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PAHs in medium and high rank Bulgarian coals – insights from aromatic indices

Съдържание на ПАВ в среден и висок ранг български въглища – връзка с ароматните им индекси

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Abstract. The study presents analyses of aromatic components in bitumen extracts from Bulgarian medium and high rank coals. Bulk samples from Balkan, Ro = 0.96%, Dobroudzha, Ro = 1.13%, and Svoge, Ro = 5.20% coal-bearing provinces, were considered. After extensive chromatographic separation and GC-MS study of the aromatic fractions, our attention was focused on polycyclic aromatic hydrocarbons (PAHs) compositions. Aromatic indices, based on quantification of individual compounds, revealed that: (i) the highest amounts of PAHs were present in Balkan and Dobroudzha samples, 219–365 μg/g TOC, and dropped to 3.5 μg/g TOC at Svoge sample; (ii) the alkylated naphthalenes and phenantrenes prevalence confirmed published data; (iii) the relationship between aromatic indices *vs.* Ro, % is in agreement with the previously obtained results, indicating their decrease with thermal maturity. For some indices only weak correlation was obtained, suggesting that PAH concentrations are not solely affected by coal rank, but also by environmental conditions and vegetation.

Keywords: coal, medium and high rank, PAHs, aromatic indices.

Introduction

Polycyclic aromatic compounds (PACs) include polycyclic aromatic hydrocarbons (PAHs), their heterocyclic analogues as well as their alkyl and aryl derivatives. In the biogeosphere, two possible origins of PACs were distinguished: biogenic and anthropogenic (Mastral, Callén, 2000; Wang et al., 2015, 2016). For organic geochemical studies in coal, PAHs are of special interest as biological markers (biomarkers) and indicators for the coal-forming palaeovegetation. In addition, they could provide valuable information for the structural reorganization of organic matter during coalification.

The occurrence and distribution of PAHs in coal largely depend on several factors, mainly coal rank, biogenic precursors, depositional environment, sedimentary settings, etc. (Achten, Hofmann, 2009). In a previous study, changes in PAHs composition depending on the coal rank have been tracked (Apostolova et al., 2022). The highest PAHs concentration was found in the bituminous coals. The study has revealed 3R/4R unsubstituted PAHs (parent PAHs) dominance in lignite and bituminous coals, and 4R/5R PAHs predominance in the subbituminous coal. The high amounts of alkylated naphthalenes (Naph) and alkylated phenantrenes (Phe) in the bituminous coals were explained by the diagenetic conversion of the plant-derived terpenoids into alkylated PAHs. The aim of the present investigation is to compare alkyl derivatives of PAHs in medium and high rank coals, and to relate aromatic indices to parent PAHs.

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Material and methods

Three bulk samples from Bulgarian coal-bearing provinces, *i.e.*, Balkan (Upper Cretaceous), Doubroudzha (Upper Carboniferous) and Svoge (Upper Carboniferous), representing medium and high coal rank, were studied. Information for basic geological settings, i.e. lithostratigraphy of the coal-bearing sediments and lithological properties of the basin's basement and provenance, could be found in Kortenski and Zdravkov (2020). The analytical methods used for ultimate, proximate analyses and vitrinite reflectance, Ro %, as well as organic matter extraction and fractionation were described in Apostolova (2018). For PAHs evaluation aromatic fractions from separations of the deasphalted bitumen extracts were considered. Gas chromatography-mass spectrometry (GC-MS) was used to identify and quantify PAHs. Absolute concentrations were determined by inner standard, 1,1'-binaphthyl application, and amounts were normalized to TOC.

Attention was focused on the distribution patterns of alkylated Naph, *i.e.*, methyl (*m/z* 142, MeNaph), dimethyl (*m/z* 156, DMNaph), and trimethyl (*m/z* 170, TriMNaph), as well as on alkylated Phe, *i.e.*, methyl (*m/z* 192, MePhe), dimethyl (*m/z* 206, DMPhe), and trimethyl (*m/z* 220, TriMPhe). Aromatic indices, *i.e.*, alkylnaphthalenes (DNR-1, TNR1 and TNR-2) and alkylphenanthrenes indices (MPI-1, MPI-3), were calculated according to Radke (1987); Radke, Welte (1981).

Results and discussion

In Table 1, the total PAHs contents, amounts of alkylated Naph homologues, Phe, and its homologues are given in μg/g TOC, together with calculated indices MPI-1, MPI-3, DNR-1, TNR-1, TNR-5, MNP and Ro% values. Except of parent PAHs, alkylnaphthalenes and alkylphenanthrenes were the most abundant compound classes in aromatic fractions (Fig. 1).

