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Internal mixing of the organic aerosol by gas phase diffusion of semivolatile organic compounds

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Abstract. This paper shows that most of the so far identified constituents of the tropospheric organic particulate matter belong to a semivolatile fraction for which gas phase diffusion in the lower troposphere is sufficiently fast to establish thermodynamic equilibrium between aerosol particles. For the first time analytical expressions for this process are derived. 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 μm this mixing process is efficient at 25°C for polar species with molecular weights up to 200 and for non-polar species up to 320. At -10°C, these values are shifted to 150 for polar and to 270 for non-polar substances. The extent of mixing of this semivolatile fraction is governed by equilibrium thermodynamics, leading to a selectively, though not completely, internally mixed aerosol. The internal mixing leads to a systematic depression of melting and deliquescence points of organic and mixed organic/inorganic aerosols, thus leading to an aerosol population in the lower troposphere which is predominantly liquid.

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