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Ubiquitous Distribution of Heterocyclic PAHs in the Large River Systems in Northern GermanyAnne-Kathrin Siemers ^{*1}, Jan Sebastian Mänz ¹, Dieter Steffen ², Wolf-Ulrich Palm ¹, Wolfgang Ruck ¹¹ Leuphana University Lüneburg, Institute of Environmental Chemistry, Scharnhorststr. 1, 21335 Lüneburg, Germany,² Lower Saxony Water Management, Coastal Defence and Nature Conservation Agency, An der Scharlake 39, 31135 Hildesheim, Germany, siemers@uni.leuphana.de

PAHs and heterocyclic PAHs are known as the predominant contaminants in groundwater at tar contaminated sites. Beyond these local sources, especially concentrations and the distribution of heterocyclic PAHs in environmental samples, such as rivers, in particular have received less research attention. Concentrations in samples of this type are assumed to be far below those from highly polluted areas, making a sensitive analytical method for the reliable quantification necessary. An analytical method for aqueous samples in low ng/l range, sediment samples and suspended matter in the range of 1 µg/kg was developed. GC-MS and LC-MSMS were used in the simultaneous analysis of 86 heterocyclic PAHs, phenols, classical EPA-PAHs and alkylated PAHs. In preliminary experiments liquid-liquid extraction (LLE) for water samples was used at the beginning of the project. However, a high LLE-sample throughput is impractical. Therefore, a combined extraction strategy using solid phase extraction (SPE) and subsequent fractionation by pH variation on Lichrolut EN cartridges was developed. Aqueous samples were directly enriched, whereas ultrasonic extraction was adopted for solid samples with subsequent transfer of evaporated extracts onto the SPE cartridges. The given procedure separates basic nitrogen-heterocycles and possesses a suitable clean-up prior to LC-MSMS analysis for this fraction. Sensitive quantitation of phenols, PAHs, sulfur- and oxygen-heterocycles is realized by GC-MS. Mean recovery of the analytes was found to be >80%. Reproducibility of the method expressed as mean RSD was found to be below 5% for GC-MS and 10% for LC-MSMS. The method combines the benefits of GC-MS and LC-MSMS analysis and is applicable to highly contaminated groundwaters at tar-contaminated sites, river waters and sediments representing background concentrations. The method was successfully validated for EPA-PAHs sampled from river sediments by a threefold extraction of a standard reference material.

The methods were applied to numerous environmental samples taken from river waters, river sediments and particulate matter. Results from two sampling campaigns in Lower Saxony are discussed. A first campaign was performed in 2009 for the water phase, sediment and suspended matter from 26 rivers. A second campaign was implemented in 2010 with the research vessel Ludwig Prandtl in the estuaries of the rivers Weser and Elbe. Only a few general results are presented here and details and interpretations are given in the presentation. Out of the 86 compounds analyzed in the first sampling campaign, only 3- and 4-phenylpyridine, phenanthridinone and 2-hydroxycarbazole were never found to be above the detection limit in any sample. Due to high blank concentrations, cresoles were not quantified. Main heterocycles found in sediment samples were dibenzofuran (up to 39 µg/g C), dibenzothiophene (up to 11 µg/g C) and carbazole, 4-methylquinoline and acridine (in the range of 4-8 µg/g C). However, homocyclic PAHs prevailed in sediment samples. Unlike the case with solid samples, comparable sum concentrations of heterocyclic and homocyclic compounds were found in the aqueous phase, dominated especially by acridine and quinoline with concentrations of up to 20 ng/L. The interpretation of results for the second campaign is still under way and will be discussed in the presentation.