	0.73	432	m2
AS2	0.90	468	Nipan o	UL4	0.84	447	l3
AB1 *	0.80	435	Upper Wynn	UL5	0.86	445	l3
AB2 *	1.41	607	German creek	UL6	0.87	445	l3
SA1 *	0.63	434	Witbank No.2	UL7	0.87	445	l3
SA2 *	0.64	433	Witbank No.2	UL8	0.88	446	l3
US1 *	0.32	416	Wyodak Anderson	UL9	0.90	448	l3
US2 *	0.46	413	Illinois No.6	UL10	0.90	446	l3
US3	1.16	457	Upper Freeport	UL11	0.91	449	l3
US4 *	1.46	488	Pocahontas No.3	Um12	1.13	480	m3
GR1 *	0.76	429	Freya	Um13	1.15	465	m3
GR2	0.90	436	N1	Um14	1.20	481	m3
GR3	0.94	443	H2	Um15	1.21	480	m3
GR4 *	1.06	466	Zollverein	Um16	1.23	477	m3
GR5	1.08	459	Mathilde				
GR6 *	1.40	479	Wasserfall				
GR7	1.52	482	Sonnenschein				
GR8	1.72	496	Girondelle				
GR9	1.94	520	Finefrau				
GR10	2.59	605	Aachen				
GR11	2.85	604	Ibbenbüren				

* Samples analyzed by Py-GC/MS

2.4 Extraction and clean up

One gram of each sample was spiked with internal standards and extracted in an accelerated solvent extractor (ASE 200, Dionex). Extraction was performed with dichloromethane (DCM) as the extraction solvent and applying two 7-minute static cycles at 120°C and 4 MPa, as described in Bergknut et al. (2006). The DCM extracts were treated with activated copper to remove elemental sulfur, followed by de-asphalting with *n*-hexane, after Willsch and Radke (1994). The extracts were then separated using open column chromatography (packed with silica gel, 50 µm in diameter), eluting with *n*-hexane (Fraction 1: saturated hydrocarbons), DCM (Fraction 2: unsaturated hydrocarbons, including PAHs), and methanol (Fraction 3: polar compounds).

2.5 Gas-chromatography/mass-spectrometry (GC/MS)

PAH-containing purified extracts were analyzed on an Agilent 7890A gas chromatograph (GC) equipped with a DB-5 MS fused silica capillary column (60 m, 0.25 mm i.d., film thickness 0.25 µm, from J&W Scientific) coupled to an Agilent 5975C quadrupole mass spectrometer (MS) with helium as the carrier gas. The GC oven was operated under the following conditions: isothermal for 1 minute at 55°C, temperature raised at 10°C min⁻¹ to 320°C, and then isothermal for 30 minutes. Both full scan and selected ion monitoring (SIM) modes were applied.

PAHs were identified by comparing retention behavior with that of the appropriate external standard. Compounds not present in the external standard mixture were identified on the basis of retention behavior, mass spectra with reference to computerized mass spectral libraries (Wiley Registry 8th Edition/NIST 2008 (W8/N08)), and elution pattern recognition with reference to published data (e.g., Armstroff et al., 2006; Kruge, 2000; van Aarssen et al., 1999). The quantified PAHs, corresponding internal and external standards, and molecular ions are listed in Table 2. Quantitative data were determined by comparing individual peak areas using SIM data (molecular ions) with those of the corresponding internal standards. The relative response factors (RFs) were calculated from a standard mixture containing both internal and external standards (Table S1, Supplementary data). Groups of each level of alkylation were quantified using straight baseline integration within a proper retention time window and the RFs of an appropriate external standard. Details regarding quality assurance are presented in the Supplementary data (Table S2).

<Table 2>

Table 2. List of quantified PAHs with corresponding internal (IS) and external (ES) standards and molecular ions (*m/z*).

2.6 Principal component analysis

Principal component analysis (PCA) was performed using 52 PAHs (including alkylated PAHs, listed in Table 2), maceral composition, TOC content, R_o , T_{max} , and elemental composition. Prior to the PCA, all data values below the limit of detection (LOD)

Table 2

Compound	Abbreviation	m/z	ES	IS	Compound	Abbreviation	m/z	ES	IS
Naphthalene	NAP	128	NAP		Fluoranthene	FLA	202	FLA	
2-Methylnaphthalene	2MN	142	2MN		Pyrene	PYR	202	PYR	
1-Methylnaphthalene	1MN	142	2MN		Benzo[a]fluorene	BFLU	216	BFLU	
Dimethylnaphthalenes	C ₂ NAP	156	2MN		Methylpyrenes/fluoranthenes	C ₁ PYR	216	1MPYR	
Trimethylnaphthalenes	C ₃ NAP	170	2MN		Dimethylpyrenes/fluoranthenes	C ₂ PYR	230	1MPYR	
Tetramethylnaphthalenes	C ₄ NAP	184	2MN		Trimethylpyrenes/fluoranthenes	C ₃ PYR	244	1MPYR	
Acenaphthylene	ACY	152	ACY		Benzo[b]naphtho(2,1-d)thiophene	BNT	234	BNT	
Acenaphthene	ACE	154	ACE		Cyclopenta[c,d]pyrene	CPP	226	CPP	
Fluorene	FLU	166	FLU		Benzo[a]anthracene	BANT	228	BANT	
Methylfluorenes	C ₁ FLU	180	1MFLU		Chrysene	CHR	228	CHR	
Dimethylfluorenes	C ₂ FLU	194	1MFLU		Methylchrysenes/benzo[a]anthracenes	C ₁ CHR	242	3MCHR	
9,10-Dihydroanthracene	DHA	180	DHA		Dimethylchrysenes/benzo[a]anthracenes	C ₂ CHR	256	3MCHR	
Dibenzothiophene	DBT	184	DBT		Trimethylchrysenes/benzo[a]anthracenes	C ₃ CHR	270	3MCHR	
Methyl dibenzothiophenes	C ₁ DBT	198	DBT		Benzo[b]fluoranthene		252	BbFLA	
Dimethyl dibenzothiophenes	C ₂ DBT	212	DBT		Benzo[k]fluoranthene		252	BkFLA	
Trimethyl dibenzothiophenes	C ₃ DBT	226	DBT		Benzo[a]fluoranthene	BPYR	252	BaFLA	
Phenanthrene	PHN	178	PHN		Benzo[e]pyrene		252	BePYR	
Anthracene	ANT	178	ANT		Benzo[a]pyrene		252	BaPYR	
3-Methylphenanthrene	3MP	192	2MP		Dibenzo[a,h]anthracene	DBA	278	DBA	
2-Methylphenanthrene	2MP	192	2MP		Indeno-1,2,3-[c,d]pyrene		276	IPYR	
Methylanthracene	C ₁ ANT	192	2MP		Benzo[g,h,i]perylene	BPER	276	BPER	
9-Methylphenanthrene	9MP	192	2MP		Anthanthrene		276	ANTA	
1-Methylphenanthrene	1MP	192	2MP		Dibenzo[a,i]pyrene		302	DBaiPYR	
Dimethylphenanthrenes/anthracenes	C ₂ PHN	206	2MP		Dibenzo[a,e]pyrene		302	DBaePYR	
Trimethylphenanthrenes/anthracenes	C ₃ PHN	206	2MP		Dibenzo[a,i]pyrene	DBP	302	DBaiPYR	
Tetramethylphenanthrenes/anthracenes	C ₄ PHN	206	2MP		Dibenzo[a,h]pyrene		302	DBahPYR	

ES – External Standard. IS – Internal Standard

were replaced with random numbers between the compound specific LOD and its ten-fold smaller value. The PCA was then performed on the square root transformed data using JMP version 7.0 software (SAS Institute Inc.).

