

## BIOMARKERS ASSEMBLAGE OF UNBURNED COAL PARTICLES IN FLY ASHES FROM BULGARIAN THERMOELECTRIC POWER PLANTS

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**ABSTRACT.** The study aimed to assess the occurrence and composition of biomarkers in fly ashes emitted during lignite, subbituminous and bituminous coal combustion in four Bulgarian thermoelectric power plants (TPPs). A protocol for isolation, fractionation and identification of organic components in extractable organic matter was applied. Gas chromatography–mass spectrometry was used to assess organic matter sources. Data for biomarkers were quantitatively interpreted and expressed in  $\mu\text{g/gTOC}$ . Several groups of organic compounds were identified, i.e. sesquiterpanes, diterpanes, triterpanes and hopanes. Only in fly ashes from TPPs feed by lignite and subbituminous coal hopanes were registered. Their patterns of distributions were characterized by the presence of  $\alpha\beta$  and  $\beta\beta$ hopane, from C27 to C31. The predominance of  $\alpha\beta$  hopanes has indicated geochemically mature organic matter. The diterpenoids were mainly represented by cyclic hydrocarbons with beyerane, abietane and phyllocladane skeleton. Triterpanes were represented by structures typical for terrestrial vegetation, i.e. oleanane, ursane, and lupane types. The cyclic aliphatic and aromatic compounds (biomarkers) in the extracts of fly ash represent a complex mixture of compounds of different origins: - from the feed coal (petrogenic source); and, compounds formed during combustion (pyrolytic source).

**Keywords:** fly ashes, gas-chromatography–mass spectrometry, biomarkers

### СЪСТАВ НА БИОМАРКЕРИТЕ ОТ НЕИЗГОРЕЛИ ВЪГЛИЩНИ ЧАСТИЦИ В ЛЕТЛИВИ ПЕПЕЛИ ОТ БЪЛГАРСКИ ТОПЛОЕЛЕКТРИЧЕСКИ ЦЕНТРАЛИ

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**АБСТРАКТ.** Цел на изследването е да се определи състава на биомаркерите в летливи пепели от изгарянето на лигнитите, кафяви и черни въглища в четири български топлоелектрически централи (ТЕЦ). Приложен е системен ход за изолиране, фракциониране и идентифициране на органични компоненти в екстрахируемото органично вещество /ЕОВ/. За оценка на състава на биомаркерите е приложен газхроматографски – масспектрален анализ (GC-MS). Данните са количествено интерпретирани и представени в  $\mu\text{g/gTOC}$ . Установени са следните групи органични съединения: сескитерпеноиди, дитерпеноиди, тритерпеноиди, хопаноиди и др. Хопаноиди присъстват само в пробите от ТЕЦ, изгарящи лигнити и кафяви въглища. Техните модели на разпределение се характеризират с присъствието на хопани в интервала от C<sub>27</sub> до C<sub>31</sub>  $\alpha\beta$  и  $\beta\beta$  конфигурация. Преобладаване на  $\alpha\beta$  хопани е типично за зряло органично вещество. Дитерпеноидите са представени главно от циклични въглеводороди с абиетанов, байеранов и филокладанов тип скелетна структура. Установени са тритерпеноиди съдържащи структури от олеананов, урсанов и лупанов тип, които са характерни биомаркери за сухоземна растителност. Регистрираните в ЕОВ от летливи пепели циклични, алифатни и ароматни съединения (биомаркери), представляват сложна смес от съединения с различен произход: от първичните въглища (петрогенен източник); и/или съединения, образувани по време на изгарянето им (пиrolитичен източник).

**Ключови думи:** летливи пепели, газова хроматография-масспектрометрия, биомаркери

### Introduction

Coal is still the primary energy source in Bulgaria. It has been estimated that in the country production of coal ash from only coal fired power plants exceeds 10.4 Mt of solid combustion wastes and the storehouses hold more than 300 Mt ashes and slag. The huge part of coal mineral fraction is collected in cyclones (fly ash) to be stored in waste dumps or reused in building industry or landfilling. Because of this it is very important to know more details about their technological features and geochemical characteristics.

