

POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)
IN BULGARIAN COALS: OCCURRENCE, DISTRIBUTION
AND CARCINOGENICITY

Irena Kostova[#], Denitsa Apostolova, Maya Stefanova*

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Abstract

The study fills the informative gap on occurrence, distribution, and carcinogenicity of polycyclic aromatic hydrocarbons (PAHs) in Bulgarian coals. It presents quantitative data for content and carcinogenicity of PAHs in different rank raw coals from eight basins with geological age from Late Carboniferous to Late Miocene, $R_o = 0.17$ – 5.20% . The high amounts of alkylated naphthalene and alkylated phenanthrene determined in the bituminous coals reflect the diagenetic conversion of the plant-derived terpenoids into alkylated PAHs.

In this first systematic study of PAHs in Bulgarian raw coals three concentration ranges are established: for Miocene/Eocene age coal – from 1.08 mg/kg to 5.79 mg/kg; for Late Cretaceous/Late Carboniferous age coal – from 77.9 mg/kg to 137.2 mg/kg; and, for the Late Carboniferous coal – 1.85 mg/kg. The relationship of the total PAHs content vs. raw coal R_o shapes as a “bell” and matches with the published data for the native PAHs from all over the world provenance. The maximal PAHs amount of 137.2 mg/kg at $R_o = 0.96\%$ for the Late Cretaceous coal lies within the “oil-generation window”, $R_o = 0.5$ – 1.3% for the kerogen. For all raw coal studied relatively low carcinogenicity is determined based on the well correlated values for B[a]P_{eq} and TEQ parameters.

Key words: Bulgarian coals, PAHs, carcinogenicity, rank correlation

[#]Corresponding author.

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Introduction. The major local energy resource of Bulgaria is lignite coal. It is dominant in the coal production structure, accounting for 93% in 2014. Lignite coal is followed by medium rank coal at 7% and high rank coal at 0.001% (~ 300 tons). In the last decade, Bulgaria managed to substantially reduce the total amount of emissions of the main pollutants into atmospheric air from thermoelectric power plants and industrial fuel combustion. Recommendations of United Nations Economic Commission for Europe include deployment plans and implementation of a shared environmental information system that provides relevant, comprehensive, accurate and publicly accessible data and information on the state of the environment [1]. Among them polycyclic aromatic hydrocarbons (PAHs) are of special concern.

Totally, coal PAHs content depends on coal rank, types of fossil sedimentary organic matter, maceral composition, depositional environment, etc. [2–4]. The scope of this study is limited to track the changes in PAHs occurrence, composition and carcinogenicity depending only on the coal rank. The present investigation could be regarded as a continuation of our previous research on the biomarker composition and PAHs concentrations of three coal samples from Bulgarian deposits of different rank and basin locations [5]. Herein, the same analytical protocol is applied but the sample set is enriched and covers a broad reflectance index range, data are quantitatively interpreted, and PAHs carcinogenicity and mutagenicity are appreciated.

There are numerous reviews on PAHs for coals of all over world provenance [6]. Therein data for PAHs occurrence, distribution and carcinogenicity for Bulgarian coals are missing. This study aims to fill this informative gap.

Experimental. Coal samples description. Coal samples are chosen according to the rank determined based on vitrinite reflectance, R_o , %. They were picked over from the collection of the Department of Geology, Paleontology and Fossil Fuels, Sofia University “St. Kliment Ohridski” (Table 1) as “average” samples representative for the basins prepared after several coal quartering. Samples were air-dried, milled, and split in portions of 0.5 kg. For proximate, ultimate, and other chemical analyses, they were sieved to < 200 mesh, dried (12 h) and stored in a desiccator.

Proximate analysis, ultimate analysis, and total organic carbon (TOC). The proximate analysis was carried out as follows: analytical moisture (W^a) according to ISO 1015:1975 [7], ash content (A^d) according to ISO 602:2015 [8], and volatile matter (VM^{daf}) by the ISO 20360:2020 [9]. The ultimate analysis, i.e., carbon (C, %), hydrogen (H, %), and nitrogen (N, %), determination was done on a LECO-CHN-4000 instrument. Total sulphur (S_t) content was determined by the Eschka method (ISO 334:2013) [10]. The total organic carbon (TOC) was determined by using Eltra Helios C/S analyzer. The samples were preliminarily pretreated with H_3PO_4 . The measurements were duplicated, and the analytical error is $< 5\%$.