3. Results and Discussion

3.1 Petrographic characteristics

Vitrinite was the most abundant maceral in the majority of the samples (commonly 66–93 vol.%), as illustrated in the Supplementary data (Figure S2). The exceptions were four samples from the Upper Silesian (POL) and Karoo (SAF) basins which were made up of 50 to 55% inertinite, compared to 1 to 33% in the other coals. There was no liptinite in coals with $R_o > 1.1\%$ (Teichmüller and Durand, 1983), while the liptinite content in coals with $R_o < 1.1\%$ ranged from 10 to 16% in low rank coals from the Ruhr (GER), Saar (GER), Donets (UKR), and South Sumatra (IND) basins.

3.2 Elemental composition of coal as a function of coal rank and origin

The elemental composition of coal changes during the course of coalification: the carbon content increases and the oxygen and hydrogen contents decrease as a result of dehydroxylation, demethylation, and condensation reactions (van Krevelen, 1993). These systematic changes were also recorded in our sample set and are presented in Figure 2. The carbon content increased with increasing rank from 69% in sub-bituminous coal from the Powder River Basin (US1) to 95% in thermally metamorphosed samples from the South Sumatra Basin (IS7/IS8). The oxygen levels decreased accordingly with increasing rank from 23 to 2%. The hydrogen content remained fairly constant at ~5% throughout the bituminous coal range but decreased to 2-3% in anthracite and the thermally metamorphosed samples. The nitrogen content remained at around 1-2% in all samples. Sulfur levels ranged from 0.3 to 5.3%, with the highest values in coals from the Illinois (USA) and Donets (UKR) basins, reflecting a marine influence on the Illinois 6 and the m3 seams in these basins.

<Fig. 2>

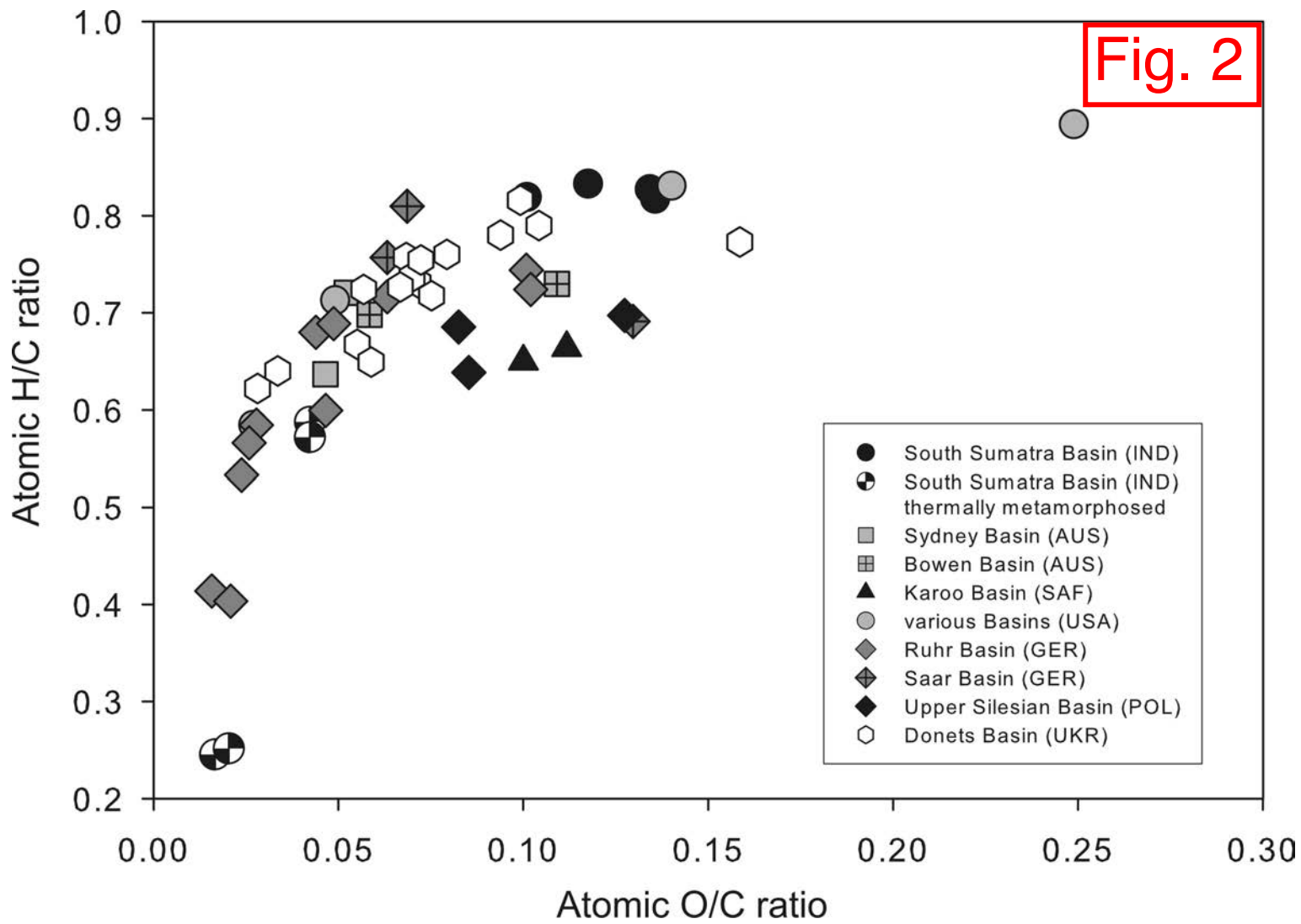
Figure 2. Progressive decrease in hydrogen and oxygen contents in relation to carbon content (van Krevelen, 1993).

3.3 Variations in the molecular signature of the coal pyrolyzates as a function of coal rank and origin

In order to further illustrate the geochemical variations that occur during coalification and their dependence on the coal origin, we investigated the proportions of aliphatic, aromatic, and oxygen-containing aromatic compounds (such as phenol, dibenzofuran (DBF), and their alkylated derivatives) in fifteen representative samples by means of Py-GC/MS.

The proportion of aromatic compounds in coal increases throughout the maturation process, whereas the aliphatic and oxygen-containing fractions decrease (Hatcher and Clifford, 1997). Similar variations were observed in the pyrolyzates of our sample set (Figure 3). The aromatic fraction varied from 23% in sub-bituminous coal from the Powder River

Fig. 2



Basin (US1) to 98% in bituminous coal from the Appalachian Basin (US4). The influence of coal origin on molecular signatures is more obvious in the lower rank samples ($R_o < 1.0\%$). For example, in the low rank, liptinite-rich Neogene coals from the South Sumatra Basin (IND) the aliphatic fraction comprised about 40%, which is consistent with the higher aliphatic structures within the liptinite maceral group (Wollenweber et al., 2006). For low rank samples from other basins the aliphatic fraction ranged between 10% in samples from the Karoo Basin (SAF) and 25% in the sample from the Powder River Basin (US1). Pyrolyzates of low rank, inertinite-rich coals from the Karoo (SAF) and the Upper Silesian (POL) basins, were dominated by the aromatic fraction, confirming the higher content of aromatic structures within the inertinite maceral group (Hatcher et al., 1992; Taylor et al., 1998). The oxygen-containing fraction was most abundant in pyrolyzates of the sub-bituminous Paleogene US coal, of which it constitutes ~52%. In the pyrolyzates of low rank, vitrinite-rich Carboniferous and Permian coals from the Ruhr (GER), Upper Silesian (POL), and Bowen (AUS) basins, the oxygen-containing fraction ranged between 25 and 32% (Figure 3).

<Fig. 3>

Figure 3. Ternary plot showing the composition of fifteen coal pyrolyzates. Aromatic fraction includes PAHs, biphenyl, and their alkylated derivatives. Aliphatic fraction contains alkanes and alkenes. Oxygen containing fraction consists of phenol, dibenzofuran, and their alkylated derivatives.

