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Aromatic indices survey in fly ashes from Bulgarian thermoelectric power plants

Изследване на ароматни индекси в летливи пепели от български топлоелектрически централи

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Introduction

In the biogeosphere to polycyclic aromatic hydrocarbons (PAHs) and their alkylated derivatives were assigned two main origins – biogenic and anthropogenic (Simoneit, 1998). Solid wastes of coal combustion in thermal power plants (TPPs) were pointed as the biggest sources of PAHs in the environment (Mastral, Callen, 2000). Worldwide few studies on the composition of PAHs, from fly ashes were performed (Fabianska et al., 2017). For the purpose full scale of alkylnaphthalene and alkylphenanthrene ratios were used for indices calculation (Radke, Welte, 1981; Radke et al., 1982, 1986)

The aim of the present study is to compare alkyl derivatives of PAHs in feed coal and fly ashes generated during lignite, subbituminous, bituminous feed coals combustion in seven Bulgarian TPPs. Attention was focused on the distribution patterns of methyl (*m/z* 142), dimethyl (*m/z* 156), and trimethyl (*m/z* 170) naphthalenes, as well as on methyl (*m/z* 192), dimethyl (*m/z* 206), trimethyl phenanthrene (*m/z* 220) and indices calculated on their intensities. The purpose was to assess their relevance in appraisal of coal organic matter transformation during combustion.

Materials and methods

Feed coals and FA samples were collected from seven Bulgarian TPPs: Maritza East 2 (ME-2), Maritza East 3 (ME-3), Maritza 3, Republika, Bobov dol (BD). Coals were sampled from the bunkers. Fly ashes (FAs) were collected at each row of the electrostatic precipitators (ESPs) of Maritza 3, Republika, BD, Russe and Varna TPPs. From ME-2 and ME-3 TPPs FAs were bulk samples.

Samples ultimate and proximate analyses as well as the protocol of organic matter extraction and fractionation were described in Kostova et al., (2020). Gas chromatography-mass spectrometry (GC-MS) was used to identify and quantify PAHs in the samples studied. PAHs absolute concentrations were determined by inner standard, 1,1'-binaphthyl. Alkylnaphthalenas and alkylphenanthrenas indices (MPI-1 and MPI-3) were calculated according to Radke et al. (1981).

Results and discussions

Except PAHs tracked by USEPA, alkylnaphthalenes and alkylphenanthrenes were the most abundant compound classes in aromatic fractions. Their detail study has provided supplemental information on feed coal maturity and glimpse on the organic matter pyrogenic transformation in dumps.

The distributions of methylphenathrenes (MePhe) in the aromatic fraction from Russe feed coal are illustrated in Fig. 1. In Table 1 were present total PAHs contents, amounts of alkylated naphthalene homologues, phenanthrene, its homologues, in μg/g TOC, calculated indices MPI-1 and MPI-3.

Our data fit well with the observations described in the literature. In low rank feed coals (Maritsa East and Pernik subbituminous coal, the feed coal of Republika TPP) Phe was absent (Table 1). It was