T a b l e 1
Coal samples bulk characteristics, amounts of EOM and aromatic fractions, ratios aromatic/aliphatic fractions content

Coal Basin, Abbreviation	Stratigraphic age	R _o (%)	Proximate analyses, %			Ultimate analyses, % daf				TOC (%)	EOM (mg/g TOC)	Arom. (%)	Ratio Aro/Alk	
			W ^a	A ^d	V ^{dat}	C	H	N	S _t					O _{diff}
Maritsa East, <i>ME</i>	Early-Middle Miocene	0.17	10.1	17.4	57.1	62.7	5.8	0.8	3.95	30.7	48.02	140.57	0.4	0.29
Stanyantsi, <i>St</i>	Late Miocene	0.20	12.5	19.0	65.5	62.3	5.8	0.3	2.82	31.6	44.40	25.12	0.9	0.31
Oranovo, <i>Or</i>	Miocene	0.36	12.5	11.5	51.6	66.1	5.6	1.0	3.55	27.3	56.03	6.14	1.8	0.23
Černo more, <i>ČM</i>	Eocene-Oligocene	0.32	9.1	12.7	52.7	68.7	5.5	1.2	1.04	24.6	54.40	42.32	1.2	0.60
Pernik, <i>Pr</i>	Late Oligocene	0.50	9.2	21.0	48.9	76.2	5.5	0.9	1.42	17.4	54.16	66.17	6.9	1.53
Balkan, <i>Bal</i>	Late Cretaceous	1.00	4.0	32.0	32.8	80.6	5.2	1.5	1.75	12.7	65.38	6.60	14.8	1.31
Dobrudzha, <i>Dob</i>	Late Carboniferous	1.10	2.1	31.1	35.4	85.3	5.0	1.6	0.99	8.1	73.88	9.67	16.3	1.73
Svoje, <i>Sv</i>	Late Carboniferous	5.20	2.4	42.7	9.1	96.3	1.2	0.4	1.05	2.1	83.17	1.42	5.5	0.12

PAHs isolation and quantification. For extractable organic matter (EOM) preparation a protocol described in a previous paper [5] was used. Briefly, ca. 5 g of coal were extracted in a Dionex ASR 200 instrument for accelerated extraction under pressure. The extracts were dissolved in a solvent mixture of hexane:dichloromethane (80:1). Further, asphaltenes therein were precipitated by centrifugation, the soluble portions (maltenes) were concentrated and using a Kohnen–Willsch MPLC were fractionated into three fractions, i.e., aliphatic (I fr.), aromatic (II fr. with PAHs presence) and polar (III fr.).

Gas chromatography–mass spectrometry (GC–MS). PAHs were analyzed by a Trace-GC equipped with a DB-5MS silica capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness) coupled to a Finnigan MAT GCQ mass spectrometer. The oven temperature was programmed to 70–300 °C with steps of 4 °C/min, followed by an isothermal period of 15 min. It was used as a carrier gas. The device was set in EI mode with a scan rate of 50–650 Da (0.7 s/scan). Identification was based on retention time and comparison of the MS with published data. PAHs absolute concentrations were determined by inner standard application, 1,1'-binaphthyl. As response factors are suggested to be 1.0, uncertainty in absolute concentrations based on differences in the responses of PAHs and 1,1'-binaphthyl must be taken into account. However, comparable fragmentation patterns of the compounds argue for minor uncertainties (< 10%). PAHs concentrations were expressed in μg/gTOC (μg/gTOC). The absolute PAHs amounts were normalized to mg/kg coal.

ΣPAHs (16 USEPA), ΣCPAHs determination and toxicity appraisal. United States Environmental Protection Agency (USEPA) has listed a total of 16 PAHs, so-called EPA PAHs, and in the environmental studies they are considered priority pollutants [11]. USEPA recommends determination of the following PAHs [11]: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (An), fluoranthene (Fl), pyrene (Py), benzo[a]anthracene (B[a]A), chrysene (Ch), benzo[b]fluoranthene (B[b]Fl), benzo[k]fluoranthene (B[k]Fl), benzo[a]pyrene (B[a]P), benzo[g,h,i]perylene (B[ghi]P), indeno[1,2,3-c,d]pyrene (In [1,2,3-cd]P), and dibenz[a,h]anthracene (DB[ah]A). Their sum amounts ΣPAHs (16 USEPA).