Variations in the molecular signatures of the pyrolyzates with increasing rank correlate with the changes in elemental composition. An increase in the aromatic fraction (and a corresponding decrease in the aliphatic and oxygen-containing fractions) is accompanied by an increase in the carbon content (and a decrease in the oxygen and hydrogen contents), as illustrated in Figure S3, Supplementary data.

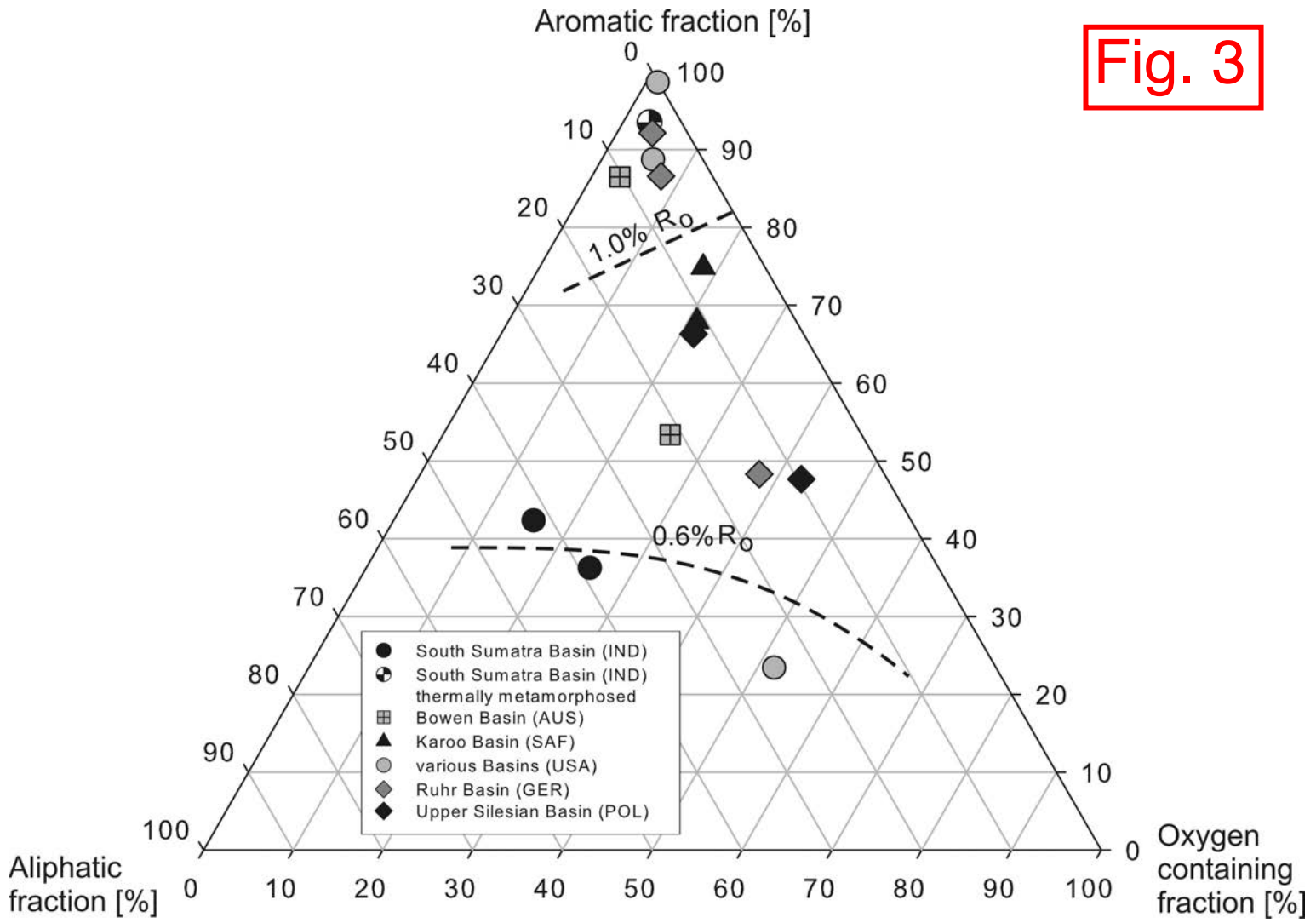
3.4 Concentration and composition of PAHs in coals as a function of rank and origin

Variations in the molecular signatures of coal pyrolyzates as a consequence of coalification are also reflected in the concentrations and compositions of PAHs in the extractable fraction (“mobile” phase). In particular reactions such as condensation, aromatization, demethylation and dehydroxylation cause (a) a decrease of the concentrations of extractable PAHs (e.g., Radke et al., 1982; Stout and Emsbo-Mattingly, 2008) and (b) variations in the composition of PAHs in the “mobile” phase, such as an increase in the concentration of low molecular weight (2-3 ring) PAHs, and a decrease in the degree of alkylation in PAHs (Stout and Emsbo-Mattingly, 2008).

3.4.1 Extractable PAH concentrations

Concentrations of extractable PAHs (PAH_{extr} , including 52 PAHs, comprising 35 individual compounds and 17 compound groups, Table 2) ranged between 14 and 2090 $mg\ kg^{-1}$. Concentrations close to 2000 $mg\ kg^{-1}$ were recorded in coals from the Saar (GER), Ruhr (GER), Sydney (AUS), South Sumatra (IND) and Donets (UKR) basins (Figure 4). Concentrations of the 16 US EPA PAHs varied from 6 to 253 $mg\ kg^{-1}$, with the highest

Fig. 3



values in two samples from the Donets Basin (UKR). The concentrations of high molecular weight (HMW) PAHs (i.e., 5-6 ring PAHs, Table 2) ranged from 1 to 94 mg kg⁻¹. The highest concentrations of HMW-PAHs (94 and 72 mg kg⁻¹) were recorded in the inertinite-rich coal samples from the Upper Silesian (POL) and Karoo (SAF) basins, respectively.

Previous studies reported that the extractable PAH concentrations formed a bell-shaped curve when plotted against coal rank, with the highest concentrations occurring when the R_o value was approximately equal to 1% (e.g., Achten and Hofmann, 2009; Radke et al., 1980). We observed a similar trend for the eleven Carboniferous coal samples from different seams in the Ruhr Basin (GER) with the vitrinite reflectance ranging from 0.76 to 2.85% (Figure 4, grey line). However, the bell-shaped curve was not observed in the samples from remaining basins investigated. Neither was such a trend evident on a multi-basin scale, including the broad set of 50 coals from diverse basins.

The Donets Basin (UKR) coals, for example, showed no relationship between PAH concentration and rank within the R_o range from 0.64 to 1.23% (Figure 4). Coals from the various basins in the USA with a R_o of 0.32–1.41%, all had similar PAH_{extr} concentrations of ~300 mg kg⁻¹, independently of the coal rank. Moreover, the samples from the USA basins (US1-US4) exhibited the lowest concentration of PAH_{extr} of the coals investigated. For instance, in the sample from the Upper Freeport coal bed, with a R_o of 1.16% (US3, Table 1) the PAH_{extr} concentration was 304 mg kg⁻¹. This concentration is significantly lower than 1790 mg kg⁻¹ of PAH_{extr} recorded in the coal from the Donets Basin in Ukraine with almost the same R_o (1.15%, Um13, Table 1). Generally high PAH_{extr} concentrations were recorded in the thermally metamorphosed Indonesian samples (IS5-IS8, Table 1) compared to coals of the same rank that had not experienced thermal metamorphism, such as Ruhr samples (with R_o>1.7%). Concretely, in the sample from the Ruhr Basin with a vitrinite reflectance of 1.72% (GR8, Table 1) the PAH_{extr} concentration was 226 mg kg⁻¹. The coal from the South Sumatra Basin with a similar vitrinite reflectance (1.78%, IS6, Table 1) had much higher PAH_{extr} concentration of 907 mg kg⁻¹ (Figure 4). We conclude therefore that the different trends in PAH concentrations are not only a function of the coal rank, but also of the coal origin.