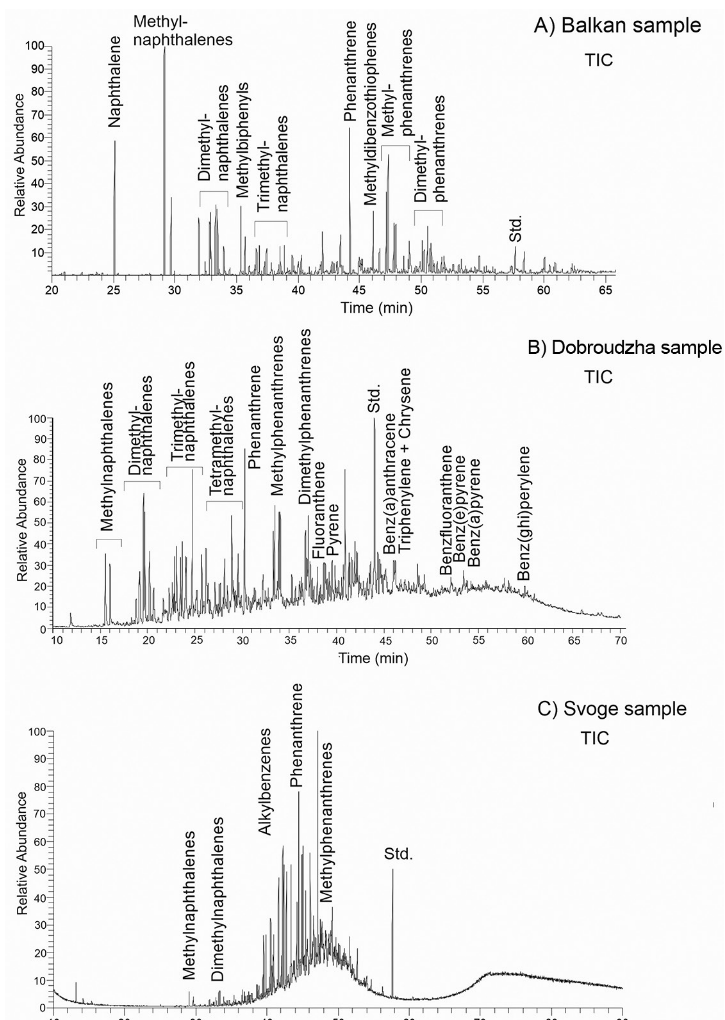

Fig. 1. TIC of aromatic fractions from the Balkan (A), Dobroudzha (B) and Svoge samples. Std., standard (1,1'-binaphthyl).

According to the literature data and our results (Table 1), the PAHs content in coal is the highest at the bituminous coal rank, followed by a considerable decrease with maturity increase to anthracite. A good positive correlation exists between PAHs concentration and coal rank. Highest PAHs concentrations were determined in Balkan and Dobroudzha samples with vitrinite reflectance (Ro) around 1% (Table 1). Our data coincide very well with the results of previous studies, indicating highest amounts of aromatic hydrocarbons (Radke et al., 1990) and USEPA-PAHs (Zhao et al., 2000) in the maturity range Ro = 0.9–1.1%.

The alkylnaphthalenes were found in the highest amounts in the Balkan coal sample (Fig. 1). In it, in addition, polycyclic sulphur aromatic compounds methyldibenzothiophenes, S-bearing analogues of Phe, were present. The amount of PAHs in Svoge anthracite was negligible (1.96 µg/g TOC).

Aromatic compounds were extensively used to follow the transformation process during OM degradation in a reductive environment – from pentacyclic triterpenoids to alkyl naphthalenes (Philp, 1985; Apostolova et al., 2017). In mature coals, a shift in the PAH distribution from high concentrations of Naph and its alkylated derivatives at low hard coal rank to a relative increase of 4–6-ring PAHs at high rank was established by Ahrens and Morrisey (2005). Petrogenic materials such as bituminous coals show a pattern of alkylated PAHs distributions where C_1-C_3 PAHs are more abundant than unsubstituted (C_0) parent PAHs. In Table 1 for bituminous coal the sums of the alkylated Phe were higher than for the parent Phe. The imprint of the biological source materials on PAH distributions in coal tends to be obscured in the high rank coal where aromatic hydrocarbon biomarkers were converted to and/or swamped by C_1–C_3 Naph and C_1–C_2 Phe with uncharacteristic chemical structures (Wang et al., 2017). Furthermore, these components, generally prevalent in bituminous coal and continuing to anthracite rank, are mostly derived from the rearrangement and fragmentation reactions that occur during coal maturation (Radke et al., 1982a, 1982b, 1990, 2000). High concentrations of C_3 substituted PAHs (1,2,5- and 1,2,7-trimethylnaphthalene) in bituminous coals were attributed to the aromatization and cleavage of the C-ring of β-amyrin in angiosperms (Strachan et al., 1988). In the anthracite, C_2-C_3 alkyl Phe were absent (Fig. 1).

