GEOCHEMICAL APPRISAL OF SEDIMENTS AND DUMP MATERIALS FROM THE DEMAGED TERRAINS OF MARITSA IZTOK BASIN, BULGARIA

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Introduction

The study is due to the scarcity of information on organic geochemistry of dump materials from open pit coal mines. Recent preliminary results prove that aliphatic and aromatic hydrocarbons, phenols etc. move through and could release out of the dump. Some of them could be regarded as potential environmental pollutants for surface and groundwater and soils. At the same time, Mini Maritsa Iztok EAD works actively on remediation of the damaged terrains and an urgent necessity of data on OM characteristics and transformation processes is obvious.

The pattern of the dump materials is complicated as they are complex compounds composed of a mineral portion (containing clay minerals mainly) and organic one. Subsequently they have undergone a number of technogenic and anthropogenic changes. In this respect OM compositions of extractable organic matter (EOM) of sediments and dump materials were appraised to estimate the scope of alteration. Our study relies on interpretation of the OM of neutral fractions with a perspective for a further considering of aromatics.

Two of the samples studied (A, B) are black clayey sediments covering the first coal seam of Trojanovo-1 and Trojanovo-North Mines. Other two samples (C, D) originate from Trojanovo-North Mine and Drjanovo Dumps of Mini Maritsa Iztok EAD. They comprise reworked and redeposited "bare" sediments and lignites without any economic value. Chloroform was used for EOM preparation. All other experimental details were described in a preliminary study (Markova et al. 2016).

Results

Samples characteristics are shown in Table 1. The sediments have close EOM yields and *n*-alkane distributions. Regular isoprenoids and values of calculated parameters vary in a relatively narrow interval. Generally, terrigenous input is a main characteristic of their OM based on pattern of distribution and CPI data. Values for P_{aq} argue for floating vegetation in addition. Hopane parameters are also comparable, all attesting OM immature state: $H_{27\beta}/H_{27\alpha}$ - close to 10 and "bio"/"geo" hopane ratio *ca.* 2.5. It was impossible to estimate the homohopane index due to the lack of recognizable peak for $H_{31}\alpha\beta S$. Hopane ratio varies from 1.3 to 1.6.

Dump GC-MS separations are strongly dominated by 16α(H)-Phyllocladane (154-388 μg/g), unlike the sediment separations in present and previous studies. Phyllocladane is already announced as the main biomarker for Maritsa-East lignites and dumps (Markova et al., 2016). The signature of *n*-alkane distribution for dumps is prevailed by the shorter homologues, CPI is close to 2 and P_{aq} values are in interval 0.50-0.52. TAR for dump samples attests aquatic vegetation additionally supported by nC_{23}/nC_{31} values >1.

Dump hopane distributions are characterized by biomarkers for immature OM: hop-17(21)-enes, neohop-13(18)-enes, $H_{27\beta}/H_{27\alpha}$ ratio varies from 5 to 9 and "bio"/"geo" hopane ratio - from 1.1 to 2.3. It was possible to estimate the homohopane index for sample D only, attesting its advanced maturation comparing to the other samples. The statement is additionally supported by "bio"/"geo" hopane value of 1.1.

Table 1 *n-Alkanes yield and distributions, regular isoprenoids and calculated parameters*

Sample	Yield, μg/g	*n*-Alkanes, %			Regular isoprenoids			Parameters			
		Short-	Mid-	Long-	Pr/Ph	Pr/nC_{17}	Pr/Ph	CPI	P_{aq}*	TAR**	nC_{23}/nC_{31}
Sediment											
A	5.70	29.13	16.66	54.20	0.96	0.27	0.22	2.07	0.57	2.21	0.94
B	5.16	27.30	13.90	58.80	0.70	0.40	0.39	3.21	0.42	3.25	0.64
Dump											
C	12.24	55.34	14.08	30.58	1.13	0.73	0.64	2.06	0.50	0.69	1.24
D	5.05	54.20	16.90	28.90	0.64	0.53	0.57	1.94	0.52	0.65	1.25

*$P_{aq} = (nC_{23}+nC_{25})/(nC_{23}+nC_{25}+nC_{29}+nC_{31})$;
**$TAR = (nC_{27}+nC_{29}+nC_{31})/(nC_{15}+nC_{17}+nC_{19})$

Contrary to long *n*-alkanes prevailance in sediments, in dump samples shorter homologues are more abundant, a hint for a possible long chain homologues destruction. In a previous study (Markova et al., 2016) such a phenomenon for dump samples was not recognized. According to "bio"/"geo" hopane ratio the dump samples in the present study refer to more immature organic matter.

Conclusions

The attempt to depict differences in OM transformation in dumps of the largest coal basin in Bulgaria as a result of mining activities on the base of geochemical data has been extended by new samples. The data will serve in the efforts to find the best decision for remediation of the damaged terrains in the region.

Acknowledgement

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Reference

Markova, K., Stefanova, M., Milakovska, Z., Marinov, S.P., 2016. A comparison of black claystones, lignites and dump materials from the Maritsa Iztok Coal Basin, Bulgaria, using organic geochemical proxies, Chemie der Erde (Geochemistry) 76, 405-417.

and, at last but not at least importance, ecological estimation of the alteration as a result of OM transformation processes of sediments and substandard lignites that are redeposited and free-heaped in dumps.

The attempt to depict differences in OM transforming in dump materials of the largest coal basin in Bulgaria as a result of technogenous and anthropogenic activities on the base of geochemical data has been extended by new samples. The data will serve in the efforts to find the best decision for the region remediation. The following items were under special concern: OM geochemical characteristics of the sediments covering the coals, OM geochemical characteristics of the dump materials, comparative analysis of OM components and indexes of sediments, lignites and dump materials; In the previous studies the geochemical analysis of dump materials from the opencast Maritsa Iztok mines, Bulgaria, were carried out based on biomarker assemblages of hydrocarbon fractions. proceeding in the dumps in comparison with Maritsa Iztok lignites.

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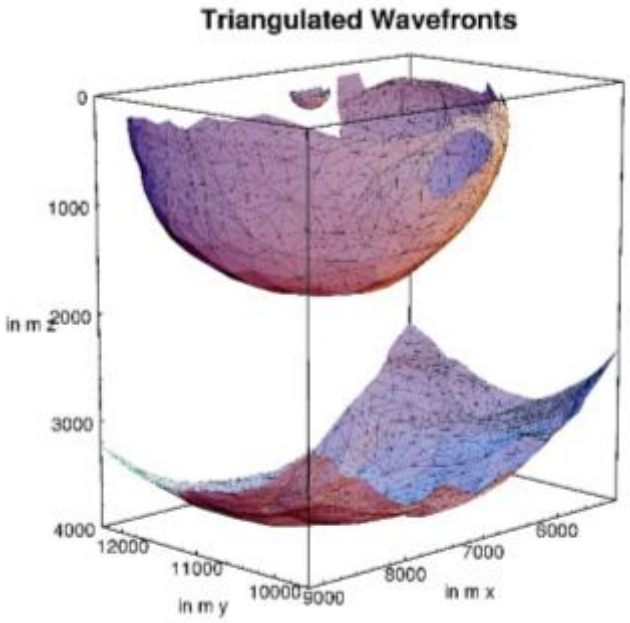

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