



## **The kinetics of gas-particle partitioning for PAHs and their interplay with multiphase chemical reactivity**

Jake Wilson (1), Gerhard Lammel (1), Ulrich Pöschl (1), Manabu Shiraiwa (2), and Thomas Berkemeier (1)

(1) Multiphase Chemistry Department, Max Planck Institute for Chemistry, 55128 Mainz, Germany., (2) Department of Chemistry, University of California, Irvine, CA, USA.

The distribution of a chemical compound between the gas phase and the particle phase is of fundamental importance in the atmosphere; it affects the lifetime, chemical transformations and health effects of a given substance. There is still lack of clear understanding of the timescales that govern the gas-particle partitioning process of semi-volatile compounds such as polycyclic aromatic hydrocarbons (PAH) [1,2]. This consideration becomes further intricate when the timescales of partitioning are compared to the timescales of chemical reactivity in both the gas and particle phases. This interplay affects the atmospheric lifetime and hence long-range transport potential of these compounds, but general rules to apply in large scale models remain elusive [3,4].

Using a kinetic double-layer model, we have investigated the equilibration timescales of partitioning of different PAHs (anthracene, pyrene, fluoranthene, chrysene, benzo(a)pyrene and benzo(e)pyrene) on black carbon-like surfaces. The sensitivity of these timescales to different atmospheric variables such as particle number concentration, temperature and surface area, is examined. It is shown that equilibration timescales can range from seconds at warm temperatures to hours at cool temperatures. We also demonstrate that equilibration timescales vary depending on the molecular size of the PAH (with larger molecules such as BaP tending to equilibrate more slowly).

After combination of this description of partitioning with chemical reaction kinetics (reactions with OH, NO<sub>3</sub> and O<sub>3</sub>), we discuss different kinetic regimes [5]. We emulate the method commonly used to treat gas-particle partitioning in global and regional chemical transport models [4], and show that depending on the model time step, it can differ significantly from the solution which accounts for mass transfer kinetics. We suggest this could be a source of error in such models, and should be examined in more detail. Our findings may not just be relevant for PAH, but for any semi-volatile substance interacting with the surface of black-carbon particles.

1. Rounds, S. A. & Pankow, J. F. Application of a radial diffusion model to describe gas/particle sorption kinetics. *Environ. Sci. Technol.* 24, 1378–1386 (1990).
2. Shiraiwa, M. & Seinfeld, J. H. Equilibration timescale of atmospheric secondary organic aerosol partitioning. *Geophys. Res. Lett.* 39, (2012).
3. Friedman, C. L., Pierce, J. R. & Selin, N. E. Assessing the influence of secondary organic versus primary carbonaceous aerosols on long-range atmospheric PAH transport. *Environ. Sci. Technol.* 48, 3293-3302 (2014).
4. Mu, Q. et al. Temperature effect on phase state and reactivity controls atmospheric multiphase chemistry and transport of PAHs. *Sci. Adv.* 4, (2018).
5. Berkemeier, T. et al. Kinetic regimes and limiting cases of gas uptake and heterogeneous reactions in atmospheric aerosols and clouds: A general classification scheme. *Atmospheric Chem. Phys.* 13, 6663–6686 (2013).