Coal ash can contain organic compounds deriving from parent coal or formed in burning process (Bailey,1992). There

are few studies reported for relatively low amounts of carbon in fly ash from coal-fired power plants (Goodarzi et al., 2002; 2005) while ash from domestic combustion contain higher amounts (Den Boer et al., 2010). Characterization of unburned carbon in fly ashes has been shown to contribute to the assessment of the possible impact of organic matter on human health and the environment.

Many compounds such as n-alkanes, acyclic isoprenoids, sesquiterpenoids, diterpenoids, steranes, tri- and pentacyclic triterpanes were established as markers of organic matter sources in coal fly ashes (Misz et al., 2007; Fabianska and Smolka-Danielowska, 2012; Ribeiro et al., 2014; Fabianska et al., 2017; Kostova et al., 2020).

The aim of the present study is to assess the occurrence and composition of biomarkers in fly ashes emitted during lignite, subbituminous and bituminous coal combustion in four Bulgarian thermoelectric power plants (TPPs).

## Materials and Methods

The fly ashes from four TPPs in Bulgaria burning coals of different rank were investigated: lignites from Maritza East-2 (ME-2) and Maritza East-3 (ME-3) TPPs, subbituminous coal for Republika TPP and bituminous coals from Russe TPP. Fly ash samples were collected at each row of the electrostatic precipitators (ESPs) of Republika, and Russe TPPs. From ME-2 and ME-3 TPPs bulk ("average") samples were studied.

The total organic carbon (TOC) determination was done by an Eltra Helios C/S analyzer on samples preliminary pretreated with H<sub>3</sub>PO<sub>4</sub>. Measurements were in duplicate, with analytical error < 5% for the respective concentrations.

The molecular compositions of feed coals and fly ashes hydrocarbons were determined by a protocol developed previously in the study of biomarker assemblages and PAHs in different rank Bulgarian coals (Apostolova et al., 2017). Briefly, ca: 5 g were extracted by dichloromethane, 1 h at 75°C and a pressure of 75 bar in a Dionex ASR 200 instrument. Asphaltenes were separated and hexane-soluble organic compounds (maltenes) were sub-divided into saturated (I fr.) and aromatic (II fr.) hydrocarbons and polar compounds using a Willsch MPLC (medium pressure liquid chromatography) instrument. Herein the saturated and aromatic hydrocarbon fractions were analyzed by a gas chromatography-mass spectrometer (GC-MS) Finnigan MAT GCQ, equipped with a DB-5MS silica

capillary column (30 m x 0.25 mm x 0.25µm), 70–300°C with steps of 4°C/min, followed by an isothermal period of 15 min. The device was set in EI mode with a scan rate of 50–650 Daltons (0.7 s/scan). The absolute concentrations were determined using deuterated tetracosane and 1,1'-binaphthyl as internal standards, respectively. Results were normalized to µg/gTOC.

## Results and Discussions

In a previous study n-alkanes present in industrial coal-derived fly ashes from the same set of samples were investigated (Kostova et al., 2020). In this study, changes in the distribution patterns of biomarker during combustion have been outlined. For lower rank coals the extraction yields of fly ashes (FAs) were high, all dominated by polar components. In fly ashes derived from the combustion of higher rank coals, extractable organic matter (EOM) were an order of magnitude lower with a considerable portion of neutral compounds (Table 1). A strong correlation ( $R^2=0.9991$ ) between TOC and C content was estimated (Kostova et al., 2020).

With the present study we complement the existing information on the composition of fly ash EOM. In all extracts aliphatic hydrocarbons strongly predominated over aromatic components. Beside n-alkanes, the dominant components in the neutral fractions, a broad range of biomarkers was found. The following compound groups, derived from feed coals lignite, subbituminous and bituminous coal, were identified in the EOM of the fly ashes (FAs): sesquiterpenoids (Sesqui-Ts), diterpenoids (DTs), triterpenoids (TTs) and hopanes (Hs) (Figure 1). Only in FAs from TPPs feed by lignite and subbituminous coals Hs were identified (Table 2).