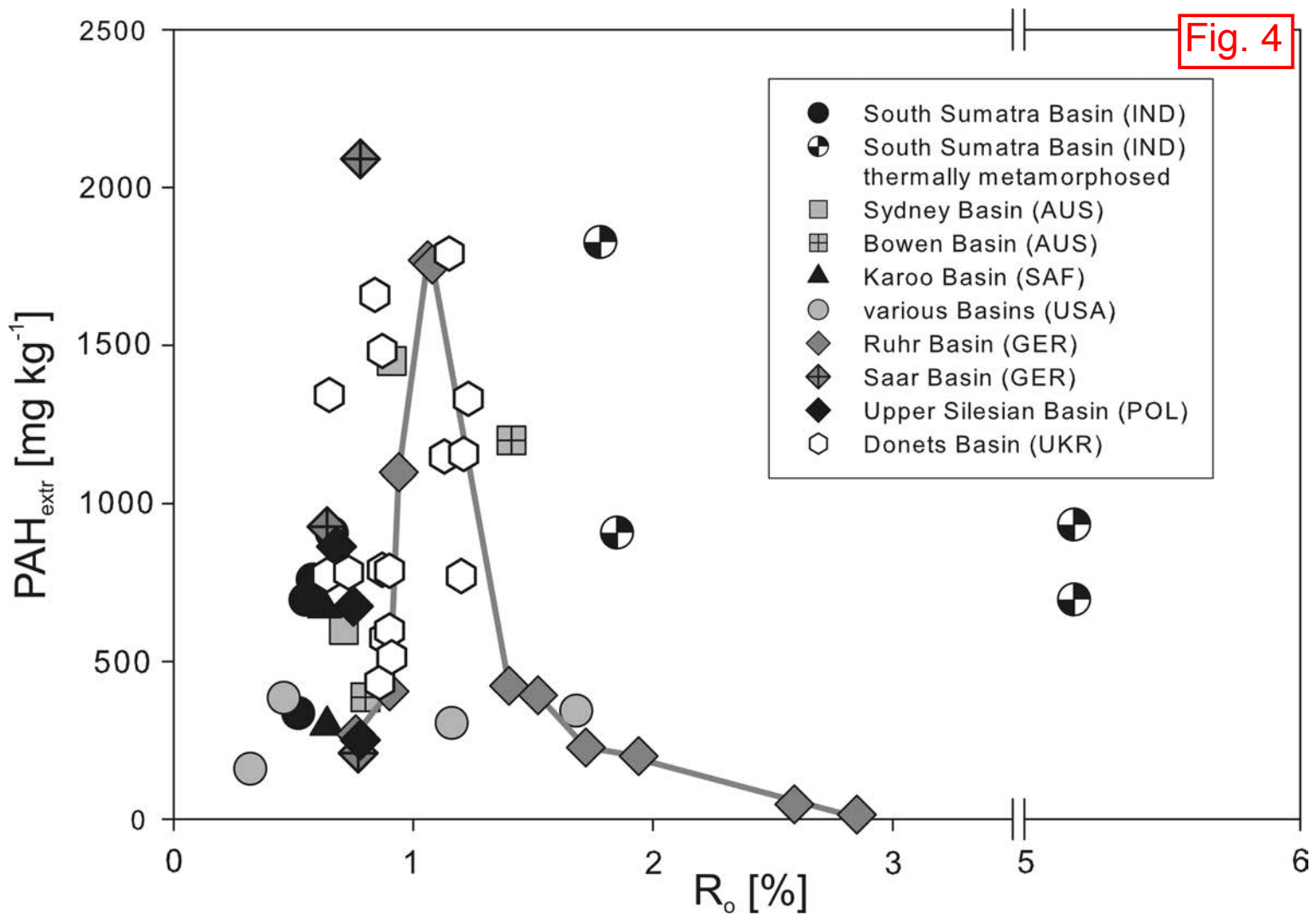
<Fig. 4>

Figure 4. Relationship between vitrinite reflectance (R_o) and the PAH_{extr} concentration in coals from different basins.

3.4.2 PAH composition

In order to investigate variations in PAH composition with respect to their molecular size (i.e., the number of fused benzene rings) we used the ratio of low molecular weight (LMW) PAH_{extr} concentrations (with 2-3 benzene rings, including their alkylated counterparts) to the concentrations of all (low and high molecular weight, AMW) PAHs, herein termed the LMW/AMW ratio. If there is a shift from a predominance of 4-6 ring PAHs towards a predominance of 2-3 ring PAHs with increasing coal rank, as indicated by Stout and Emsbo-Mattingly (2008), then this ratio should increase with increasing coal rank. When applied to our sample set, the LMW/AMW ratio increased with the rank for coals from the

Fig. 4



Donets (UKR), Bowen (AUS), and South Sumatra (IND) basins (Figure 5). The high rank thermally metamorphosed samples from the South Sumatra Basin (IS7, IS8) exhibited a LMW/AMW ratio close to 1, which indicates that the PAH composition from these samples consists almost entirely of 2-3 ring PAHs.

No trend in the LMW/AMW ratio with increasing coal maturity was discerned in coal samples from other basins, most likely due to the samples not covering a sufficiently broad range of vitrinite reflectance. The LMW/AMW ratio for coals from the Ruhr Basin (GER), however, increased with rank to reach a maximum at 1.4% R_o , but then decreased below 0.5 at the anthracite stage (Figure 5). This indicated that these two anthracite samples are dominated by HMW PAHs, just opposite to the two above mentioned Indonesian anthracites (IS7, IS8). This implies that PAH composition with respect to their molecular size does not depend only on the coal maturity, but also on the coalification history, evident for the coals at higher maturity stage.

<Fig. 5>

Figure 5. Dependence of the LMW/AMW ratio (low molecular weight PAHs over all molecular weight PAHs) on the coal rank.

In order to explore variations in the degree of alkylation we used the ratio between the concentrations of parent and monomethylated naphthalenes and phenanthrenes (C_0 - C_1 NAP&PHN) and the sum of parent, monomethylated, dimethylated, trimethylated, and tetramethylated naphthalenes and phenanthrenes (C_0 - C_4 NAP&PHN), herein termed the $(C_0-C_1)/(C_0-C_4)$ NAP&PHN ratio.

Within the investigated set of coals with diverse origins an increase in the $(C_0-C_1)/(C_0-C_4)$ NAP&PHN ratio was observed with increasing coal rank, reflecting the decrease in abundance of the more alkylated compounds with increasing coalification. This trend was observed within those basins for which we had sufficient samples to provide a range of ranks but, more interestingly and unlike the LMW/AMW ratio, the same trend was also evident for the entire sample collection (Figure 6a).

The majority of samples showed a predominance of alkylated phenanthrenes and naphthalenes over their parent compounds (C_0), producing a bell-shaped profile (Figure 6b) and having the $(C_0-C_1)/(C_0-C_4)$ NAP&PHN ratios ≤ 0.5 . Thermodynamically less stable alkylated (C_2 - C_4) NAP&PHN (Budzinski et al., 1993) are more abundant than their unsubstituted counterparts (C_0 NAP&PHN) in coals with a vitrinite reflectance $\leq 1.6\%$. In more mature samples with the $R_o > 1.6\%$ (with one exception of a sample from the South Sumatra Basin (IND)), the $(C_0-C_1)/(C_0-C_4)$ NAP&PHN ratio was > 0.5 , indicating a predominance of thermodynamically more stable C_0 - C_1 NAP&PHN (Budzinski et al., 1993). A closer look into the distribution of NAP&PHN and their alkylated derivatives in these samples revealed that monomethylated (C_1) compounds indeed predominate (Figure 6c). Another distinctive sample was the one from the Ruhr Basin (GR10), which even showed a predominance of the parent compounds (C_0), producing a sloping profile (Figure 6d).