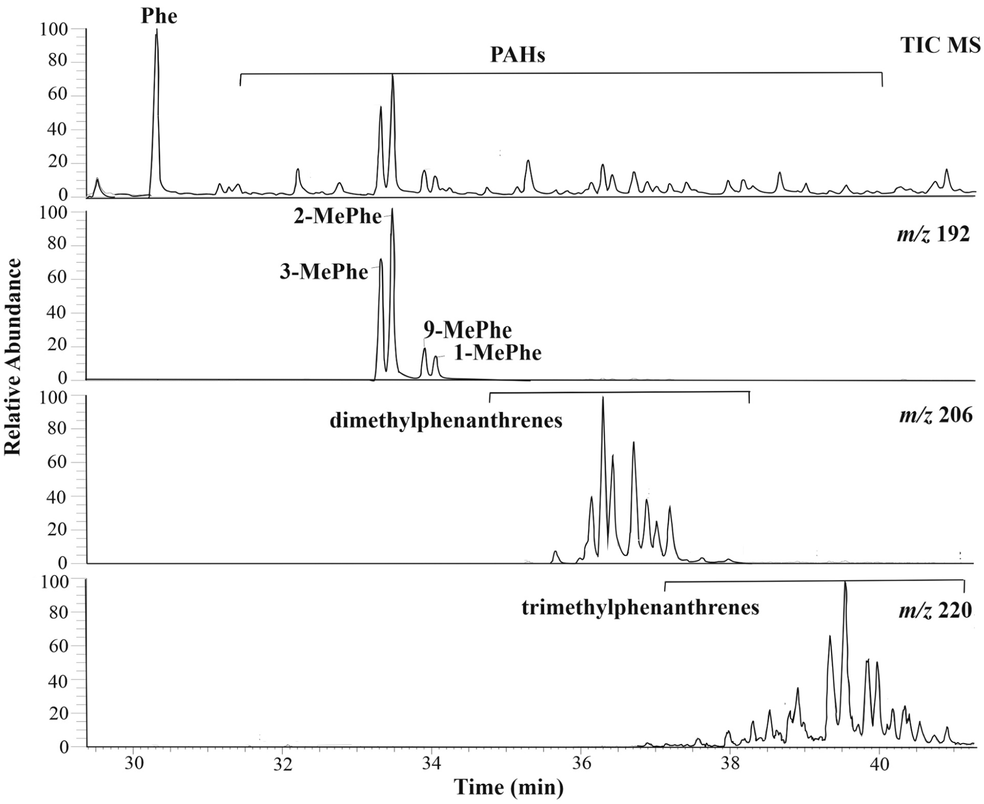

Fig. 1. Distribution of methylphenathrenes (MePhe) in the aromatic fraction from Russe TPP feed coal

present in the higher rank feed coals. As a result of pyrogenic syntheses Phe was generated in FAs samples from lower rank coals, i.e., ME, Republika. For the FAs from higher rank feed coal pyrogenic Phe has rested lower than petrogenic one. For petrogenic/pyrogenic PAHs definitions see Stogiannidis and Laane (2014).

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). In Table 1 for BD feed coal the sum of alkylated Phe were higher than for the parent Phe. The pattern was $C_0 < C_1 < C_2 < C_3$.

Pyrosynthesis of small active radicals as anthracene or methyl anthracene generated during coal organic matter pyrolysis was proposed by Mastral and Callen (2000) as the main pathway of PAHs formation. In pyrogenic materials alkyl PAHs show the opposite distribution pattern: $C_0 \gg C_1 > C_2 > C_3$, often zero (Table 1, Fig. 1). This observation was valid for higher rank feed coals and their FAs, while for the lower rank coal the tendency was somewhat obscured possibly due to the higher number of PAHs of biogenic origin, i.e.q perylene, phenyl naphthalene, triphenyls, etc.

In coal samples, 9- and 1-MePhe are often highly abundant, with 9-MePhe being predominant (Radke et al.,1986). With maturity increase, 2- and 3-MePhe become more prominent, due to their enhanced thermal stability. Normally, 2-MePhe is present in higher proportions than 3-MePhe. Based on these observations, the MePhe ratios (MPI-1 and MFI-3, Table 1) were established, showing excellent correlation with feed coals rank - higher values for higher rank feed coals and lower ones for low rank coals. MPI values for some FAs were clearly too low, perhaps due to the low concentration of isomers, which led to the integration error.

Conclusions

Except PAHs monitored by the USEPA, alkylnaphthalenes and alkylphenanthrenes were highly abundant compound classes in aromatic fractions, especially in bituminous coals extractable organic matters. Their detail study has supplied supplemental information on feed coal maturity and glimpse on the organic matter pyrogenic transformation during combustion.

Some data for alkyl phenanthrenes distributions in feed coals and FAs from combustion were confirmed, namely, petrogenic PAHs set was dominated by alkylated Phe and pyrogenic by Phe itself. The study was able to distinguish the two men-

Table 1. Total PAHs content, amounts of alkylated naphthalene homologues, phenanthrene, its homologues, in μg/gTOC, calculated MPI-1 and MPI-3 indices

