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Correlation Patterns of PAHs and Heterocyclic PAHs in Sediment Samples from Northern Germany - Point Sources and Diffuse Immissions

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PAHs are extensively investigated and classified as priority hazardous substances within the Water Framework Directive of the European Union (EU-WFD, besides anthracene five representative compounds and in addition naphthalene and fluoranthene, classified as priority compounds). Unlike the highly lipophilic PAHs much less is known about the related class of heterocyclic PAHs. To investigate the general importance of especially heterocyclic PAHs numerous environmental samples taken 2009 from river waters, river sediments and particulate matter were analyzed in our group (sampling campaigns in Lower Saxony, Germany). For comparison purposes a special point source in the River Lippe (from a highly contaminated site in Lünen, Ruhr area, Germany) was used. In a first step concentrations from sediment samples (bulk fraction normalized to carbon content) were used. Analytical data for 81 compounds (16 EPA PAHs, 12 phenols, 21 N-heterocycles, 7 O-heterocycles, 5 S-heterocycles and 20 related PAHs such as methylated compounds or hydroxy- or keto-derivatives) at 35 EU-WFD sampling points in Lower Saxony, 2 particulate matter sampling stations and 5 sampling points before, at and behind the local source in Lünen were used (in sum 3400 concentrations). The following main questions were addressed:

- Which correlations exist between the compounds at different sampling points (more than 6500 potential correlations were examined).
- Which compounds out of the chosen spectrum of 81 substances were never found and are assumed to be not important (with respect to an analytical screening)?
- Which heterocyclic PAHs were found to be most important in sediment samples?
- Do correlations exist between heterocyclic PAHs and homocyclic PAHs? Is it possible to define priority compounds which can be used e.g. as markers?
- High concentrations were determined at the local point source (but in general not for all compounds).

Besides the question of the influence of such a point source on the background concentration the difference in compound patterns was investigated using cluster analysis.
Due to the high dynamic in concentrations logarithmic values were used and only linear correlations are discussed here. 22 compounds were found without correlation (defined as R >0.9) with any other compound. This group includes 3 compounds with very high blank concentrations (cresols and 2,3,6-trimethylphenol) and 11 compounds never detected above detection limit in any sample (3- and 4-phenylpyridine, phenanthridinone and 2-hydroxycarbazole) or only in less than 3 samples (e.g. 1,8-dimethylnaphthalene, 2-methylbenzofuran, 2,3-dimethylbenzofuran, xanthene, 8-methylquinoline). Compounds found at least in more than 17 samples but without any correlation to other compounds include for instance acenaphthylene, indene, benzofuran, or 2-naphthol. Due to their high solubility most phenols were found only in few samples and in addition with bad correlations.
Not surprisingly superb correlations (R >0.99) were found for numerous EPA-PAHs as for pyrene (with fluoranthene) or for isomers such as 1,2-dimethylnaphthalene (with 1,4-dimethylnaphthalene). Correlations for heterocycles with R >0.97 were found for instance for 1-benzothiophene (with naphthalene), dibenzofuran (with fluorene) or dibenzothiophene (with phenanthrene).
Details, first interpretations and the comparison between concentrations at the local source with background samples are discussed on the poster.