Based on the $(C_0-C_1)/(C_0-C_4)$ NAP&PHN ratio, which in the whole sample set generally increases with increasing maturity of coals, we demonstrated a decrease in alkylation as coalification progresses. Furthermore, we revealed that there is not a complete

loss of alkylated PAHs, but rather a shift towards the dominance of monomethylated compounds over the observed range of coal ranks.

<Fig. 6>

Figure 6. (a) Relationship between vitrinite reflectance (R_o) and the degree of alkylation; (b) Example of a bell-shaped profile with a maximum at C_2 compounds (sample UL5); (c) Example of a bell-shaped profile with a maximum at C_1 compounds (sample US4); (d) Example of a sloping profile (sample GR10) of NAP alkylation series.

3.5 Principal component analysis

A principal component analysis (PCA) was applied to further investigate the relationship between coal composition (PAHs, macerals, bulk geochemistry) and origin. Most of the variance (70%) of the dataset was explained by the first three principal components. The resulting second and third principal components (PC2 and PC3) accounted for 18% and 12% of the variance respectively, and were geochemically the most informative.

The eigenvector for the PC2 showed a strong negative contribution from C_4 naphthalenes and phenanthrene/anthracene isomers, as well as from anthracene and C_1 anthracene (Figure 7b). In contrast, the PC2 eigenvector showed a positive contribution from C_0 - C_2 naphthalenes as well as from C_0 - C_1 phenanthrenes such as 2MP and 3MP (refer to Table 2 for the full compound name), which are thermodynamically more stable than C_0 - C_1 anthracenes (Radke et al., 1982). A decrease in the degree of alkylation and the formation of thermodynamically more stable compounds during coalification have been described previously (Radke and Welte, 1981; Stout and Emsbo-Mattingly, 2008) and were illustrated in our sample set through the sensitivity of the PC2 to coal rank. Furthermore, strong negative contributions from the bulk oxygen and hydrogen contents and a positive contribution from the carbon content, vitrinite reflectance, and Rock Eval T_{max} were observed in the eigenvector for the PC2, providing additional confirmation of the dependence of the PC2 on the coal rank. Finally, the liptinite content (a hydrogen-rich maceral, more abundant in less mature coals) appeared to have a strong negative contribution to the PC2, which is consistent with the correspondingly higher hydrogen content and the higher degree of alkylation.

The eigenvector corresponding to the PC3 indicated a strong positive contribution from the HMW parent PAHs (5-6 ring PAHs, Figure 7b), and a negative contribution from the 2-3 ring PAHs and their alkylated derivatives. We therefore conclude that the PC3 is sensitive to the ring number in PAHs. In addition, the inertinite content had a strong positive contribution to the PC3 eigenvector (Figure 7b). This confirms that the PAH composition and concentration are not only a function of coal rank (and corresponding R_o values, and the C, H, and O contents), but also of the coal's maceral composition and therefore is strongly influenced by the origin of the coal.

<Fig. 7>

Figure 7. (a) PCA for PAHs, bulk parameters, and maceral composition: the second principal component (PC2) accounted for 18% of the variation in the data set, and the third principal component (PC3) accounted for 14% of the variation. (b) Loadings of PCA results in Figure 7a.