Consistent with USEPA the following PAHs are considered carcinogenic: B[a]A, Ch, B[b]Fl, B[k]Fl, B[a]P, In[1,2,3-cd]P and DB[ah]A. Their sum amounts ΣCPAHs. Sample's toxicity is appraised by the Benzo[a]pyrene equivalent concentrations (B[a]P_{eq}), in mg/kg) calculated by the sum of the individual PAHs concentrations and their comparative potency as carcinogens [12]:

$$B[a]P_{eq} = B[a]P + BFl \times 0.07 + B[a]A \times 0.06 + DB[a, h]A \times 0.6 + In(1, 2, 3-cd)P \times 0.08,$$

where BFl is the sum of all benzofluoranthene isomers.

For comparison, toxic equivalency quantities (TEQ, in mg/kg), are added using toxic equivalence factors (TEFs) proposed by NISBET and LAGOY [13]. Inas-

much as not all carcinogenic PAHs are present in EOM, the formula is simplified to:

$$\text{TEQ} = 0.001 \times (\text{Fl} + \text{Phe} + \text{Py}) + 0.01 \times (\text{An} + \text{Ch}) \\ + 0.1 \times (\text{B[a]A} + \text{B[k]F} + \text{In[1, 2, 3-cd]P}) + 1 \times \text{B[a]P}.$$

Results and discussion. Yields of EOM in mg/gTOC, amounts of aromatic fractions, in %, and ratios of the aromatic over aliphatic fractions are given in Table 1. Coal-bearing provinces and stratigraphic ages are determined according to [14, 15]. The fractional compositions of all EOM are strongly dominated by the sum of NSO components in the third fractions plus asphaltenes. It is ~ 98% for the lower rank coals and slowly decreases to 74–75% for coals from *Bal* and *Dob* basins, accompanied by the highest amounts of aromatic compounds, 14.8–16.3%. The fractional compositions of EOM for medium rank (*Pr*) and high rank (*Bal*, *Dob*) coals also reflect in higher values for the ratio of aromatic over aliphatic components, values > 1.0 (Table 1).

GC-MS study of all aromatic fractions revealed that except PAHs there are aromatized sesqui-, di-, and triterpenoids. All of them have already been discussed as coal biomarkers in the previous study [5]. Here we focus our attention only on PAHs abundance, distribution, and carcinogenicity.

In Table 2 are given amounts of each PAH identified in coal aromatic fractions, data expressed in µg/gTOC. After PAHs concentrations were normalized

T a b l e 2
PAHs in coal samples studied (µg/gTOC)

PAHs	Coal basin							
	<i>ME</i>	<i>St</i>	<i>ČM</i>	<i>Or</i>	<i>Pr</i>	<i>Bal</i>	<i>Dob</i>	<i>Sv</i>
Phenanthrene	0.74	0.28	0.42	0.23	n.d.	19.20	9.96	0.62
Anthracene	0.21	0.12	n.d.	0.01	n.d.	n.d.	n.d.	n.d.
2-Phenyl-naphthalene	n.d.	0.17	0.30	0.05	1.28	6.54	2.08	n.d.
Fluoranthene	n.d.	0.16	0.27	0.04	n.d.	2.58	1.32	0.69
Pyrene	1.54	0.12	0.57	0.07	n.d.	1.95	2.49	0.63
Benzo(ghi)fluoranthene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Benz(a)anthracene	n.d.	n.d.	n.d.	n.d.	0.17	0.90	1.52	0.02
Triphenylene	0.87	0.17	0.60	0.18	1.89	0.82	0.85	n.d.
Chrysene	1.57	0.16	n.d.	n.d.	n.d.	1.95	1.10	n.d.
Benz(k)fluoranthene	n.d.	0.11	n.d.	0.03	1.14	0.22	1.51	n.d.
Benz(e)pyrene	0.47	0.04	0.61	0.02	2.35	0.54	1.39	n.d.
Benz(a)pyrene	0.33	0.07	1.39	0.03	1.31	0.41	0.83	n.d.
Perylene	0.57	0.13	1.76	0.04	2.83	0.24	0.66	n.d.
Benz(ghi)perylene	n.d.	n.d.	0.99	0.18	n.d.	n.d.	0.31	n.d.
Total	6.3	1.53	6.87	0.88	10.96	35.34	24.02	1.96

