

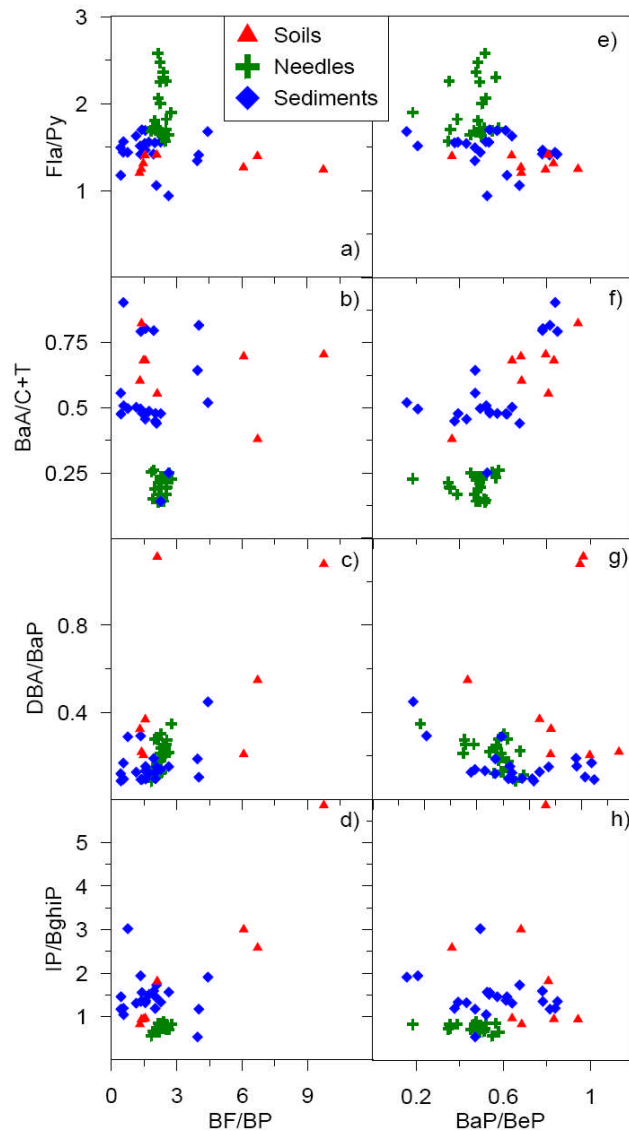
PAH RATIOS IN DIFFERENT ENVIRONMENTAL SAMPLE MATRICESOliver PAECH¹, Birgit NABELFELD^{1,2}, Gunnar KÜHN¹ and Lorenz SCHWARK¹

1. *Institute of Geology, University of Cologne, Germany*
2. *present address: Curtin University of Technology, Perth, Australia*

Polycyclic aromatic hydrocarbons (PAH) comprise the most abundant and diverse group of anthropogenically emitted and dispersed environmental pollutants. Their behaviour in the environment as a function of biological, chemical and physical processes as well as their source recognition and apportionment is often investigated using specific PAH-ratios (for reviews see e.g. Howsam and Jones, 1998, Yunker et al., 2002 and references therein). Ratios of individual PAH, if used for source recognition are strongly dependent on the physicochemical properties of the components used for calculation. For PAH disseminated preferentially by atmospheric pathways the boiling point and vapour pressure are most critical, as they partition PAH in classes transported predominantly in the gas or particulate phase. Therefore, it is recommended for source allocation to utilize PAH ratios where compounds are of similar physicochemical characteristics, i.e. ratios should be calculated where PAH with identical number of rings are used. It must also be considered that fractionation and modification of PAH occurs during transportation and accumulation in and on various matrices, e.g. sediment/soil/vegetation/man-made surfaces, which will affect PAH source ratios. In several investigations, frequently employed PAH ratios are applied in uncritical fashion and matrix differences are not accounted for. We here compare frequently used PAH source ratios in different environmental matrices in a case study of the Cologne conurbation.

In this study 22 samples of pine needles (*pinus nigra*), 22 sediment samples taken from 7 lakes and 8 soil samples were collected in summer and winter of the year 2002 and 2004 within an area spanning <350 km². The region is affected by various urban and industrial emission sources. The samples were analysed for the 16 EPA primary pollutant PAHs plus triphenylene, benzo[a]fluoranthene, benzo[j]fluoranthene and benzo[e]pyrene.

Source-relevant PAH ratios were calculated whereby the ratios are based exclusively on molecules with identical ring number and similar physicochemical properties. Relationships between selected ratios were inspected by using binary plots of two key ratios for 5-ring PAH, BF/BP (benzo[a+b+j+k]fluoranthene/benzo[a+e]pyrene) and BaP/BeP (benzo[a]pyrene/benzo[e]pyrene) versus ratios of 4-, 5- or 6-ring-PAH, Fla/Py (fluoranthene/pyrene), BaA/C+T (benz[a]anthracene/chrysene+triphenylene), DBA/BaP (dibenz[ah]anthracene/benzo[a]pyrene), IP/BghiP (indeno[1,2,3-cd]pyrene/benzo[ghi]perylene).



Results show that as expected ratios are matrix-affected in a different manner. Variability of PAH ratios in pine needles is lowest, as one transport mechanism is dominant and degradation effects on pine needles occur in a similar fashion. Soils show a higher variability as there are variations in PAH degradation conditions (pH, Eh, soil microbiota) and lake sediments are affected by these effects as well but also receive PAH by variable transport mechanism (atmospheric and fluvial input, the latter strongly depending on K_{ow}). For certain binary plots strongly opposing trends in variation were noted. The ratio of Fla/Py is highly variable for needles but nearly constant for soils, whereas the ratio BF/BP behaves opposite with high variability for soils and low for needles. On the contrary the relationship between BaP/BeP and BaA/AC+T is

almost linear. The pine needle cluster according to the BaA/AC+T ratios is well separated from the soil and sediment ratios. If compared to the BF/BP ratio it shows low variability for the latter but if compared to the BaP/BeP it reveals a high variability. The differences in the behaviour of the individual PAH ratios can be explained and will be discussed based on their susceptibility towards photolytic degradation, water solubility and K_{ow} , microbial degradation, transport partitioning, and other environmental processes.

REFERENCES

- Howsam, M. and Jones, K.C. (1998) Sources of PAHs in the Environment. In: NEILSON, A.H. [Edt.] *The Handbook of Environmental Chemistry, Vol. 3: Part I: PAHs and related compounds - Chemistry Berlin, Heidelberg*, 412 S.
- Yunker, M.B., MacDonald, R.W., Vingarzan, R., Mitchell, H., Goyette, D. and Sylvestre, S. (2002) PAHs in Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry*, 33, 489-515