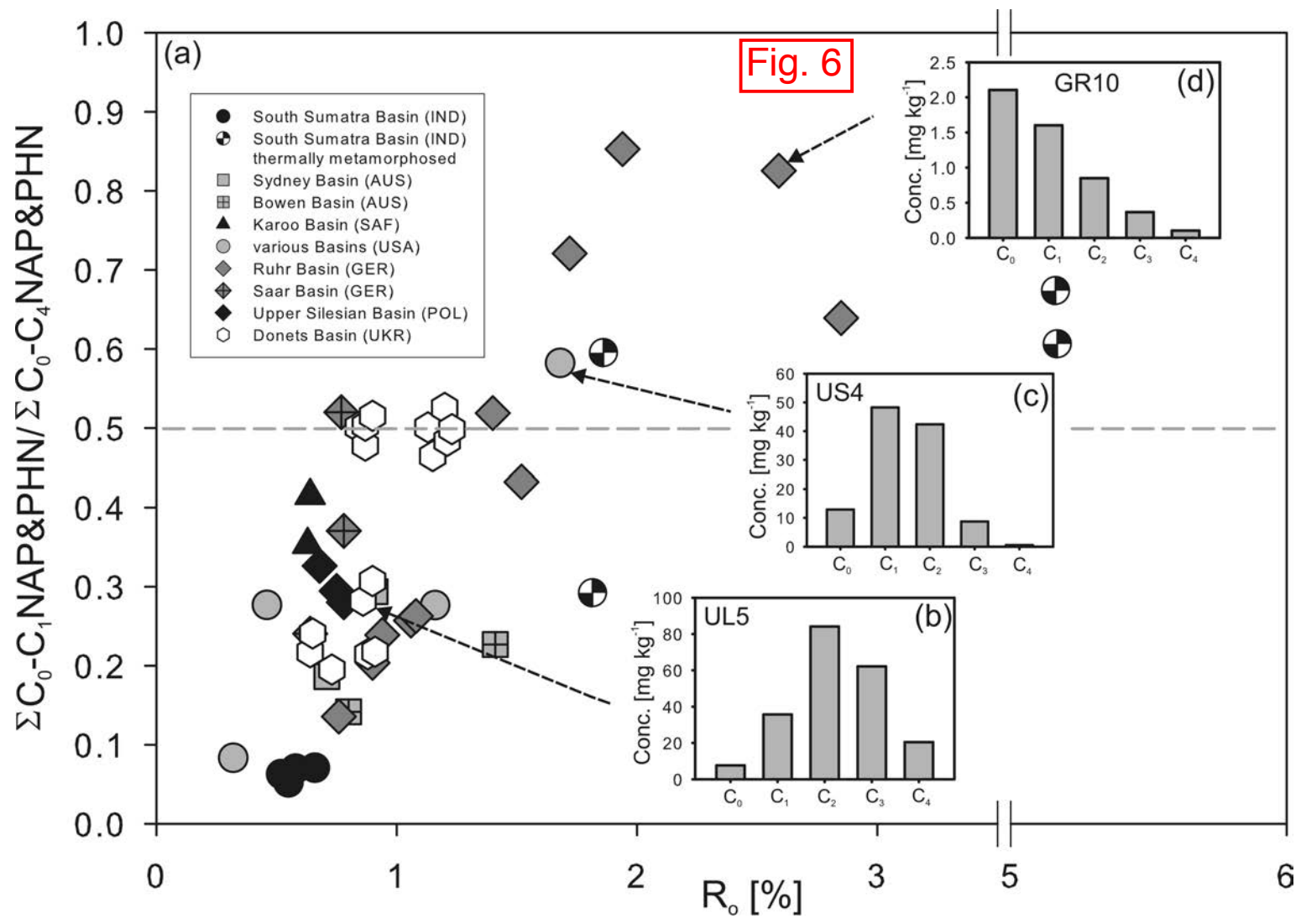
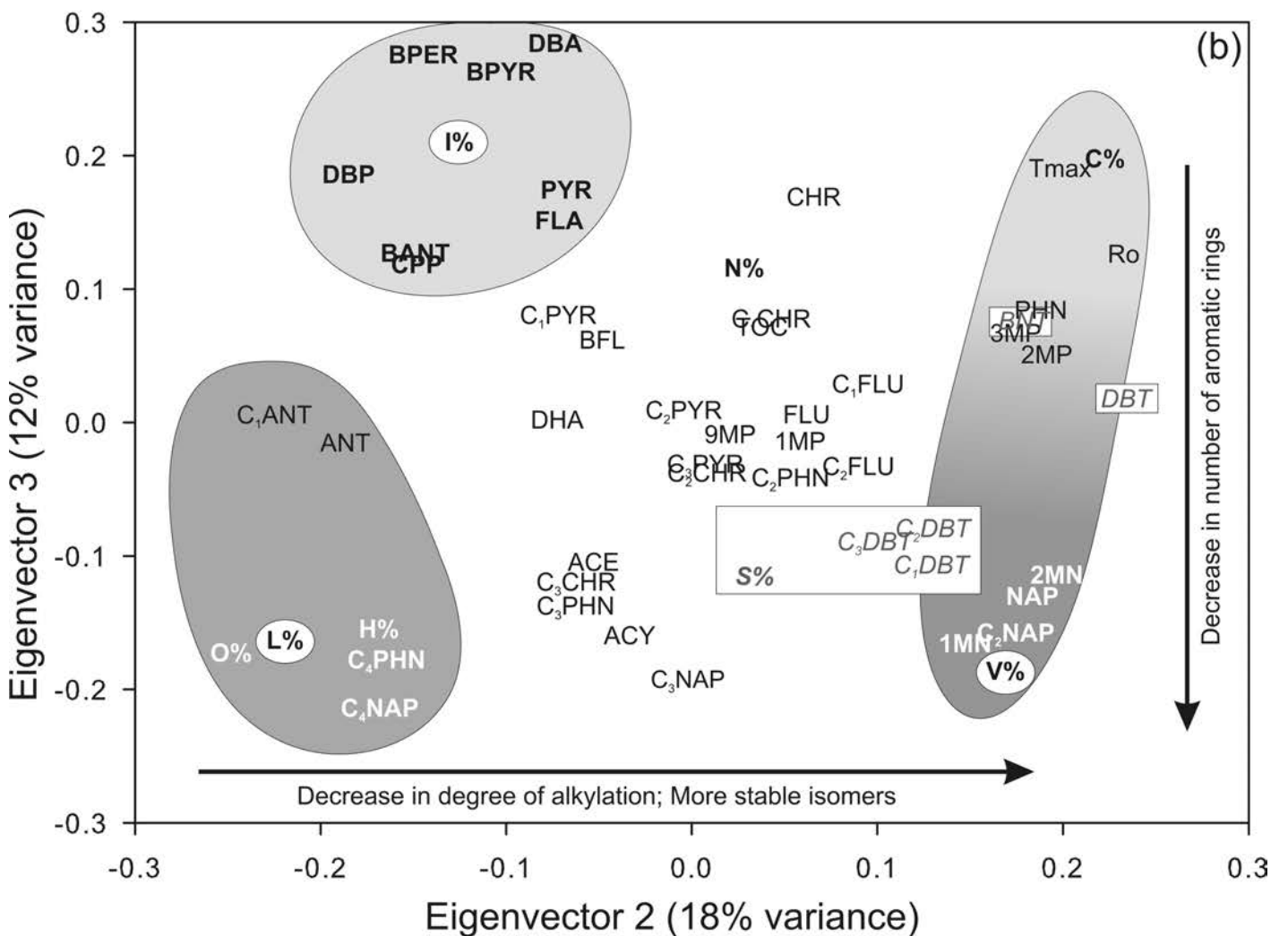
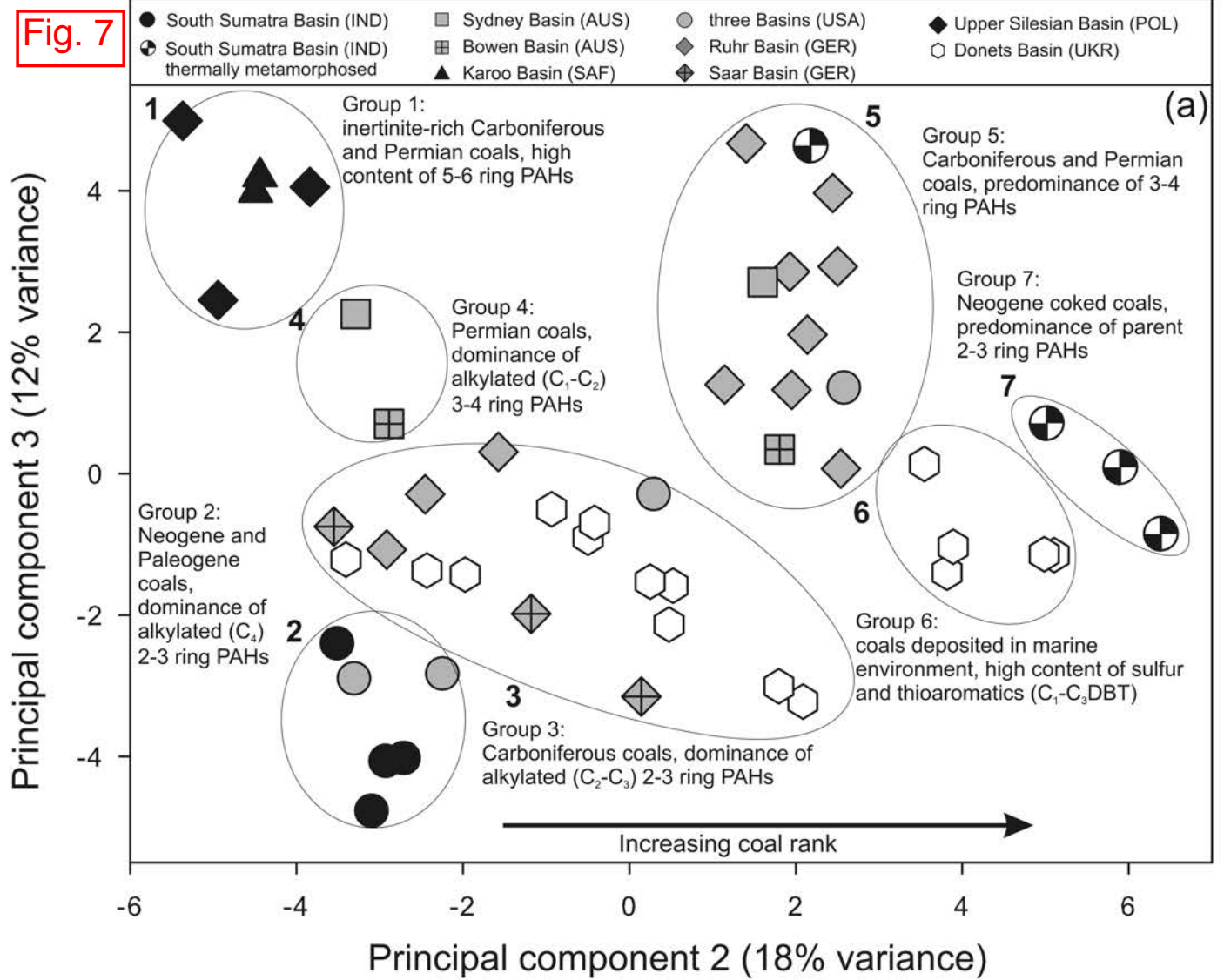


Fig. 7

The set of samples used in this study has been divided into seven groups according to their rank and origin on the basis of their bulk geochemistry, their PAH and maceral content, and maturity indices (Figure 7a). Coals with a high inertinite and HMW-PAH content, such as the samples from the Karoo (SAF) and Upper Silesian (POL) basins, comprise Group 1. Low rank, liptinite-rich Neogene coals from the South Sumatra Basin (IND) (0.52-0.66% R_o) and the two low rank coals from the USA basins (0.32-0.46% R_o) fall into Group 2 (clustering in the lower left part of Figure 7a). The samples in Group 2 are dominated by C_4 naphthalenes and phenanthrenes. Less mature Carboniferous coal samples mainly from the German basins and the m2 and l3 seams in the Donets Basin (UKR), make up Group 3 (0.64-0.9% R_o) and are characterized by a predominance of 2-3 ring PAHs and their methylated (C_2 - C_3) derivatives. Group 4 consists of the low rank Permian coals from the Bowen and Sydney basins (AUS) (0.7-0.8% R_o), which exhibited a predominance of 3-4 ring PAHs. The higher rank Carboniferous coals from the German, Australian, Ukrainian, and USA basins (1.0-2.85% R_o) fall into Group 5 and plot in the upper right of Figure 7a. Group 6 includes all samples from the m3 seam, deposited in a marginal-marine environment (Sachsenhofer et al., 2003) in the Donets Basin (UKR). These samples are characterized by a high sulfur content and sulfur-containing heterocycles such as alkylated dibenzothiophene (DBT1-3). Three of the thermally metamorphosed Neogene coals from the South Sumatra Basin (IND) (1.85 - 5.18% R_o) make up Group 7, plotting on the right in Figure 7a, with a high rank and high naphthalene and phenanthrene content (see also Figure 5).

