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Atmospheric
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Discussions

Interactive comment on “Effects of the physical state of tropospheric ammonium-sulfate-nitrate particles on global aerosol direct radiative forcing” *by* S. T. Martin et al.

S. T. Martin et al.

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"An Estimate of the Effects of Organic Molecules on the Phase Transitions of Sulfate, Nitrate, and Ammonium Particles" by Scot T. Martin and Allan K. Bertram

Knowledge of the molecular composition of atmospheric particle-phase organic molecules is limited. Furthermore, there is limited laboratory data on the role of organic molecules in phase transitions. These two facts hinder predictions of the effects of organic molecules on the phase transitions of sulfate, nitrate, and ammonium particles. Nevertheless, calling upon the limited laboratory data, literature reports, and several assumptions, we provide below an initial estimate.

Based upon the IPCC SC1 scenario for 2000 (Table 5.14, Penner et al., 2001), the atmospheric burden comprises 0.78 TgS as sulfate, 0.09 TgN as nitrate, and 0.42 TgN

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as ammonium. (These values compare to our respective estimates of 0.37, 0.05, and 0.29 Tg. See Sect. 2.2.) The SC1 scenario then provides (0.15 + 1.52 = 1.67) Tg of organic molecules (i.e., the sum of carbon, hydrogen, and oxygen). As an upper limit of the effect of organic molecules, we assume that they are water soluble and internally mixed with the inorganic constituents. We assume that the organic molecules do not crystallize. We do not consider heterogeneous nucleation and the possible effects of surfactants, which could influence the hygroscopic properties and the physical state of the particles. Further work is needed to determine the accuracy of these assumptions.

For phase transitions, instead of mass, the appropriate concentration scale is mole fraction because the deliquescence water activity of an ideal solution is linear in mole fraction. Using molecular weights for sulfur (32), nitrogen (14), and organic molecules (150), we obtain relative global mole burdens of 2.4 for sulfate, 0.64 for nitrate, and 1.1 for organics. (We omit ammonium because we assume that the sulfate and nitrate occur as molecular units combined with ammonium or proton.) The organic molecular weight of 150 is chosen assuming an average monomeric chemical unit of CH2O and an average of five units in each molecule. This estimate seems reasonable considering the organic molecules commonly identified in atmospheric aerosol particles; nevertheless, this estimate is a source of uncertainty in our analysis. Following from the relative global mole burdens, the average organic mole fraction is calculated as (1.1)/(2.4 + 0.64 + 1.1) or 0.27, which appears to provide an upper limit because the actual extent of internal mixing and water solubility are below 100

Based on the above analysis and assumptions, we conclude that the inorganic system represents a baseline, to which the organic molecules are a perturbation of up to 0.27. For mole fractions below 0.35, the changes in the deliquescence relative humidity (DRH) and the crystallization relative humidity (CRH) due to organic molecules are anticipated to be minor (Brooks et al., 2002; Braban and Abbatt, 2003; Parsons et al., 2003). In this case, the CRH and DRH values depend first on the inorganic composition, which is then modified slightly by the organic molecules. We conclude that the

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inorganic system is a baseline for estimating the major effects on hygroscopic growth between the upper and lower sides (US and LS) of the hysteresis loop.

The analysis above assumes a globally averaged aerosol particle chemical composition. In reality, there is great variability among individual atmospheric particles as well as large regional differences such as organic enriched particles coming from biomass burning in Africa versus sulfate enriched outflows from heavy coal usage in China. Certainly, there exist individual particles having high organic content. For these particles, the hygroscopic and phase transition properties depend upon the concentrations and the physicochemical properties of the organic molecules.

Clearly more research is needed to develop an accurate description of how organic molecules modify the phase transitions of inorganic particles.

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