n.d. – not determined, in grey – “other” PAHs

T a b l e 3

PAHs content in coal samples studied, B[a]P_{eq} and TEQ (mg/kg)

Sm.	PAHs						Σ **	Ratio			Carcinogenicity	
	Total	USEPA	Other*	Alk. Phe	Alk. Nap	Carcino.		***	****	B[a]P _{eq}	TEQ	
												1
<i>ME</i>	3.02	2.12	0.90	1.49	0.84	0.91	5.35	0.42	0.3	0.16	0.17	
<i>St</i>	0.68	0.45	0.23	0.36	0.17	0.15	1.21	0.51	0.22	0.03	0.06	
<i>Or</i>	0.49	0.33	0.16	0.38	0.21	0.03	1.08	0.48	0.06	0.02	0.05	
<i>ČM</i>	3.74	1.96	1.78	1.69	0.36	0.76	5.79	0.91	0.20	0.76	0.76	
<i>Pr</i>	5.93	1.42	4.51	8.66	3.06	1.42	17.65	3.18	0.24	0.76	0.78	
<i>Bal</i>	23.1	17.78	5.32	61.89	52.44	2.27	137.43	0.30	0.10	0.31	0.37	
<i>Dob</i>	12.95	10.26	2.69	3.89	29.09	2.67	77.93	0.26	0.21	0.55	0.54	
<i>Sv</i>	1.04	1.04	0	0.49	0.32	0.01	1.85	0	0.01	0	0	

*Sum of 2-Phenylnaphthalene, Triphenylene, Perylene, Benzo[e]pyrene;

**Sum of all PAHs GC-MS identified in aromatic fractions (1+4+5)

***Ratio "other" PAHs/USEPA PAHs (3/2);

****Ratio CPAHs/PAHs (6/1);

to mg/kg coal in Table 3. Therein data were differentiated in ΣPAHs, ΣPAHs (16 USEPA), "other" PAHs, ΣCPAHs and sums of alkylated Nap and alkylated Phe. The portion of "other" PAHs comprise the sum of 2-Phenyl Nap, Triphenylene, Perylene and B[e]P. The ratio "other" PAHs/USEPA PAHs illustrates the fact that in the analyzed mixture of aromatic components often the so-called "other" PAHs prevail (ratio 3.18 for *Pr*) or approach EPA PAHs (0.4–0.9 for *Me*, *St*, *Or* and *ČM*) (Table 3). This is not valid for PAHs from high rank coals (*Bal* and *Dob*) where 16 EPA PAHs are dominant, and ratio drops to 0.26–0.30. In Table 3 are also given ratios for CPAHs/PAHs and at the same time, as it were, the values do not depend on coal rank, because the range is relatively narrow, 0.2–0.3. Therefore, only 20–30% of all PAHs are toxic and can be regarded as an environmental threat.

The highest PAHs content is registered for the higher rank (bituminous) coals, while the lowest – for the lignites. The PAHs study reveals three rings over four rings (3R/4R) unsubstituted PAHs dominance in lignite and bituminous coals, and 4R/5R PAHs predominance in the subbituminous coal. The high amounts of alkylated Nap and Phe in shape as a "bell" and is in a perfect coincidence with the published data for the raw coals and PAHs concentration [6]. The maximal PAHs amount of 137.2 mg/kg is measured for the Late Cretaceous coal with $R_o = 0.96\%$ falling within the kerogen "oil-generation window", $R_o = 0.5\text{--}1.3\%$ (Fig. 1) [16,17]. Data for extractable PAHs concentrations in coals are in accordance with the published data [6,18–20].

