Toxic semivolatile substances (PAHs, their nitro and oxy derivatives, brominated flame retardants) in ambient particulate matter in the inner tropics, India: Gas-particle partitioning and wash-out by monsoon rains

G. Lammel^{1,2}, P. Shahpoury¹, S.S. Gunthe³, O. Audy², J. Kohoutek², P. Kukučka² and A. Muthalagu³

¹Max Planck Institute for Chemistry, Multiphase Chemistry Department, 55128 Mainz, Germany ²Masaryk University, Research Centre for Toxic Compounds in the Environment, 62500 Brno, Czech Republic ³Indian Institute of Technology, Environmental and Water Resources Engineering, Chennai 600036, India

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The carriers of aerosol samples' toxicity (molecular level) are still unknown. Mutagenicity of PM is linked to polycyclic aromatic hydrocarbon (PAH) content (e.g., Vu et al., 2012) and up to 20% or so of the toxic equivalent is attributable to nitro-PAHs (NPAHs; Albinet et al., 2008). Many halogenated compounds bioaccumulate along food chains to toxic levels.

For most lipophilic semivolatile organic compounds, wet deposition is dominated by wet scavenging of the particulate mass fraction. In temperate climates typically only a few percent or less of the airborne PAHs are washed out during a precipitation event (Škrdlíková et al., 2011; Shahpoury et al., 2015). The efficiency of transfer of airborne semivolatile organics by precipitation in the tropics has hardly ever been studied.

High-volume air sampling (on quartz fibre filter and in polyurethane foam plugs) and rainwater sampling was conducted 100 km inland at a rural mountain site, Munnar (10.09°N/77.07°E, 1600 m a.s.l.,), before, during and after the onset of the southwest monsoon 2014. Air masses were advected across India and the Arabian Sea before, and across the Indian Ocean and the Arabian Sea after onset.

Analysis of PAHs, their derivatives and polybrominated diphenyl ethers (PBDEs) was by GC-MS/MS in AP mode, of hexabromocyclododecane (HBCD) by LC-MS/MS (negative EI mode).

Mean particulate Σ_{27} PAH, Σ_{13} NPAH and Σ_{9} OPAH concentrations were 17.6, 0.37 and 0.37 ng m⁻³, respectively, and the mean particulate mass fractions, $\theta = c_p / (c_p + c_g)$, were 0.21(0.00-1.00 for individual species), 0.29(0.00-1.00) and 0.33(0.00-0.59), respectively. Mean particulate Σ_9 PBDE and Σ_3 HBCD concentrations were 8.3 pg m⁻³ ($\theta = 0.33$) and 0.023 pg m⁻³ ($\theta = 0.05$), respectively. PBDEs were dominated by BDE209 (not quantified) and HBCD by γ -HBCD. Molecular processes determining gas-particle partitioning (GPP) were investigated using GPP models, such as pp-LFER.

The substance patterns in the aerosol gas and particulate, and the rainwater dissolved and particulate phases differed largely (Fig. 1). Mean PAH, NPAH and OPAH particle scavenging ratios, $W_p = 10^3 c_{rwp}/c_p$, were 1.3(0.8-50)×10³, 0 and 23(0-3540)×10³, respectively. W_t of PBDEs and HBCD isomers ranged (90-4540)×10³.



Figure 1. Mean PAH (above) and brominated substances (below) substance patterns in the aerosol particulate phase and in rainwater (values <LOQ replaced by LOD/2).

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