The PCA has thus permitted the origin of coal samples to be distinguished graphically on the basis of their PAH and maceral content and their bulk parameters (TOC content, T_{max} , R_o , and elemental composition).

4. Conclusion

Coal particles and coal by-products may introduce related pollutants, including PAHs, into environments impacted by an extensive coal mining and usage. The amount and composition of the pollutants that could possibly be released vary with the rank and origin of coals.

In this study we showed that the molecular composition in coal pyrolyzates reflects differences in the maceral composition of samples with different origins. Aliphatic compounds were dominant in the liptinite-enriched samples from the South Sumatra Basin (IND); aromatic compounds were more abundant in the inertinite-rich samples from the Karoo Basin (SAF), whereas oxygen-containing compounds were only dominant in the sub-bituminous coal from the Powder River Basin (USA).

Our study additionally showed that numerous parameters used for principal component analysis (PAH_{extr} , elemental and maceral composition) serve well in separating the investigated set of coals into seven groups according to their rank and origin.

The composition of PAHs in the extractable portion of coals characterized by a predominance of 2-3 ring PAHs throughout the entire range of coal maturity, irrespective of the coal origin. Only in the anthracites from the Ruhr Basin in Germany (GR10, GR 11) the higher molecular weight (4-6 ring) PAHs dominated. Furthermore, we revealed that di- and trimethylated compounds dominate in the less mature coals ($R_o < 1.6\%$), while

monomethylated compounds dominate in the coals with $R_o > 1.6\%$ in our sample set. This progressive lowering of the degree of alkylation does not lead to a complete loss of alkylated PAHs, but to a dominance of mono- methylated compounds as the coalification proceeds.

Regarding the relationship between PAH_{extr} concentrations and coal rank, we revealed that this relationship is apparent in samples within a single coal basin (Ruhr Basin, GER). However, there is no evidence for such a relationship on a multiple-basin scale, when the entire set of 50 coals from different basins was investigated. We demonstrated that the PAH_{extr} concentrations vary by an order of magnitude between coals of almost identical maturity, but which derive from different basins. This implies that possible environmental risks of PAHs related to unburnt coal particles in the environment do not depend on the coal maturity solely, but also on the coal origin. Moreover, as we showed that less mature coal samples are dominated by 2-3 ring PAHs with C₂-C₃ methylated moieties (compounds less water soluble compared to the C₀-C₁ methylated counterparts) and therefore believe that these coals can create less risks regarding the mobilization of PAHs, compared to the more mature samples, if there is a prolong exposure of coals to aqueous environments. Nevertheless, this does reflect the overall environmental risks, since less mature coals (such as subbituminous coals) account other potentially toxic compounds than PAHs, such as, biphenyls, N-, O-, and S-containing heterocyclic compounds, aromatic amines, various non-aromatic compounds, and phthalates, that may be mobilized and transported via co-eluting humic-like substances.

Acknowledgments

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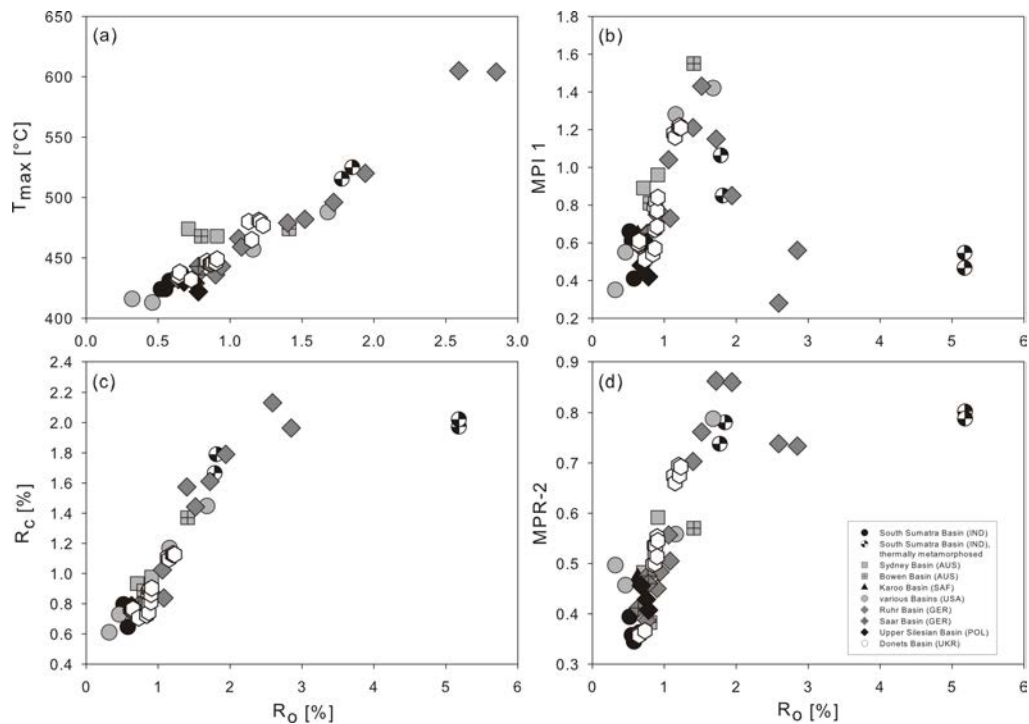
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Supplementary data

Variations in concentrations and composition of polycyclic aromatic hydrocarbons (PAHs) in coals related to the coal rank and origin

Laumann, S., Micić, V., Kruge, M.A., Achten, C., Sachsenhofer, R.F., Schwarzbauer, J., Hofmann, T.

Figure S1. Correlation of the vitrinite reflectance (R_o) with (a) T_{max} derived from Rock Eval pyrolysis; (b) methylphenanthrene index MPI-1[†], (c) calculated mean reflectance R_c ^{*}, (d) methylphenanthrene ratio MPR-2[‡].



$$^{\dagger} \text{MPI-1} = 1.5 \cdot (2\text{-MP} + 3\text{-MP}) / (\text{PHN} + 1\text{-MP} + 9\text{-MP})$$

$$^* R_c = 0.60 \cdot \text{MPI 1} + 0.40 \text{ (for } R_o < 1.35\%); R_c = -0.60 \cdot \text{MPI 1} + 2.30 \text{ (for } R_o > 1.35\%)$$

$$^{\ddagger} \text{MPR-2} = (2\text{-MP} + 3\text{-MP}) / (1\text{-MP} + 9\text{-MP} + 2\text{-MP} + 3\text{-MP})$$

MP – methylphenanthrene

PHN - phenanthrene

Table S1. Response factors (RFs) for the quantification of target compounds.

