



Observation of the suppression of water uptake by marine particles

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ARTICLE INFO

Article history:

Accepted 20 March 2010

Keywords:

VH-TDMA
Hygroscopic growth
Organic films
Marine aerosols

ABSTRACT

A 4 week intensive measurement campaign was conducted in March–April 2007 at Agnes Water, a remote coastal site on the east coast of Australia. A Volatility-Hygroscopicity-Tandem Differential Mobility Analyser (VH-TDMA) was used to investigate changes in the hygroscopic properties of ambient particles as volatile components were progressively evaporated. Nine out of 18 VH-TDMA volatility scans detected internally mixed multi-component particles in the nucleation and Aitken modes in clean marine air. Evaporation of a volatile, organic-like component in the VH-TDMA caused significant increases in particle hygroscopicity. In 3 scans the increase in hygroscopicity was so large it was explained by an increase in the absolute volume of water uptake by the particle residuals, and not merely an increase in their relative hygroscopicity. This indicates the presence of organic components that were suppressing the hygroscopic growth of mixed particles on the timescale of humidification in the VH-TDMA (6.5 secs). This observation was supported by ZSR calculations for one scan, which showed that the measured growth factors of mixed particles were up to 18% below those predicted assuming independent water uptake of the individual particle components. The observed suppression of water uptake could be due to a reduced rate of hygroscopic growth caused by the presence of organic films or organic-inorganic interactions in solution droplets that had a negative effect on hygroscopicity.

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1. Introduction

Organic compounds can comprise a significant and sometimes dominant fraction of the atmospheric aerosol in all types of natural and polluted environments, including pristine marine environments (Blanchard, 1964; O'Dowd et al., 2004). Marine Organic Aerosol (OA) has both primary and secondary production mechanisms. The primary mechanism occurs when organic material concentrated at the ocean surface is collected by rising bubbles which subsequently burst to generate sea spray aerosol enriched with organic matter (Facchini et al., 2008; Keene et al., 2007; Modini et al., 2010). The secondary formation of marine OA results from

the chemical processing of biogenic volatile organic compounds (BVOCs) into condensable organic vapours that subsequently enter the aerosol phase, probably through condensation rather than nucleation (O'Dowd and de Leeuw, 2007). Secondary marine OA formation is likely to occur frequently over coastal waters, where marine biota is often enriched. For example, marine OA has been indirectly observed in freshly nucleated particles (5–25 nm) at coastal sites on the west coast of Ireland (Vaattovaara et al., 2006) and on the east coast of Australia (Johnson et al., 2005; Modini et al., 2009).

The climatic impact of marine OA may be very large due to the fact it is being emitted or formed in the pristine marine boundary layer (MBL) where particle concentrations are relatively low (200–500 cm⁻³) and the potential for the OA to effect marine cloud formation is, therefore, high. In order to assess the climatic impact of a marine OA source it is necessary to know how organic compounds affect the water uptake properties of atmospheric aerosol. Implicit in this

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understanding is knowledge of the mixing state of organic and inorganic components in the marine aerosol. In addition to affecting cloud condensation nuclei (CCN) concentrations, OA effects on hygroscopicity will also influence marine aerosol size, phase (Marcolli et al., 2004), radiative forcing (Randles et al., 2004), chemical reactivity and lifetime. This article will focus on sub-saturated hygroscopic measurements of OA (i.e. relative humidity (RH) < 100%).

Experimentally, the hygroscopic properties of a range of organic aerosols have been studied extensively over the last decade or so in the laboratory and the field. A thorough review of these studies is provided in section 7 of Kanakidou et al. (2005) and in Swietlicki et al. (2008). Depending on water solubility, organic compounds may or may not cause a significant reduction in the deliquescence relative humidity (DRH) of mixed organic-inorganic particles compared to purely inorganic particles. At higher RHs the hygroscopic growth factors of mixed (soluble or insoluble) organic-inorganic particles are lower than what would be expected for the inorganic components alone because measurements have so far indicated that organic aerosols are less hygroscopic than inorganic aerosols above deliquescence.

