

Modelling the interaction of semi-volatile organic compounds with multiphase aerosol particles using polyparameter linear free energy relationships

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Gas-particle partitioning (GPP) is an important mechanism which affects the transport, fate, and bioavailability of semi-volatile organic compounds (SOCs). The preferential partitioning of SOCs in the atmosphere depends on parameters such as the compound's molecular structure as well as particulate matter (PM) physical and chemical properties. The various organic and inorganic PM constituents interact with SOCs depending on their molecular structures. Previous studies considered PM as a homogenous bulk and used a typical organic solvent (i.e. octanol) as a surrogate to simulate such interaction. In the present study we applied polyparameter linear free energy relationship (ppLFER) to address this process following a multiphase aerosol scenario. ppLFER models have been developed for various organic solvents (Abraham *et al.*, 2010) and inorganic surfaces (Goss *et al.*, 2003). The models consider all types of molecular interactions (e.g. dispersion forces, hydrogen bonding) between solute and sorbent at equilibrium.

We considered three different phases of particulate organic matter (OM): (A) high molecular mass organic soluble (OS) OM (mass mixing ratio in OM: 0.05), (B) low-mid molecular mass both water soluble (WS) and OSOM (0.55), and (C) high molecular mass organic polymers (OP) (0.40) (Rogge *et al.*, 1993). An appropriate ppLFER model was used for each phase – i.e. hexadecane-air, dimethyl sulfoxide-air, and polyurethane ether-air, respectively. In addition, SOC adsorption to soot and soluble salt particles, namely ammonium sulphate and ammonium chloride, were included using corresponding ppLFER equations. Partitioning constants (K_p ; $\text{m}^3_{\text{air}} \text{g}^{-1}_{\text{PM}}$) determined with this model were corrected using the measured fractions of OM, soot, and the salts, and compared with the experimental K_p for parent, oxy-, and nitro-PAHs, and nitrophenols from three central European sites - i.e. Košetice, Grenoble, and Mainz.

As can be seen from Figure 1, the model made good predictions for semi-volatile pyrene (PYR), fluoranthene (FLT), 9,10-anthraquinone (9,10-ATQ), benzo(a)fluorenone (BAFLON), 9-nitroanthracene (9-NANT), and 3-nitrophenanthrene (3-NPHE), with 74 - 96% of the data points predicted within one order of magnitude accuracy (Table 1). The analysis indicated that adsorption was the main process in the substance GPP, dominated by the contribution of low-mid

molecular mass WSOSOM. Despite being assigned substantially different OM mass mixing ratios, OSOM and OP contributed less than 5% to the overall absorption process, although the contribution from OP was relatively higher. Finally, partitioning onto soot dominated the adsorption process, suggesting that the contributions from soluble salts may be neglected when studying the target analyte GPP. The PM phase state is an additional parameter to be included in future parameterizations of the GPP process.

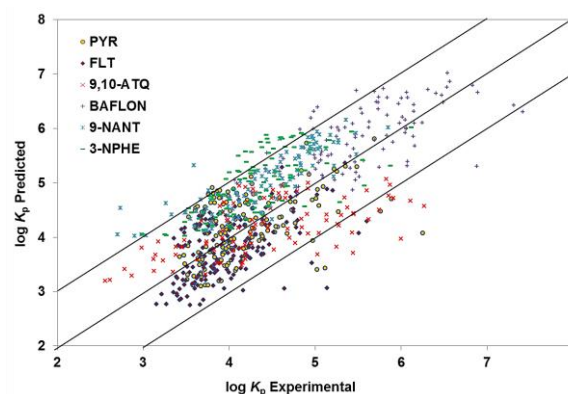


Figure 1. Comparison between experimental and predicted $\log K_p$ ($\text{m}^3 \text{g}^{-1}$).

Table 1. Experimental $\log K_p$ and percentage of predictions within one order of magnitude accuracy

	$\log K_p$ range	% Predicted
PYR	3.4 – 6.2	94
FLT	2.9 – 7.1	96
9,10-ATQ	2.6 – 6.3	85
BAFLON	4.0 – 7.4	92
9-NANT	2.7 – 5.8	90
3-NPHE	3.0 – 6.1	74

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