Table 1. Characteristics of EOM of FAs (according Kostova et al., 2020)

TPP	ESP row	Yield		Fractional composition, %			
		mg/gTOC	wt.%	I fr.**	II fr***	III fr.****	Asph.
ME-2	avr. *	8.88	0.0121	7.8	1.0	83.4	7.8
ME-3	avr.	2.74	0.0103	35.7	11.9	51.2	1.2
Republika	I	7.27	0.0088	5.4	9.5	70.3	14.8
	II	15.05	0.0102	25.8	11.8	42.4	20.0
	III	19.87	0.0117	13.1	1.0	77.8	8.1
Russe	I	0.8	0.0145	21.8	1.8	59.8	16.6
	II	1.91	0.0308	37.9	1.5	45.7	14.9
	III	0.23	0.0154	28.0	0.6	55.0	16.4

\*average sample; \*\* neutral; \*\*\* aromatic; \*\*\*\* polar

Table 2. Biomarkers assemblage of EOM of fly ashes (µg/g TOC)

TPP	ESP row	Sesqui-Ts	DTs	TTs	Hs	H <sub>ββ</sub>	H <sub>αβ</sub>	Ratio H <sub>ββ</sub> / H <sub>αβ</sub>	Hop-(17,21)-en
ME-2	avr.	2.00	70.21	0.37	2.08	0.47	1.60	0.29	0.49
ME-3	avr.	2.76	104.93	3.25	4.99	1.82	3.17	0.57	1.93
Republika	I	0.30	14.98	-	1.71	0.70	1.01	0.69	0.00
	II	45.88	205.53	-	17.83	3.09	14.74	0.21	0.00
	III	5.78	273.82	-	13.62	1.99	11.64	0.17	1.12
Russe	I	0.70	2.40	0.23	-	-	-	-	-
	II	2.53	1.18	0.11	-	-	-	-	-
	III	0.06	0.40	0.03	-	-	-	-	-

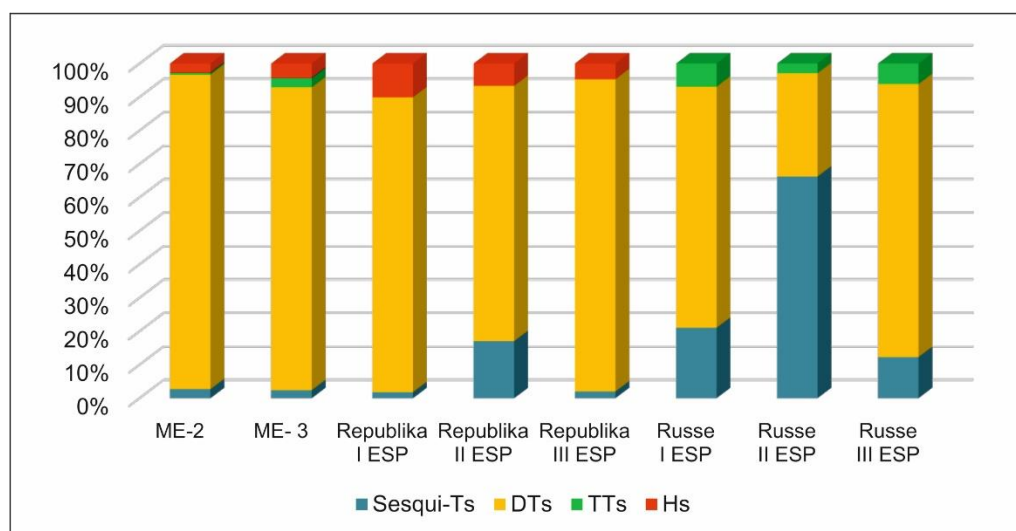


Figure 1. Distribution of the biomarkers in EOM of fly ashes, studied, in rel.%

Saturated and monounsaturated sesqui-Ts, including the C14 and C15 compounds, related to the cadinene, eudesmane and drimane types were identified. Aromatic sesqui-Ts were dominated by curcumene, cuparene, cadalene and isocadalene structures. In most samples cadalene, C15H18, predominate over the other aromatic sesqui-Ts.

