Elevated PAHs concentration and risk assessment in floodplain soils impacted by coal mining

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Introduction: Carbonaceous geosorbents like coal can be one very strong geosorbent in soils and sediments. They occur due to dislocation during large flood events in areas impacted by coal mining. In addition, coal is not only a strong geosorbent but also may contain elevated native polycyclic aromatic hydrocarbons (PAHs) concentrations. Mobility of PAHs associated with different geosorbents, controls especially coal particles, their sorption/desorption, bioavailability and further environmental risk.

Methods: Aiming for the source allocation, we determined 45 PAHs including alkylated PAHs, and n-alkanes in different soil samples. Soil samples were separated according to their grain size and density. To further identify the dominant geosorbents, organic petrography was applied. Sorption batch experiments were performed with different size and density fractions of soil samples. Using supercritical solvent extraction (SFE), desorption kinetics of PAHs in different fractions of soils were studied.

Results: Elevated PAH concentrations (up to 120 mg/kg for EPA PAHs and 200 mg/kg for 45 PAHs) were found in soils along the Mosel River floodplain. According to ratios of alkylated PAHs to parent PAHs, and other typical PAH ratios, both petrogenic and pyrogenic sources were indicated. The light fractions of soils, although with little soil mass, represented most of total PAHs mass with extremely high PAHs concentrations up to 2400 mg/kg.



Fig. 1: Photomicrographs of carbonaceous particles identified by organic petrography techniques in light fractions ($< 2 \text{ g cm}^{-3}$) of soil samples collected from Mosel River floodplain, Germany.

Organic petrographic analysis with the use of light fractions found that the anthropogenic organic materials including coal and coal-derived particles were abundant (Figure 1). In our samples the optical properties of the coal particles are typical of particles from the industrial activity related to coal mining.

Discussion: Both TOC/BC content and OM petrographic composition revealed two distinct domains of carbonaceous geosorbents for PAHs: (1) coal particles transported by flood events; (2) coal-derived particles mostly present in the upstream region. Both of them were derived from former coal mining and coal industrial activity in the neighboring region.

Sorption study revealed that the light fraction had the highest sorption capacity comparable to low rank coals. In addition, the light fraction contributed most for the sorption of Phe in total soil samples. Moreover, sorption was strongly non-linear and a combined partitioning – pore filling model gave a better fit than the Freundlich sorption model.

Desorption data from sequential SFE were successfully described using a two-site model. Desorption rate constants were one order of magnitude lower than those of "slow" and "very slow" desorption rates from other studies. This suggests very slow and extremely slow desorption. We demonstrate that, despite high soil PAH concentrations which are due to coal and coalderived particles, the environmental risk is reduced by the very slow and extremely slow desorption rates.

In conclusion, for the establishment and development of soil quality criteria (SQC) it is important to understand the environmental behavior of PAHs, especially if associated to heterogenous geosorbents like coal and coal-derived particles.

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