TPPs	Feed coal FA, EPS row	ΣPAHs μg/gTOC	AlkylNapht μg/gTOC	Phe μg/gTOC	AlkylPhe μg/gTOC	*MPI-1	**MPI-3
ME-2	coal	23.3	2.61	0.00	3.27	0.55	0.36
	FA	0.14	0.24	0.07	0.87	0.00	0.00
ME-3	coal	4.58	3.06	0.00	0.00	0.00	0.00
	FA	0.61	0.59	0.12	4.56	0.57	1.80
Maritza 3	coal	33.44	3.03	0.00	2.80	0.00	0.00
	FA I	1.46	1.21	0.39	2.48	0.00	0.00
	II	6.60	2.64	2.13	33.48	0.29	1.64
	III	4.38	1.04	0.75	4.55	0.00	0.00
Republika	coal	79.39	40.90	0.00	22.85	0.00	0.00
	FA I	0.11	0.00	0.11	1.40	0.00	0.00
	II	4.78	6.02	2.86	18.37	0.39	1.29
	III	0.29	0.64	2.29	6.60	0.00	0.00
BD	coal	20.47	10.17	1.57	0.00	0.00	0.00
	FA I	0.00	0.00	0.11	1.24	0.00	0.00
	II	0.00	0.00	0.00	1.05	0.00	0.00
	III	0.27	0.30	0.15	3.40	0.00	0.00
Russe	coal	25.87	0.40	5.83	13.58	1.43	5.56
	FA I	0.55	0.25	0.40	0.00	0.00	0.00
	II	1.13	0.36	0.46	0.00	0.00	0.00
	III	0.21	0.08	0.14	0.00	0.00	0.00
Varna	coal	3.26	0.58	0.46	1.52	1.01	2.00
	FA I	0.43	0.42	0.31	0.09	0.21	1.00
	II	0.41	0.29	0.28	0.03	0.40	1.43
	III	0.36	0.09	0.25	0.00	0.49	0.93
	IV	0.36	0.11	0.36	0.00	0.00	0.00
	V	0.20	0.10	0.17	0.03	0.00	0.00

Abb.:AlkylNaph, alkylnaphthalenes; Phe, phenathrene; AlkylPhe, alkylphenanthrenes;
*MPI-1 = 1.5(2-MePhe + 3-MePhe)/(Phe +1- MePhe + 9- MePhe);
**MPI-3 = (2-MePhe + 3-MePhe)/(1-MePhe + 9-MePhe)

tioned types. The difference was appreciable for waste materials from bituminous coal combustion where PAHs concentrations were considerable. For lower rank feed coals and FAs the aromatic indices survey supplied information was limited. The MePh indices, i.e., MPI-1 and MPI-3, increase with rank of feed coals while for FA samples the tendencies were not so well expressed.

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References

Fabiańska, M. J., B. Kozielska, J. Konieczyński. 2017. Differences in the occurrence of polycyclic aromatic hydrocarbons and geochemical markers in the dust emitted from various coal-fired boilers. – *Energy & Fuels*, *31*, 2585–2595.

Kostova, I., D. Apostolova, M. Stefanova (in press). Geochemical features of unburned coal particles in fly ashes from thermal power plants in Bulgaria. – In: *6th World Multidisciplinary Earth Sciences Symposium (WMESS 2020)*. 7–11 September 2020, Prague, Czech Republic.

Mastral, A. M., M. S. Callen. 2000. A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. – *Environmental Science & Technology*, *34*, 3051–3056.

Radke M., D. H. Welte. 1981. The Methylphenanthrene Index (MPI): A maturity parameter based on aromatic hydrocarbons. – In: *Advances in Organic Geochemistry 1981*, 504–512.

Radke M., H. Willsch, D. Leythaeuser, M. Teichmüller. 1982. Aromatic components of coal: relation of distribution pattern to rank. – *Geochim. Cosmochim. Acta*, *46*, 1831–1848.

Radke, M., D. Welte, H. Willsch. 1986. Maturity parameters based on aromatic hydrocarbons: influence of the organic matter type. – *Organic Geochem.*, *10*, 51–63.

Simoneit, B. R T. 1998. Biomarker PAHs in the environment. – In: Neilson A. H. (Ed). *The Handbook of Environmental Chemistry, PAHs and Related Compounds*. 3, Part I., Berlin, Springer-Verlag, 176–221.

Stogiannidis, E., R. Laane. 2014. Source characterization of polycyclic aromatic hydrocarbons by using their molecular indices: An overview of possibilities. – *Rev. Environmental Contamination and Toxicology*, *234*, 49–133.