In general, this behaviour is adequately captured in state-of-the-art thermodynamic models that predict the hygroscopic properties of mixed organic-inorganic particles. This is despite the difficulty these models face in representing the physicochemical properties and non-ideality of the vast range of organic compounds potentially existing in atmospheric aerosol. To get around this issue, for example, some models rely on functional group contribution models for predicting the activity coefficients of organic compounds (e.g. UNIFAC: Fredenslund et al., 1975). There is also the issue of organic-inorganic interactions in aerosol solution droplets. Some models have explicitly treated organic-inorganic interactions that influence the water activity of the total solution droplet (Clegg et al., 2001; Erdakos et al., 2006; Ming and Russell, 2002; Zuend et al., 2008). However the development of these models is restricted by a lack of experimental data on relevant interaction parameters. This problem is avoided in models that assume a simple additive approach for the water activities of organic and inorganic components in solution (e.g. the ADDEM model: Topping et al., 2005). The assumption that inorganic and organic components in solution act independently of each other (i.e. no interactions) is known as the ZSR approximation (Chen et al., 1973; Stokes and Robinson, 1966).

Aside from its use in detailed thermodynamic models like ADDEM, the ZSR principle has been used to predict the hygroscopic growth of mixed particles from hygroscopic data for pure compounds (e.g. Brooks et al., 2004; Gysel et al., 2007; Meyer et al., 2009; Prenni et al., 2003). Comparisons between such ZSR-based predictions and measurements have indicated that the ZSR principle is frequently valid and therefore useful as a first order approximation. However, there are a few notable discrepancies. A number of laboratory based studies have found both positive and negative differences between measured and ZSR-predicted growth factors for mixed particles (Chan and Chan, 2003; Cruz and Pandis, 2000; Svenningsson et al., 2006; Zardini et al., 2008). These differences can be as large as 20% (Cruz and Pandis, 2000). Failure of the ZSR assumption indicates that interac-

tions between organic and inorganic components have had an effect on the water activity of a solution droplet. For example the water solubility of some organic compounds can decrease/increase with increasing salt concentration in solution (salting out/salting in effects). Another intriguing interaction possibility is the formation of organic micelles capable of forming complex aggregates with inorganic cations, which effectively takes them out of solution (Tabazadeh, 2005).

In addition to affecting the equilibrium size of a mixed particle at a given RH (which may or may not be predictable with the ZSR principle), organic components can also affect the time that particle requires to grow (or shrink) to this equilibrium size. These are so called kinetic or mass-transfer effects (Chan and Chan, 2005). Organic components that delay the hygroscopic growth of particles have been investigated in the laboratory (Chan and Chan, 2007; Sjogren et al., 2007) and observed in a small fraction (0–2%) of particles in a polluted, urban environment (Chuang, 2003). In the supersaturated regime, two recent field studies have observed delayed cloud droplet activation of mixed particles relative to ammonium sulphate particles (Ruehl et al., 2008; Shantz et al., 2010). Kinetic effects can potentially arise if an organic component is present as a film (Gill et al., 1983) or solid enclosure (Sjogren et al., 2007) that reduces the rate of water vapour transfer between the environment and soluble portion of a particle. These effects are important because they can affect the ability of particles to act as cloud condensation nuclei (CCN) due to the finite time available for particles to activate into cloud droplets in a rising air mass. This in turn can affect cloud microphysical properties (Chuang et al., 1997; Feingold and Chuang, 2002).

A promising method for investigating the hygroscopic properties of mixed organic-inorganic particles in the field and the laboratory is the Volatility Hygroscopicity- Tandem Differential Mobility Analyser (VH-TDMA) (Johnson et al., 2004). This technique is able to probe changes in the hygroscopic properties of particles as volatile organic components are progressively evaporated (Fletcher et al., 2007; Johnson et al., 2005; Meyer et al., 2009; Meyer and Ristovski, 2007; Ristovski et al., 2010; Sellegri et al., 2008; Villani et al., 2009). For example in the ambient study of Johnson et al. (2005), increases in the hygroscopic growth factors (HGF) at 84–92% RH of marine particles in the nucleation, Aitken and accumulation modes were observed after the removal of volatile organic species. Furthermore, the authors calculated that the changes in HGF were explained by an increase in the absolute amount of water uptake by the residuals, and not merely an increase in their hygroscopicity. This result indicates that there was a real suppression of water uptake by the marine OA component on the timescale of humidification in the VH-TDMA system employed in that study (5–10 s). This observation of water uptake suppression may have occurred due to negative organic-inorganic interactions in solution (e.g. 'salting out' effect) or kinetic effects (e.g. organic film formation).

In this paper we report new observations of water uptake suppression by marine particles. These observations were made with a VH-TDMA during a measurement campaign conducted at the remote coastal location of Agnes Water on the east coast of Australia.

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