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## Influence of Two Tar-Contaminated Sites on Adjacent Rivers: Quantitation of PAHs, Heterocyclic PAHs and Phenols in the Aqueous Phase

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Over the past century, the anthropogenic use of coal as important resource of industrial products often resulted in soils and groundwater contamination at manufacturing plant sites. Tars and tar oils are formed as byproducts during coking processes and are known to be of high toxicological relevance. The major portion of a typical coke oven coal tar is represented by unpolar, homocyclic aromatic compounds, such as the well known EPA-PAHs. Additionally, even more polar compounds such as phenols and heterocyclic aromatic compounds are present at low mass percentages of up to 10%. Over the last decade, these polar compounds played an increasing role in the groundwater-soil system of tar-contaminated sites and were subject of governmentally funded research projects in Germany (KORA, RUBIN). As an extension of these projects, the presented work investigates the importance of tar-contaminated sites as point sources to adjacent rivers. Therefore, a sensitive method for the quantitation of 86 heterocyclic PAHs, phenols and homocyclic PAHs was developed and applied to groundwater samples on the river bank of tar-contaminated sites and samples from related rivers.

Groundwater samples and river water samples were taken at two tar-contaminated sites and their adjacent rivers in Germany:

- Former coal mining and coke oven plant site (A): 5 sampling points on the adjacent river, 3 groundwater wells on the river bank of the contaminated site.
- Former steel works site (B): 3 sampling points on the adjacent river, 5 groundwater wells on the river bank of the contaminated site, 1 reference well outside the contaminated zone.

All water samples were acidified on-site to pH 1-2 by adding hydrochloric acid and stored at 4°C until preparation. The following solid phase extraction procedure (groundwater: 100 ml, river water: 1000 ml) was performed using Lichrolut EN SPE Cartridges (Merck, Germany) with a vacuum extraction manifold. River samples were initially filtrated using 1.6 µm glass fiber filter pads to prevent clogging of the cartridges. After loading, the cartridges were eluted in two fractions under acidic (fraction 1: neutral analytes) and basic conditions (fraction 2: basic PANHs). Quantitative analysis of the resulting and finally concentrated extracts were performed by GC-MS for fraction 1 and LC-MSMS for fraction 2. The method provides a reliable reproducibility (5-10% RSD) and a mean recovery of more than 80%. Limits of detection achieved are in the low ng/l range. For further information, a schematic overview of the sample preparation procedure will be presented on the poster. The analysis of groundwater samples from the river bank of site (A) show high sum concentrations of up to 10 mg/l in two wells and minor concentrations of 0.4 mg/l in the third well. Main contaminants found are the homocyclic aromatics indane, indene, 1-methylnaphthalene and acenaphthene. Especially, sulfur- and oxygen heterocycles, such as 1-benzothiophene and dibenzofurane were found in high concentrations as well. Increased concentrations of the compounds mentioned were also found in the river adjacent to the contaminated site (A). Measurements of samples from the former steel works side (B) and further data processing is still under way.