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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Internal mixing of the organic aerosol by gas phase diffusion of semivolatile organic compounds" *by* C. Marcolli et al.

Anonymous Referee #1

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The work reported here is a useful contribution to the current research efforts to understand the partitioning of organic species in atmospheric aerosol. The theoretical analysis of the partitioning process is new and a good analysis for trying to understand the processes occurring in ideal terms and makes a significant contribution to bridging laboratory observations, field observations and current thermodynamic models.

One aspect of the paper which I think could do with some improvement is the analysis of the potential errors and limitations to the conclusions of the work. Areas for which I think this is important are outlined below in my specific comments, but in particular I think the attribution of molecular weight ranges for which compounds may be considered semi-volatile being a major conclusion stated in the abstract, should have a range

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or error associated with them. The figures are not fully convincing that such strong boundaries are reasonable.

There is a substantial literature concerning partitioning of semi-volatile organics in the atmosphere and their long range transport that the authors should compare their conclusions with.

Specific:

Abstract and page 5800 (Conclusions): The phrase “equilibration by gas-phase diffusion leads to selective - albeit not complete - internal mixture of the organic aerosol” is ambiguous and should possible be made clearer, particularly in the Abstract.

p. 5790 The postulate that the phase of the organic components of atmospheric aerosol being liquid down to very low relative humidity, primarily rests on laboratory and chamber studies in the absence of potential heterogeneous crystallisation nuclei (e.g. soot, mineral dust), though ammonium sulphate has been shown not to be an efficient heterogeneous nuclei for some dicarboxylic acids. Also, the absence of a significant fraction of insoluble solid organic species, e.g. the major fraction of humic acid-like substances, oxalate salts have not been considered. There is little direct evidence yet that a predominately organic aerosol particle in the troposphere is a liquid. However, this paper shows quite nicely that it does seem likely that treating the particles as liquid may be used to predict properties of the partitioning and re-distribution of organic molecules, in agreement with Pankow.

p.5976: It is not clear why the compounds whose vapour pressures are shown are restricted to the 6 groups as there is much data in the literature on other organics, e.g. PCBs, PCDDs, PBDEs, nitro-aromatics, terpenes, carbonyls, and lipids, amongst many other chemical groups, all of which have been shown to be present in tropospheric aerosols at varying mixing ratios.

p. 5799: In the field study by Mochida et al. which is cited, the chemical formation

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and reaction of organic species to form or remove oxalic acid was also considered to explain some changes in oxalic acid distribution, perhaps the authors could comment on the lifetime of some species with respect to chemical formation and degradation compared to thermodynamic equilibration.

p.5800, Section 3.4 and figure 3. The conclusion of this section, should have some caveats. For example is the major fraction of adipic or azelaic acid likely to be in the water soluble organic fraction in an aerosol given the relatively low solubility of these species in water and their surfactant properties? It is also not surprising most organics are not saturated in aerosol particles.

Technical Comments

p. 5793 Is a subscript on beta missing in equation 7?

p. 5795: first line: Figs.1 c and d not Fig 4.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5789, 2004.

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