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Comparison between measured and predicted CCN concentrations at Egbert, Ontario: Focus on the organic aerosol fraction at a semi-rural site

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Abstract

Aerosol–cloud condensation nuclei (CCN) closure was studied in a semi-rural location 80 km north of Toronto, Canada at the Centre for Atmospheric Research Experiments outside of Egbert, Ontario during the fall of 2005. This site is subject to both polluted air from southern Ontario and clean air from the north. The purpose of the investigation was to evaluate the degree to which closure is attained at a supersaturation of 0.32% when size-resolved aerosol compositions from an Aerodyne Quadrupole Aerosol Mass Spectrometer are made alongside measurements of CCN number density and aerosol size distribution. Attention was given to assessing the sensitivity of closure to assumptions made concerning the water solubility and surface tension of the organic fraction of the aerosol in the Köhler analysis. By assuming that the organics are insoluble and that the growing droplet has the surface tension of water, a good overall degree of closure is attained throughout the analysis time period, with the predicted numbers of CCN within 15% of the modelled numbers, which is within our estimated systematic uncertainties. However, for the specific periods during which the organic content of the aerosol is high, the degree of closure is significantly lower. Sensitivity analyses indicate that some degree of organic water solubility and/or surface tension reduction is necessary to achieve the best agreement and least variance between the modelled and measured numbers of CCN. A general conclusion is that significant uncertainties arise in predicting CCN levels only when the level of soluble inorganic species is below approximately 25% by mass.

Keywords: Cloud condensation nuclei; Organic aerosols; Köhler theory; Closure study

1. Introduction

Although it is well known that aerosols can affect climate indirectly by acting as cloud condensation or ice nuclei, uncertainties remain in quantitatively connecting the chemical composition of aerosol particles to their ability to promote hygroscopic growth. For cloud condensation nuclei (CCN), it is known that soluble inorganic ions promote droplet activation through vapour pressure lowering of the growing droplet (e.g. Pruppacher and Klett, 1980). However, the role of the organic fraction of the aerosol, a substantial component of tropospheric aerosol mass, is more difficult to assess (e.g.

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Novakov and Penner, 1993; Corrigan and Novakov, 1999; Dinar et al., 2006). This arises primarily from varying water solubility of the organic fraction. Other factors to consider include the rate at which organics go into solution (Shantz et al., 2003), the effect that surface-active organics have on the mass accommodation coefficient of water (Chuang, 2003) or on the surface tension of the droplet (Shulman et al., 1996; Facchini et al., 1999), and the organic fraction's density and ability to dissociate.

Many of these factors have been systematically explored through laboratory studies of pure organic and mixed organic–inorganic aerosols. These experiments have confirmed that the solubility of the organic is of crucial importance (Cruz and Pandis, 1997; Hori et al., 2003; Bilde and Svenningsson, 2004). Interestingly, a number of less soluble species are also good CCN, which is thought to be because they exist in either supersaturated or supercooled meta-stable states so that all the organic material is available for activation (Raymond and Pandis, 2002; Bilde and Svenningsson, 2004; Broekhuizen et al., 2004a; Huff Hartz et al., 2006). This makes them appear to activate as though they are fully soluble even though their thermodynamic solubility is low. Also, the degree of internal mixing of a soluble species plays a crucial role. If only a few percent of a soluble species are added to a largely insoluble particle, the particle becomes more CCN active (Raymond and Pandis, 2003; Shantz et al., 2003; Bilde and Svenningsson, 2004; Broekhuizen et al., 2004a). Lastly, oxidation of the organics also increases its CCN activity (Broekhuizen et al., 2004b).

While laboratory studies can identify the specific mechanisms by which organics affect activation, field studies can evaluate the relative importance of each mechanism and assess the overall ability of organics to promote CCN activity. Such studies are referred to as aerosol–CCN closure experiments, where measured ambient CCN concentrations are compared to predicted values in order to test our understanding of droplet activation. Ambient concentrations are measured with a CCN counter and predicted concentrations are calculated from aerosol chemical composition and size distribution information that are measured in parallel. A successful closure study is one in which these two quantities are comparable within the experimental uncertainties and demonstrates the suitability of the droplet activation model. A series of successful studies conducted under varied aerosol types and loadings but using the same Köhler model assesses the model's robustness and appropriateness for inclusion in a climate model.

For assessing the role of organics in droplet activation, the best closure studies are those that span a wide range of aerosol compositions so that the same Köhler model can be used to determine the degree of closure when the aerosol mass is dominated by soluble inorganics as well as when it is dominated by organics. From past studies, closure is not always obtained within experimental uncertainties and there is no consensus on how to treat the organics within the Köhler model. Also, the degree of closure needs to be carefully assessed since there are many assumptions and uncertainties involved in the calculations and measurements. A more complete survey of closure studies is given in Broekhuizen et al. (2006), Medina et al. (2007) and Stroud et al. (2007). What follows below is a brief summary, with a focus on the organic fraction.

In remote regions where the organic fraction may be low, it can sometimes be excluded from the calculations altogether (Liu et al., 1996). Similarly, closure has been reported in one study if particles at cloud level are assumed to be completely composed of ammonium sulphate with no organic component (VanReken et al., 2003).

At sites with a moderate organic content, some information about the size-resolved chemical composition is needed. Both in the Indian Ocean (Cantrell et al., 2001) and in the lower Amazon basin (Roberts et al., 2002), closure was achieved by incorporating an insoluble organic fraction, derived from multistage cascade impactors, into a Köhler model.

The organic fraction can change rapidly in polluted or semi-urban environments such that chemical compositions highly resolved in time and aerosol size are necessary to account for CCN activity. This is now possible with recent advances in the aerosol mass spectrometer (AMS) manufactured by Aerodyne. By assuming an insoluble organic component at urban and semi-urban sites, closure can be achieved using aerosol populations with multiple modes (Broekhuizen et al., 2006; Medina et al., 2007; Stroud et al., 2007).

In understanding how experimental results from the laboratory can be applied to ambient measurements, only a few closure studies have managed to account for organics (Cantrell et al., 2001;