Gas/Particle Partitioning of Polycyclic Aromatic Hydrocarbons in a Canadian Rural Area

Yushan Su[1], Frank Wania[1], Tom Harner[2], Ying Duan Lei[1], Mahiba Shoeib[2]

[1]Department of Physical and Environmental Sciences, University of Toronto at Scarborough
[2]Meteorological Service of Canada, Environment Canada

Partitioning of polycyclic aromatic hydrocarbons (PAHs) between air and aerosol is an important inter-media exchange process, especially for PAHs with intermediate volatility. An understanding of gas-particle partitioning is thus a key component in improving our understanding of PAH atmospheric transport, pathways and effects. 24-hour high-volume air samples of 750 ~ 900 m^3 volume were taken simultaneously in a deciduous forest and a nearby clearing every twelve days in a rural region of southern Ontario, Canada between October 2001 and November 2002. Gaseous and particle-bound PAHs were analyzed separately in a total of 70 air samples.

The gas/particle partitioning behavior of PAHs in all samples was studied with two equations. The fraction ϕ in the particle phase measured during each sampling event was related to the sub-cooled liquid vapour pressure P using the Junge-Pankow equation $\phi = 10^{m \cdot \log P + b'}/(1+10^{m \cdot \log P + b'})$, either allowing for the slope m to deviate from –1 (two-parameter model) or not (one-parameter model). This fitting procedure is superior to linear logarithm regressions involving dimensionless gas/particle partitioning coefficients log K_p, because the latter tends to ignore a significant amount of analytical information while giving undue weight to highly uncertain data points. The reason is that ϕ can still be calculated when either gaseous or particle-bound concentration is 0, whereas log K_P cannot be defined for PAHs that are either completely in the gas phase or entirely bound to particles - even though such data points often have a low uncertainty. Fitting the data from this study also showed that linear logarithm regression involving K_p' give too much weight to data points involving small concentrations above the detection limit in either the gas or particle phase. It is believed that this issue has not been sufficiently appreciated in previous analyses of gas/particle partitioning data set; therefore, we suggest that the values of many of the regression parameters reported in the literature may have been over-interpreted in light of their considerable uncertainty.

The experimental data fit is good for both the one and two-parameter equation, and discrepancies between experimental data and models relate to sampling/experimental artefacts. In particular, samples taken close to the freezing point appear to suffer from blow-off artefacts. The magnitude of the differences in the model fitting parameters between sampling events is consistent with the reported variability in the nature (surface area, organic matter content) and concentration of atmospheric particles. The one-parameter equation fit is similar to that of the two-parameter equation. Interrelation between the fitting parameters m and b' in the two-parameter equation further lends support to the suggestion that the performance of the one-parameter equation is comparable to the two-parameter equation in interpreting gas/particle partitioning data of PAHs, although two parameters may provide additional theoretical insight into the partitioning mechanisms. Statistical analysis of fitting parameters for both equations reveals that PAH gas/particle partitioning behavior is not significantly different at the two sites.