

# Organic geochemistry of solutions liberated during weathering of stock-piled lignite and bituminous coal

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During natural weathering of coal, oxygen-rich functional groups are formed in the porous structure. Oxygen enrichment can induce structural modifications that may negatively influence the utilization of the coal e.g. in coke-making (Rouzaud *et al.*, 1991). The products of the atmospheric alteration of stock-piled coals are weathered coal residues and numerous organic and inorganic compounds. Some of these compounds are easily released into solutions. These solutions can move and can enter the surface waters, as well as interact with soil systems. We suppose that especially humic-like compounds (HLC), carboxylic acids (CA), phenolic compounds (PC) and polycyclic aromatic hydrocarbons (PAHs) are released from coals during weathering. The goal of this study is to identify organic compounds from field-sampled solutions and to evaluate their concentrations.

## Methods

At Bílina (Most lignite basin, Czech Republic) and Libušín (Kladno coal basin, Czech Republic) experimental sites fluids circulating in lignite and bituminous coal piles are sampled using zero tension lysimeters. Comparative series of samples are prepared by leaching coal samples with acidified water in the laboratory. Dissolved organic carbon (DOC), pH and major ions concentrations are determined periodically in untreated water samples. HPLC analyses of collected solutions were carried-out for PAHs concentrations. Separation of HLC was carried-out using Amberlite XAD-8 resins.

## General characteristics of investigated coals and sampled solutions

Stock-piled lignite carbon content is 71%, sulphur 0.71%, huminite reflectance 0.41%. Huminite is a major maceral (about 71%) in investigated stock-piled lignite. Bituminous coal contains 80% carbon

0.76% sulphur, vitrinite reflectance is about 0.66%. Vitrinite is a major maceral (about 60%) in investigated stock-piled coal. H/C nor O/C ratio of both investigated coals does not change significantly in the course of two-years weathering (Sýkorová, unpublished).

In the case of lignite, macroscopic crystalline accumulations of marcasite are present in the material. Seladonite and glaukonite represent major clay minerals present in lignite, kaolinite is major clay mineral in bituminous coal.

At both experimental sites, liberated solutions are characterized by high conductivity (1.6 mS/cm<sup>2</sup> and 0.9 mS/cm<sup>2</sup>). pH values range between 5.6 and 6.9. At Bílina mean DOC concentrations are 21 mg/l, high concentrations about 40 mg/l have been measured during 1997 summer period. Lower concentrations of DOC are liberated in solutions from bituminous coal from experimental pile situated at Libušín (mean concentration 5.6 mg/l).

Sulphates are dominant anions in lignite originating solutions, with mean concentration 880 mg/l, and maximum 1540 mg/l during 1997. Sodium and calcium are dominant cations (mean annual concentration 141, resp. 146 mg/l). Extremely high concentrations of sulphates originate from marcasite weathering and dissolution, hydrogen ions originating from this reaction are exchanged with clay sodium ions. At Libušín, solutions liberated during the weathering of bituminous coal contain high concentrations of sulphates (mean annual concentration 310 mg/l) and sodium is the dominant cation (mean annual concentration 111 mg/l).

## Organic compounds from liberated solutions

At Bílina, total concentrations of PAH in solutions liberated from lignite piles are in order of two to fourth hundreds ng/l, with october maximum of about one thousand ng/l. At the beginning of the

experiment (Spring 1997) fluorene, fenantrene and pyrene are dominating PAHs, during winter 1997 (from November to January) fenantrene and naphthalene become the most important PAHs.

Relatively high concentrations of PAHs occur in rainwater samples: total PAH content is about 400 ng/l. Lower PAH content in solutions from stock-piled coal reflect an immobilization process related probably to PAHs interaction with clays and fine and porous coal particles. Higher concentrations of PAHs are found in solutions from room-temperature experimentally leached lignites (about 500 ng/l). About one order higher is the content of PAHs in experimentally leached highly oxidised (palaeo-oxidized) lignites (about 6000 ng/l). Such lignites (forming a deposit near Duchcov, 5 km from Bilina) have been altered to a mixture of humic compounds. Observed differences in PAH concentrations reflect different character of the leaching processes, and the influence of the immobilization through the sorption of organic molecules.

At Libušín total concentrations of PAH in solutions liberated from bituminous coal piles vary from 20 to 90 ng/l, with an october maximum of about one hundred ng/l. At the beginning of the experiment (Spring 1997) fenantrene, naphthalene and fluorene are dominating PAHs, during fall 1997 higher concentrations of fenantrene and naphthalene have been observed.

Due to observed chemical characteristics (pH,

DOC, sulphate concentration) it is supposed that organic anions play only a minor role in acid-base equilibrium of investigated systems. Obtained results indicate that PAHs represent an important group of organic compounds in rainwater from highly industrialised Central and Northern part of Bohemia. Low concentrations of PAHs and HLC are released from bituminous coal to the stock-pile output. Concerning the output from lignite piles, no general trend has been observed indicating general evolution of total PAHs concentrations to be correlated with the degree of weathering.

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