Di-Ts in the samples were represented mainly by hydrocarbons with beyerane, abietane and phyllocladane type skeleton. Their amounts in EOM of FAs were found to be higher for subbituminous and lignite and lower for bituminous coal (Table 2). The following Di-Ts were identified in the non-aromatic hydrocarbon fractions of EOM: norpimarane, beyerane, pimarane,  $\alpha$ -phyllocladane, abietane and  $\beta$ -phyllocladane. The  $\alpha$ -phyllocladane has been usually found in conifers except of Pinaceae (ten Haven et al., 1992) and was regarded as a typical biomarker of Araucariaceae, Cupressaceae, and Taxodiaceae. In all samples studied, the aromatic tricyclic Di-Ts, i.e. norabietatriene, dehydroabietane, simonellite, retene and methyl retene were identified. Simonellite was the dominant aromatic Di-T in the FAs from TPPs feed by subbituminous coal.

Non-hopanoid TTs were found in very low amount only in FAs from TPPs feed by lignite and bituminous coals. TTs containing the structures typical of the oleanane, ursane, or the lupane type derivatives were considered as biomarkers for angiosperms (Karrer et al., 1977). Compounds of these series were identified in the saturated and aromatic hydrocarbon fractions. They included des-A degraded and pentacyclic TTs of oleanane-, ursane-, and lupane-types.

Only in FAs from TPPs feed by lignite and subbituminous coal hopanes were registered. Their patterns of distributions were characterized by the presence of  $\alpha\beta$  and  $\beta\beta$  hopane (H), in the range from C27 to C31. The predominance of  $\alpha\beta$ -H indicates geochemically mature organic matter. C28 was not detected. Hop-17(21)-ene was detected in high amounts in the EOM from ME-2 TPP, ME-3 TPP and Republika TPP, III ESP row, consistent with the low rank of the feed coal. In contrast to the ratio of  $17\beta$ (H), $21\beta$ (H)-hopanes to  $17\alpha$ (H), $21\beta$ (H)-hopanes ( $H\beta\beta/H\alpha\beta$ ) found in ME feed coal ( $\geq 1$ ), in FAs ratios  $\leq 1$  were obtained, a hint for serious modification in hopanes distributions induced by combustion.

$18\alpha$ (H)-22,29,30-trisnorhopane (Ts) and  $17\alpha$ (H)-22,29,30-trisnorhopane (Tm) were absent. In all samples studied moretanes were not registered. During maturation moretanes were transformed in  $\alpha\beta$ -hopanes and finely disappeared from coal extracts or oils (Peters et al., 2005; Misz et al., 2007).

The absence of steranes and high content of DTs in all EOM indicate that, most of the organic matter present in the fly ashes reflects their biogenic origin and depositional environment. DTs were indicators for conifer input into sedimentary organic matter (Noble et al., 1985; Otto and Simoneit, 2001). They were registered in feed coals from Maritza East and Pernik basins (Dodova-Angelova et al., 1985; Stefanova et al., 2002; Bechtel et al., 2005; Stefanova et al., 2016; Apostolova et al., 2016; Atanassova et al., 2017).

Geochemical features of the EOM studied have indicated a mixture of compounds derived from feed coals and combustion products (Fabianska and Danielowska, 2012). The biomarkers common in most humic coals and kerogen-type III (terrestrial organic matter), was described for coals from the Maritza East and Pernik coal basins. However, hopanes distributions were seriously altered by combustion. The strong dominance of  $\beta\beta$ -hopanes characteristic for the feed coals of Maritza East basin has disappeared and was replaced by considerable amounts of  $\alpha\beta$  stereoisomers.

## Conclusion

Several coal biomarkers were found to be well preserved in EOM of unburned coal in FAs from four Bulgarian TPPs. The study has demonstrated that the distributions of aliphatic components in FAs generated during combustion of lignite, subbituminous and bituminous coal show a significant similarity to feed coal. For compounds registered in the EOM of coal-derived fly ashes two origins were distinguished: compounds from the feed coal and components formed in combustion process or with thermal-induced changes in stereochemistry.

In conclusion, EOM biomarker assemblages kept the features of the feed coals. Thus, they could be successfully used in surveys for potential pollutants in the environment.

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