# Native polycyclic aromatic hydrocarbons (PAHs) in coals with different rank

# Природни полициклични ароматни въглеводороди (ПАВ) във въглища с различен ранг

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The structure of coal can be described as a two phase system, which includes a macromolecular network (an insoluble) and a “mobile” (soluble) parts, both of them contain PAHs (Given, 1987; Haenel, 1992). The macromolecular phase consists of aromatic structural units that enclose the “mobile” phase, which consists of relatively small molecules (including 2–6 ring PAHs). The PAHs in the “mobile” phase are of particular environmental concern since they can be more easily released in to the environment than those that are trapped within the macromolecular network (Haenel, 1992; Achten, Hofmann, 2010). PAHs in coals are usually present as complex mixtures with a range of physicochemical properties and the composition of PAHs is therefore variable. Sixteen of the PAHs in the “mobile” phase are particularly toxic and carcinogenic, and therefore defined by the US Environmental Protection Agency (USEPA) as priority pollutants. In addition to the 16 USEPA PAHs, toxic effects are also observed with some alkylated counterparts (http://monographs.iarc.fr/ENG/Monographs/vol92/mono92.pdf), as well as with dibenzopyrenes (Siemiatycki et al., 2004). Radke et al. (1980) was among the first publications discussing the composition of PAHs in the “mobile” phase of coals and reporting that trends in PAHs concentration and composition are not monotonic with variations in coal rank. In fact, PAHs concentrations reach their maximum at bituminous coal rank, and then decrease with coalification.

Three samples from Bulgarian deposits, i.e Maritsa East, Oranovo-Simitli and Balkan Basin, representing lignite, subbituminous, and bituminous coals, respectively, were studied. The investigation includes determination of vitrinite (huminite) reflectance and concentration of PAHs. Gas chromatography-mass spectrometry (GC-MS) was applied to identify and quantify PAHs in the studied samples. Coal rank was determined on the basis of vitrinite reflectance, Ro (%).

Vitrinite (huminite) reflectance values (Ro) of studied coal samples are 0.17% for Maritsa East, 0.36% for Oranovo-Simitli, and 0.96% for Balkan Basin. These data are in compliance with ICCP classification for lignite, subbituminous and bituminous coals and also correspond to the results reported by Šiškov et al. (1982).

Extracted PAHs (PAH extracted, i.e. 16 PAHs defined by USEPA as priority pollutants plus alkylnaphthalenes and alkylphenanthrenas) were determined in the lowest concentrations in the Oranovo-Simitli coal (1.97 μg/g TOC), followed by Maritsa East (11.06 μg/g TOC) and were in the highest amount in the Balkan Basin (219.92 μg/g TOC). Considering the chemical processes during coalification, a systematic relationship between PAHs concentrations and coal maturity is expected. The exception is the lower concentration of extracted PAHs in the subbituminous coal sample from Oranovo-Simitli, than lignites from Maritsa East. However, if coals of similar origin are considered, the maximum total aromatic hydrocarbon yield (Radke et al., 1990) and maximum EPA-PAH concentrations (Zhao et al., 2000) were observed at 0.9% Ro and 1.1% Ro, respectively. These conclusions are also confirmed in the high rank bituminous coal from Balkan Basin (Ro 0.96%). The increasing PAHs concentration can be explained by increasing condensation, carbon concentration and aromatization of coal with increasing maturity. The concentrations of the 16 USEPA PAHs increase from lignite (0.88 μg/g TOC) to subbituminous coal (6.30 μg/g TOC), and highest values are found in high rank bituminous coal (35.34 μg/g TOC). The low molecular weight (LMW) PAHs concentrations (i.e., 2–3 ring PAHs) increase in the order: subbituminous < lignite < bituminous coals.

The high molecular weight (HMW) PAHs concentrations (i.e., 4, 5, 6 ring PAHs) increase in the same order like LMW.

In the studied coal samples of different rank, 13 from 16 EPA-PAHs are found including phenanthrene, anthracene, 2-phenylnaphthalene, fluoranthene, pyrene, benzo(a)anthracene, triphenylene, chrysene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)-pyrene, perylene and benzo(ghi)perylene. Not only PAHs concentrations but also PAHs patterns change with increasing rank. Bituminous coals contain PAHs, predominantly three cyclic PAHs, i.e. phenanthrene (19.20 μg/g TOC), 2-phenylnaphthalene (6.54 μg/g TOC), and four cyclic PAHs, i.e. fluoranthene (2.58 μg/g TOC), pyrene (1.95 μg/g TOC), chrysene (1.95 μg/g TOC), benzo(a)anthracene (0.90 μg/g TOC) and triphenylene (0.82 μg/g TOC). In lignite PAHs of the highest concentration are chrysene (1.57 μg/g TOC), perylene (1.54 μg/g TOC), triphenylene (0.87 μg/g TOC), and phenanthrene (0.74 μg/g TOC). PAHs in subbituminous coals only occur in trace amounts. Detected compounds include phenanthrene (0.23 μg/g TOC), triphenylene (0.18 μg/g TOC) and benzo(ghi)-perylene (0.18 μg/g TOC). Benzo(ghi)perylene are found only in subbituminous coal from Oranovo-Simitli Basin. During coalification, PAHs patterns change because primary products of higher thermodynamic stability are generated at the expense of less stable compounds. Bicyclic, tricyclic and tetracyclic PAHs are formed mainly in the high rank bituminous coal from Balkan Basin and provide a pattern of compounds showing a structural relationship to natural precursor molecules, e.g. phenanthrene derivatives, which are thought to be derived from plant resins and steroids (Püttmann, Schaefer, 1990).The exception is perylene (1.54 μg/g TOC), which has been found only in lignite. With increasing maturity, a shift occurs in the PAHs pattern from high concentrations of naphthalene and its alkylated derivatives at bituminous coals.

PAHs concentrations and patterns in coals depend on the organic matter type, as well as temperature and pressure conditions during the coalification processes (Achten, Hofmann, 2009).

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