



Source Identification of Polycyclic Aromatic Hydrocarbons by Diagnostic Ratios and Positive Matrix Factorization

A. Dvorska (1), J. Jarkovsky (1), G. Lammel (1,2), and J. Klanova (1)

(1) Masaryk University, Research Centre for Environmental Chemistry and Ecotoxicology, Kamenice 3, 62500 Brno, Czech Republic, (2) Max Planck Institute for Chemistry, J.-J.-Becher-Weg 27, 55128 Mainz, Germany

Although polycyclic aromatic hydrocarbons (PAHs) are also of natural origin, in many regions their environmental concentrations have strongly increased due to human activities. These semivolatile organic compounds are generally formed during incomplete combustion. Other sources include volatilization from unburned petroleum or tire abrasion in road traffic. Among all pollutants PAHs pose the highest human health hazard in Europe (WHO, 2003).

A multivariate statistical method, positive matrix factorization (PMF; Paatero, 1997), and diagnostic ratios of individual PAHs (e.g. Yunker et al., 2002) are used for PAH source identification in central Europe.

To minimise confounding factors such as differences in volatility, water solubility, adsorption etc., diagnostic ratios should be restricted to PAHs of similar molecular mass (Readman et al., 1987). Furthermore, different reactivities are limiting. Nevertheless, the application of PAH diagnostic ratios is often inconclusive, because substance patterns (profiles) have not been reported for all sources and ranges for various sources overlap.

The complete profiles are made use of by statistical methods such as factor analysis, UNMIX and PMF (Tauler et al., 2006). However, these methods can be unreliable, because of incomplete knowledge of source profiles and the analysis' sensitivity to the data distribution.

A unique 12-year data set of concentrations of PAHs (16 individual substances, 2 phases, weekly) in air, measured at the regional observatory Košetice, Czech Republic, is examined, together with shorter time series from Leipzig (urban background) and Schwartemberg (subalpine mountain background), Germany. Also, retene and coronene as specific source markers measured in Košetice from 2006 on are included into the analysis. An extensive literature search on PAH emission profiles was conducted. This data set was accomplished by measurements at sites in the Zlínsko region, Czech Republic, which are strongly dominated by a single, well defined PAH source. By determination of the total PAH concentrations (sum of gas and particulate phases) the propagation of sampling artefacts related to PAH partitioning into statistical errors is avoided.

The main results are: Major PAH source categories exhibit a significant seasonality, coronene as a marker for traffic (Bi et al., 2003) should be used with care. Long-term trends of the major PAH sources are insignificant.

Literature:

Bi X.H., Sheng G.Y., Peng P., Chen Y.J., Zhang Z.Q., Fu J.M., 2003. Distribution of particulate- and vapor-phase n-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. *Atmos. Environ.* 37, 289-298.

Paatero P. (1997): Least square formulation of robust non-negative factor analysis, *Chemometrics Intelligent Lab. Systems* 37, 23-35.

Readman J.W., Mantoura R.F., Rhead M.M., 1987. A record of polycyclic aromatic hydrocarbon (PAH) pollution obtained from accreting sediments of the Tamar estuary, UK: evidence for non-equilibrium behaviour of PAH. *Sci. Total Environ.* 66, 73-94.

Tauler R., Paatero P., Hopke P., Henry R.C., Spiegelman C., Park E.S., Poirot R.L., 2006. State of the art in methods and software for the identification, resolution and apportionment of contamination sources In: *Summit*

on Environmental Modelling and Software (Proceedings of the iEMSs 3rd Biennial Meeting; Voinov A., Jakeman A.J., Rizzoli A.E., eds.), International Environmental Modelling and Software Society, Burlington, USA.

WHO (2003) - World Health Organization: Health risks of persistent organic pollutants from long-range transboundary air pollution. WHO Regional Office for Europe, Copenhagen, 252 pp.

Yunker M.B., Macdonald R.W., Vingarzan R., Mitchell R.H., Goyette D., Sylvestre S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* 33, 489-515.