Compound	RFs	IS
Naphthalene	1.03	Naphthalene D8
2-Methylnaphthalene	0.74	
Acenaphthylene	0.91	
Acenaphthene	0.57	
Fluorene	0.70	
1-Methylfluorene	0.44	
9,10-Dihydroanthracene	0.48	
Dibenzothiophene	0.97	
Phenanthrene	1.10	Phenanthrene D 10
Anthracene	0.99	
2-Methylphenanthrene	0.82	
Fluoranthene	1.15	
Pyrene	1.19	
Benzo[a]fluorene	0.75	
1-Methylpyrene	0.79	
Benzonaphthothiophene	1.11	
Benzo[a]anthracene	0.96	
Cyclopenta[cd]pyrene	0.84	
Chrysene	1.12	
3-Methylchrysene	0.73	
Benzo[b]fluoranthene	1.37	
Benzo[k]fluoranthene	1.49	
Benzo[a]fluoranthene	1.04	
Benzo[e]pyrene	1.33	
Benzo[a]pyrene	1.13	
Indeno[1,2,3-cd]pyrene	1.50	
Dibenzo[a,h]anthracene	1.28	
Benzo[g,h,i]perylene	1.34	
Anthanthrene	0.85	
Dibenzo[a,l]pyrene	0.65	
Dibenzo[a,j]pyrene	0.74	
Dibenzo[a,i]pyrene	0.46	
Dibenzo[a,h]pyrene	0.43	

IS – internal standard

Table S2. Relative standard deviations for duplicate measurements (RSD), limit of detection (LOD) and limit of quantification (LOQ) for each target compound.

Compound	Abbreviation	RSD [%]	LOD [mg kg ⁻¹]	LOQ [mg kg ⁻¹]
Naphthalene	NAP	3.61	0.0052	0.0172
2-Methylnaphthalene	2MN	/	0.0072	0.0241
Methylnaphthalenes	C ₁ NAP	6.49	/	/
Dimethylnaphthalenes	C ₂ NAP	12.73	/	/
Trimethylnaphthalenes	C ₃ NAP	9.36	/	/
Tetramethylnaphthalenes	C ₄ NAP	13.04	/	/
Acenaphthylene	ACY	7.44	0.0014	0.0047
Acenaphthene	ACE	8.17	0.0021	0.0068
Fluorene	FLU	13.81	0.0121	0.0403
1-Methylfluorene	1MFLU	/	0.0148	0.0494
Methylfluorenes	C ₁ FLU	15.37	/	/
Dimethylfluorenes	C ₂ FLU	12.00	/	/
9,10-Dihydroanthracene	DHA	9.86	0.0107	0.0010
Dibenzothiophene	DBT	14.16	0.0048	0.0161
Methyldibenzothiophenes	C ₁ DBT	14.12	/	/
Dimethyldibenzothiophenes	C ₂ DBT	12.39	/	/
Trimethyldibenzothiophenes	C ₃ DBT	11.03	/	/
Phenanthrene	PHN	7.60	0.0063	0.0211
Anthracene	ANT	5.21	0.0071	0.0237
2-Methylphenanthrene	2MP	/	0.0203	0.0678
Methylphenanthrenes/anthracenes	C ₁ PHN	3.43	/	/
Dimethylphenanthrenes/anthracenes	C ₂ PHN	6.48	/	/
Trimethylphenanthrenes/anthracenes	C ₃ PHN	5.49	/	/
Tetramethylphenanthrenes/anthracenes	C ₄ PHN	5.30	/	/
Fluoranthene	FLA	7.49	0.0195	0.0649
Pyrene	PYR	5.80	0.0164	0.0546
Benzo[a]fluorene	BaFLU	7.82	0.0121	0.0403
1-Methylpyrene	1MPYR	/	0.0220	0.0733
Methylpyrenes/fluoranthenes	C ₁ PYR	4.73	/	/
Dimethylpyrenes/fluoranthenes	C ₂ PYR	9.19	/	/
Trimethylpyrenes/fluoranthenes	C ₃ PYR	9.48	/	/
Benzo[b]naphtho(2,1-d)thiophene	BNT	8.04	0.0047	0.0156
Cyclopenta[c,d]pyrene	CPP	8.26	0.0129	0.0821
Benzo[a]anthracene	BaANT	7.74	0.0247	0.0870
Chrysene	CHR	11.69	0.0261	0.0431
3-Methylchrysene	3MCHR	/	0.0289	0.0962
Methylchrysenes/benzo[a]anthracenes	C ₁ CHR	9.67	/	/
Dimethylchrysenes/benzo[a]anthracenes	C ₂ CHR	8.58	/	/
Trimethylchrysenes/benzo[a]anthracenes	C ₃ CHR	9.00	/	/
Benzo[b]fluoranthene	BbFLA	20.31	0.0152	0.0506
Benzo[k]fluoranthene	BkFLA	13.11	0.0112	0.0373
Benzo[a]fluoranthene	BaFLA	9.78	0.0015	0.0051
Benzo[e]pyrene	BePYR	12.64	0.0187	0.0623
Benzo[a]pyrene	BaPYR	11.85	0.0158	0.0526
Indeno-1,2,3-[c,d]pyrene	IPYR	16.43	0.0212	0.0707
Dibenzo[a,h]anthracene	DBA	6.47	0.0007	0.0022
Benzo[g,h,i]perylene	BghiPER	10.76	0.0147	0.0489
Anthanthrene	ANTA	15.04	0.0121	0.0404
Dibenzo[a,l]pyrene	DBalPYR	15.94	0.0089	0.0297
Dibenzo[a,e]pyrene	DBaePYR	8.78	0.0032	0.0108
Dibenzo[a,i]pyrene	DBaiPYR	11.27	0.0125	0.0415
Dibenzo[a,h]pyrene	DBahPYR	15.56	0.0113	0.0376
16 US EPA PAHs		6.41	/	/
PAH _{extr}		5.41	/	/

PAH_{extr}= total concentrations of extractable PAHs.

Figure S2. Ternary diagram showing the maceral compositions of the investigated coals.

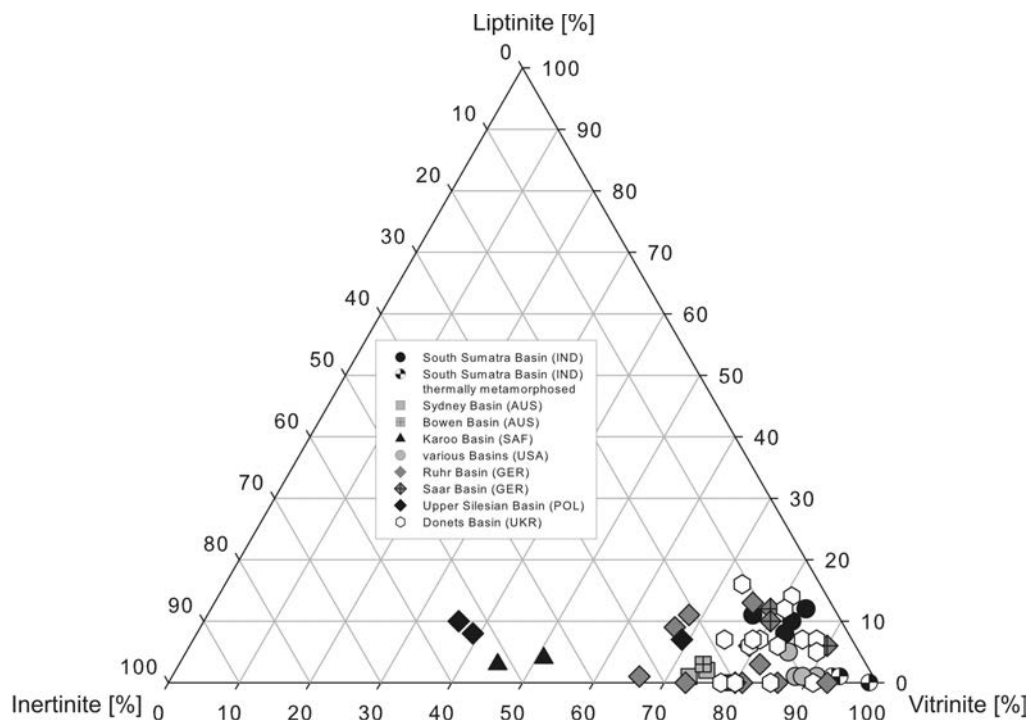


Figure S3. Relationship between (a) carbon content and aromatic fraction, (b) oxygen content and oxygen containing fraction, (c) hydrogen content and aliphatic fraction. Arrows indicate direction of increasing coal rank.

