POLAR AROMATICS IN GANGUES AND LIGNITES FROM MARITSA IZTOK COAL BASIN

M. Stefanova[1], Z. Milakovska[2]

[1]Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria
[2] Geological Institute, Bulgarian Academy of Sciences, Sofia, Bulgaria

Introduction

In previous studies an insight into the composition of polar constituents in low rank coals (lignites) from Maritsa Iztok Basin (MIB) was described. Lately, new polar diterpenoids in coal and gangue extracts were identified and tracked with depth (Stefanova *et al.*, 2016). Unequivocal proves for Cupressaceae/Taxodiaceae or Podocarpaceae as dominant palaeoflora in the mire were also obtained. Herein, the polar aromatic compositions of samples from different mire facieses will enhance the scope of knowledge. The attention will be stressed, on one hand, on the information for the organic matter (OM) characteristics in the palaeoswamp. On the other hand, these results will contribute to depict polar aromatic transformation in MIB dumps.

Samples of Troyanovo-North Mine (MIB) were studied: two - from the third coal seam, one - of gangues. Bitumens were prepared by chloroform Sohxlet extraction, asphaltenes were precipitated and maltenes are fractionated by mini-SiO_2 columns into neutrals (*n*-hexane elution), polar aromatics (DCM) and polars (acetone). Fractions were trimethylsilylated. 5α-cholestane was added prior to analysis. The gas chromatograph was fitted with a Rtx-5MS column (30 m, 0.25 mm i.d., 0.25 μm film thickness, 5 m of column guard). The GC operating conditions were: 40° C (1 min) to 120° C at 30° C min^{-1}, then from 120° to 300° C at 3° C min^{-1}, hold 30 min. Samples were injected in splitless mode, with the injector temperature set at 280° C. He was the carrier gas in constant flow mode at 1 ml/min.

Results

Samples characteristics are shown in Table 1. GC-MS patterns of the separations of polar aromatics are comparable. Aromatic phenols, ketophenols accompanied by a broad series of dicarboxylic fatty acids, nC_3 to nC_{26}, are identified in all samples studied. Isophyllocladene, 28.7 μg/g C_{org}, is registered only in sample 1.

Table 1 *Samples characteristics, yields of bitumens and fractional compositions*

Sample	Depth (m)	A^d	Rock Eval				Bitumen	Fractions, %		
		%	T_{max}	TOC	HI	OI	mg/g C_{org}	Neutrals	Polar aromatics	Polars
1	70.0 -70.1	45.9	355	52.0	299	31	149.2	10.6	39.2	36.3
2	71.0-71.5	47.4	370	31.5	153	79	172.9	11.8	45.0	27.2
3	74.5-75.0	28.3	369	42.2	240	68	98.7	12.0	56.6	22.4

Identified polar diterpenoids are typical for Maritza East lignites. Ferruginol, sugiol and hinokione are common constituents of modern species of Cupressaceae/Taxodiaceae and Podocarpaceae, but rare in the other conifer families. Herein, variations in amounts of polar aromatics are visible (Fig.1). With depth. the amounts of sugiol and 7-ketototarol are increased, while for the others (ferruginol, 6,7-dehydroferruginol, 5,6-dehydrosugiol) changes are moderate. An exception is salvinolone with fivefold increase in depth. Generally, magnitudes determined for polar aromatics in the previous study are compatible with lignites but much lower (ca. 5 folds) with gangues.

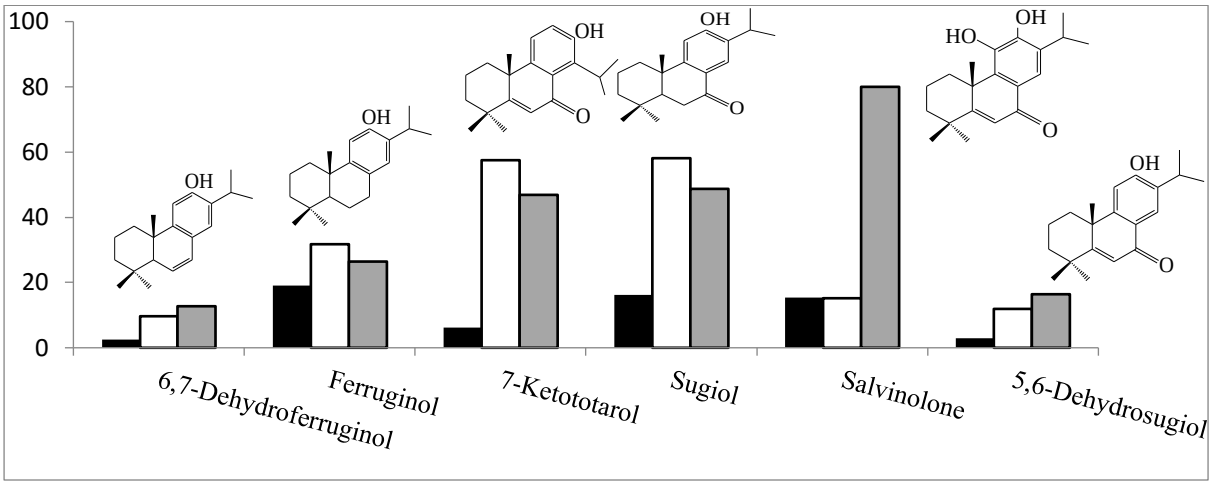

Figure 1 *Amounts of polar aromatics in samples studied, µg/gC_{org}*
(black - sample 1; white - sample 2; grey - sample 3)

Dicarboxylic fatty acids are highly abundant. They are firstly identified in the extractable matter of samples from MIB. The signatures are strongly prevailed by the long chain homologues, *n*C_{16}-*n*C_{26} (86-96%) with CPI (4.9-2.8) decreasing with depth. Distributions have maximized at different homologues, at *n*C_{18}, *n*C_{20} for the sample 1 and shifted to *n*C_{22}, *n*C_{24} for the deeper ones. It is admitted that high molecular weight *n*FAs are mostly derived from plant leaf and needle cuticular waxes, and all the other oxygenated compounds as dicarboxylic fatty acids, very probably from the suberin of roots and/or twigs and branches.

Conclusions

The new information obtained for polar aromatics reveals two types of compounds varying with depth, polar diterpenoids and dicarboxylic fatty acids. Results are encouraging and will contribute in OM characteristics and tracking secondary processes in dumps.

Acknowledgement

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Reference

Stefanova, M., Simoneit, B.R.T., Marinov, S.P., Zdravkov, A., Kortenski, J., 2016. Novel polar biomarkers in the Maritza-East lignite, Bulgaria. Organic Geochemistry 96, 1-10.