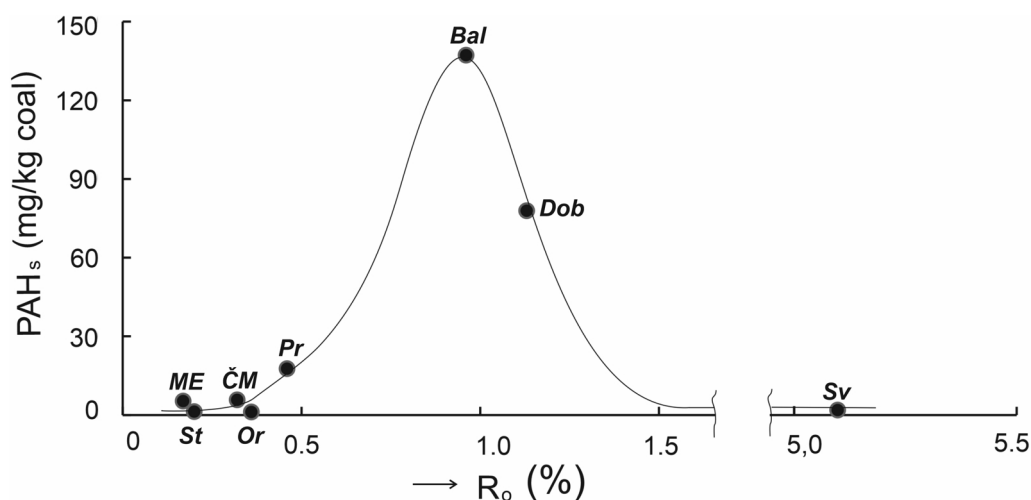


Fig. 1. Correlation of total PAHs vs. R_o

Conclusions. The study offers the first quantitative data for content and carcinogenicity of broad rank Bulgarian coals. We examined raw coals from eight Bulgarian basins with geological age from Late Carboniferous to Late Miocene characterized by R_o from 0.17% to 5.20%. The highest PAHs concentration is registered for the higher rank (bituminous) coals, while the lowest – for the lignites. The PAHs study reveals 3R/4R unsubstituted PAHs dominance in lignite and bituminous coals, and 4R/5R PAHs predominance in the subbituminous coal. The high amounts of alkylated Nap and alkylated Phe in the bituminous coals reflect the diagenetic conversion of the plant-derived terpenoids into alkylated PAHs.

In this first systematic study of PAHs in Bulgarian different rank raw coals three series for PAHs concentrations are determined: for Miocene/Eocene age coal – from 1.08 mg/kg to 5.79 mg/kg; for Late Cretaceous/Late Carboniferous age coal – from 77.9 mg/kg to 137.2 mg/kg; and, for the Late Carboniferous coal – 1.85 mg/kg. The relationship of the total PAHs content vs. R_o shapes as a “bell” and is in a perfect match with the published data for the native PAHs. The maximal PAHs amount of 137.2 mg/kg at $R_o = 0.96\%$ for the Late Cretaceous coal lies within the “oil-generation window”, $R_o = 0.5\text{--}1.3\%$.

For all raw coal studied relatively low carcinogenicity is determined assumed by the values for the well correlated B[a]P_{eq} and TEQ parameters. Inasmuch as there is not a promulgated regulation for PAHs content in coal, we refer to the soil norms where 0.15 mg/kg soil is fixed as a background for PAHs. Hence, data for ME, St, Or point negligible CPAHs contents, contrary to Pr, ČM and partly Dob characterized by appreciable amounts of B[a]P in the mixture.

Totally, comparing to the published data for PAHs concentration in coals from different Bulgarian coal basins are characterized by lower PAHs amounts.

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*Department of Geology, Paleontology
and Fossil Fuels
Faculty of Geology and Geography
Sofia University “St. Kliment Ohridski”
15 Tsar Osvoboditel Blvd
1504 Sofia, Bulgaria
e-mails: irenko@gea.uni-sofia.bg
dapostolova@gea.uni-sofia.bg*

**Institute of Organic Chemistry
with Centre of Phytochemistry
Bulgarian Academy of Sciences
Akad. G. Bonchev St, Bl. 9
1113 Sofia, Bulgaria
e-mail: Maya.Stefanova@orgchm.bas.bg*