Various indices based on parent and alkylated Naph or Phe were used for medium and high rank coal characterization. They depend on stabilities of the alkyl groups at different positions on the molecules. The β-positions are more thermodynamically stable (*e.g.*, 2- and 3-methyl Phe) compared to the α-positions (*e.g.*, 1- and 9-methyl Phe), and their relative contents increase with maturation (Willsch, Radke, 1995). The distributions of methylated Naph and Phe can be used for the assessment of thermal maturity because they are strongly controlled by rank, especially for coal with Ro > 0.9%, where biomarker parameters generally fail. The indices in Table 1 decrease with coal rank increase, *i.e.*, MPI-1, MPI-3, DNR-1, MNR, all of them indicative for a thermal maturity increase. For TNR-5, a potential

Table 1. Vitrinite reflectance (Ro), PAHs content, amounts of alkylated naphthalenes and phenanthrenes and calculated indices

		Sample		
		Balkan	Dobroudzha	Svoge
Ro, %		0.96	1.13	5.2
PAHs, in µg/g TOC	PAHs, except Phe	16.14	14.06	1.34
	Alkyl Naph	170.01	102.56	0.92
	Phe	19.20	9.96	0.62
	Alkyl Phe	159.78	92.35	0.60
Total PAHs		365.13	218.93	3.49
Aromatic indices	MPI-1[1]	1.19	0.70	0.49
	MPI-3[2]	1.91	1.05	1.00
	DNR-1[3]	2.14	1.05	1.50
	TNR-1[4]	1.18	0.83	1.08
	TNR-5[5]	0.28	0.66	0.60
	MNR[6]	2.89	1.21	1.40

(1)MPI-1 = 1.5(2-methyl Phe + 3-methyl Phe)/(Phe +1-methyl Phe+ 9-methyl Phe); thermal maturity;
(2)MPI-3 = (2-methyl Phe + 3-methyl Phe)/(1-methyl Phe + 9-methyl Phe); *m/z* 192; thermal maturity;
(3)DNR-1 = (2,6-dimethyl Naph+2,7-dimethyl Naph)/1,5-dimethyl Naph; *m/z* 156, thermal maturity;
(4)TNR-1 = (1,3,7-trimethyl Naph + 2,3,6-trimethyl Naph)/(1,3,5- trimethyl Naph + 1,4,6-trimethyl Naph + 1,3,6-trimethyl Naph); *m/z* 170, thermal maturity;
(5)TNR-5 = 1,2,5-trimethyl Naph/(1,2,5-trimethyl Naph+ 1,2,7-trimethylNaph + 1,6,4-trimethylNaph); *m/z* 170, source;
(6)MNR = 2-methyl Naph/1-methyl Naph; *m/z* 142; thermal maturity.

source index, an increase was documented. However, the values for Dobroudja and Svoge samples, both of Late Carboniferous geological ages, were comparable (0.60–0.66) despite of a broad difference in Ro (1.13–5.20%). Obviously, the PAHs composition was strongly influenced by other factors, the characteristics of the coal-forming vegetation for example.

Conclusion

The study of PAHs in Bulgarian coals of different rank has revealed: (i) the highest amounts of PAHs are presented in a high rank bituminous coal, in the range of 219–365 μg/g TOC and sharply dropped at the anthracite stage of maturation to 3.5 μg/g TOC; (ii) the prevalence of alkylated naphthalenes and phenantrenes in the aromatic fraction is in accordance with published data and was assigned to the diagenetic conversion of the plant-derived terpenoids into alkylated PAHs; (iii) the relationship between aromatic indices and Ro% is in agreement with previously obtained results, indicating their decrease with thermal maturity. Namely, decrease in MPI-1, MPI-3, MNR values with thermal maturity was registered. For the other indices, weak correlations were obtained, suggesting that PAH concentrations are not solely affected by coal rank, but also by their origin (*e.g.*, location, geological age, vegetation).

At the moment, the aim of this study was limited to obtain insights into relationships between coal rank and PAH occurrences. Possible influencing factors on composition of PAHs remain to be clarified by subsequent investigations.

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