

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

**C. Marcolli et al.**

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We agree with the reviewer that there are no strong boundaries between semivolatile and nonvolatile substances. Nevertheless, we decided to give numbers as benchmarks in the abstract and conclusions. We certainly do not want these numbers to be taken as strict boundaries. We therefore change the text in the abstract and the conclusions.

Abstract: "Inspection of vapor pressure data of a series of organic substances allows a rough estimate for which substances this mixing process must be considered. As general benchmarks we conclude that for typical aerosol radii between 0.1 and 1 micrometer this mixing process is efficient at 25C for polar species with molecular weights

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up to 200 and for non-polar species up to 320.”

Conclusion: “Inspection of vapor pressure data for a series of organic substances allows a rough estimate for which substances this mixing process must be considered. As general benchmarks we conclude that this mixing process is efficient for polar species with molecular weights up to 200 and for non-polar species up to 320 at 25C, shifting to 150 and 270 at -10C, respectively”

The main focus of our investigation is particle / particle partitioning of semivolatile species by gas phase diffusion. We therefore discuss studies that reported size distribution of organic species or single particle data. We think that it is not within the scope of this paper to review the literature on gas / particle partitioning of semivolatile organic species. There is one more recent article that describes redistribution of semivolatile organic species from small particle to larger particle sizes during dust events. We add a sentence that refers to this paper. Page 5799, we insert after line 3: “Likewise, Falkovich et al. (2004) describe the redistribution of low-molecular-weight PAH and pesticides from small particle to larger particle sizes during dust events. High-molecular-weight PAH as well as levoglucosan always remained in the submicron particle size bins, in which they were originally emitted to the atmosphere.”

Abstract and p. 5800: We change the phrases in the abstract and the conclusions to make them clearer. To give further explanation of the state of mixing resulting from thermodynamic equilibration by gas phase diffusion, we add a paragraph that compares this mixing process with coagulation. Page 5790, line 10: we replace the sentence from “Furthermore” to “thermodynamics” by: “The extent of mixing of this semivolatile fraction is governed by equilibrium thermodynamics, leading to a selectively, though not completely, internally mixed aerosol.” Page 5800, line 24: we add after organic aerosol: “,whereby the degree of mixing is given by the activity of the semivolatile species in the aerosol phases.”

p. 5790 The organic aerosol in the lower troposphere is liquid without being super-

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saturated if it consists of a high enough number of miscible components (Marcolli et al., 2004). This finding follows from thermodynamic considerations and can be understood in terms of a melting point depression. It is in agreement with the continuous water uptake and release of atmospheric aerosols observed in several field studies by HTDMA experiments. Based on solubility data and the concentration of individual organic species in tropospheric aerosols, only the most abundant organic species such as oxalic acid or oxalate salts might be supersaturated and effloresce. Humic acid like substances are present as liquids or amorphous solids and take up water and other gases at any RH as Chan and Chan (2003) have shown for humic and fulvic acid samples. We are therefore confident that treating the organic aerosol as a liquid is adequate for most situations in the lower troposphere.

p. 5796 We agree that much more data could be added to Figure 2. However, we do not think that this would make the Figure more concise. It was our aim to include major substance classes covering hydrophilic as well as hydrophobic compounds. We hope that Eqs. (7) and (9) of the manuscript will be used by the community to calculate equilibration times between particles by gas phase diffusion for substances and conditions that are not covered in the manuscript.

p. 5799 We estimated that the dicarboxylic acids investigated by Mochida et al. establish thermodynamic equilibrium between particles within minutes. Based on literature (e.g. Chebbi and Carlier, 1996), we assumed longer timescales for formation by chemical reactions and deposition.

p. 5800 Based on the octanol-water partition coefficient ( $P$ ), adipic acid ( $\log P = 0.08$ ) is distributed almost equally between hydrophilic and hydrophobic phases whereas azelaic acid ( $\log P = 1.57$ ) partitions indeed preferably into the hydrophobic phase. Therefore, we show in Figure 3 the solubility in an ideal solvent and not the one in water.

Technical comments:

p.5793 Since the subscript of beta refers to the radius  $r$ , there is no subscript needed when  $r_1 = r_2$  as is assumed starting from equation (5).

p. 5795 Thank you for pointing this out. We will correct it.

#### References:

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Chebbi, A. and Carlier, P.: Carboxylic acids in the troposphere, occurrence, sources, and sinks: a review, *Atmos. Environ.*, 30, 4233 - 4249, 1996.

Falkovich, A. H., Schkolnik G., Ganor. E., and Rudich, Y.: Adsorption of organic compounds pertinent to urban environments onto mineral dust particles, *J. Geophys. Res.*, 109, D02208, doi:10.1029/2003JD003919, 2004.

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

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