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Hygroscopic and Volatile Properties of Ultrafine Particles in the Eucalypt Forests: Comparison with Chamber Experiments and the Role of Sulphates in New Particle Formation.

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Abstract. Simultaneous measurements of the volatile and hygroscopic properties of ultrafine particles were conducted in a Eucalypt forest in Tumbarumba, South-East Australia, in November 2006. These measurements were part of an intensive field campaign EUCAP 2006 (Eucalypt Forest Aerosols and Precursors). The particles exhibited a 2 step volatilisation with the first component starting to evaporate at temperatures above 50°C. With the onset of evaporation of the first component the hygroscopic growth factor increased. This indicated that the particle was composed of a less volatile, but more hygroscopic core, which was coated with a more volatile, but less hygroscopic, coating. The fraction of the more hygroscopic component was proportional to the measured maximum SO₂ concentration indicating the role of gaseous H₂SO₄ in new particle formation. As the volatilisation temperature of the second more hygroscopic component was above that for H₂SO₄ it is likely that this component is partially or fully neutralised H₂SO₄. Comparison with α -pinene smog chamber experiments shows an excellent agreement with the first step volatilisation indicating its origin in the photooxidation of a monoterpene precursor.

Key Words: VH-TDMA, volatilisation, hygroscopic growth, α -pinene, eucalypt forest

INTRODUCTION

A number of recent studies have shown that formation of new particles is a frequent phenomenon in the atmosphere (see for example a review by Kulmala et al. 2004[1]). In order to understand the mechanisms underlying these new particle formation events it is of utmost importance to determine the chemical composition of the particles. However to estimate the composition of particles below 20 nm remains a complex task. Very frequently indirect methods such as the measurement of particle hygroscopic properties and/or volatility are used to infer the composition of even the smallest particles below 20 nm.

Recently a new technique, the VH-TDMA has been developed that simultaneously measures the particle volatile and hygroscopic properties². Although the VH-TDMA system measures physical properties such as the volatilisation temperature and hygroscopic growth, chemical properties can be inferred from the measurements, as well as information about the mixing state of the aerosol

The task of identifying the mechanisms responsible for aerosol formation and quantifying their contribution to aerosol production is accomplished by comparing the physicochemical behaviours observed in field measurements with that of reference aerosols generated in the laboratory.

EXPERIMENTAL SETUP

Measurements were conducted at the Tumbarumba flux station that is located in a tall open Eucalypt forest in south eastern New South Wales in November 2006 (5-12.11.06). The dominant species are *E. delegatensis* (Alpine Ash) and *E. dalrympleana* (Mountain Gum), and the average tree height is 40 m. The instruments were located in a shed on the ground with inlet at 2 m height. The size distribution was measured with an Air Ion Spectrometer (AIS; Airel LTD, Estonia) (0.34 to 40 nm) and with an SMPS (TSI 3936) (5 to 160 nm). During the 1 week period a number of new particle formation events were observed.

The volatile and hygroscopic properties were measured using the VH-TDMA². Once the nucleation events was observed and the newly formed particles reached a relatively stable size of 20-30nm, this mode was selected and analysed by the VH-TDMA. The thermodenuder temperature was scanned from room temperature until the particles completely volatilised. The maximum thermodenuder temperature necessary for complete volatilisation ranged from 150 to 180°C. The change in the hygroscopic growth factor was measured simultaneously with the increasing temperature. The relative humidity during temperature scans was kept constant at $RH = 90 \pm 0.2\%$.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 presents the VH-TDMA spectra of the 3 nucleation events observed on the 8th, 9th, 10th of November. The analysed particle size was around 25nm in all three cases. The particle volatilisation is presented through the volume fraction remaining $V/V_0 = D_v/D_{v0}$, where D_v is the particle diameter at temperature T, and D_{v0} particle diameter at room temperature (left y-axis). The change in the hygroscopic properties after volatilisation is

presented through the dependence of the growth factor $G_h = D_h/D_v$, on the thermodenuder temperature (T_d), where D_h is the particle diameter after volatilisation and subsequent humidification (right y-axis). Open and closed symbols correspond to V/V_0 and G_h respectively.

The first step volatilisation starts at around 50°C and finishes at around 80°C. 30-50% of the volume is lost in this first step volatilisation. During this first step volatilisation the hygroscopic growth factors remains constant. With the removal of the first volatile species, above 80°C, the hygroscopic growth factors start to increase. This indicates that the particles are coated with a more volatile but less hygroscopic compound that suppresses the particle growth. Similar observations were made with the VH-TDMA in the marine environment³. The second less volatile but more hygroscopic component volatilises at temperatures above 100°C. For the measurements on the 8th and the 9th the particle size drops down to below 10nm at temperatures of around 150°C. This still does not indicate that the second less volatile component had fully evaporated as 10nm was the lowest particle size detectable by the CPC's used (3010). It is likely that the first more volatile component is of organic origin and a product of photo oxidation of monoterpenes which are relatively abundant in this environment. The second compound is most likely in the form of sulphate.

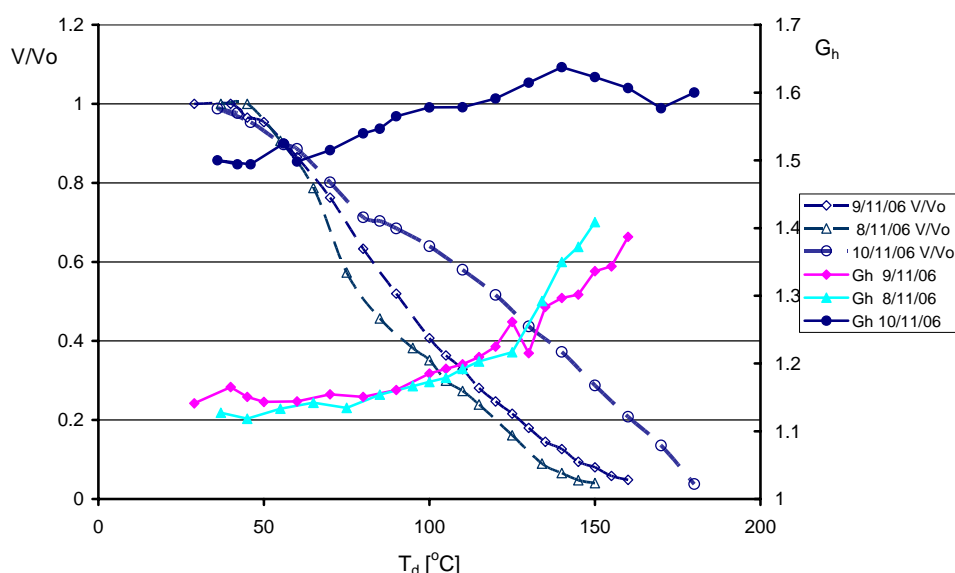


Figure 1. VH-TDMA spectra of the 3 nucleation events observed on the 8th, 9th, and 10th of November. Initial particle size was 25nm and the RH was kept constant at 90%. Empty symbols and dashed lines represent volume fraction remaining (V/V_0), and full symbols and full lines hygroscopic growth factors (G_h).

There is a distinct difference in both volatilisation and hygroscopic growth for the nucleation event observed on the 10th of November. During this event the observed hygroscopic growth factor was significantly higher at room temperature than on the other dates. The presence of the more hygroscopic but less volatile species was much more pronounced on this day.

The reason for this could be in the role that the sulphuric acid plays in the new particle formation events. It has been recently documented⁴ that the measured G_h , in boreal forests, correlate positively with the gaseous sulphuric acid concentration. The maximum measured SO_2 concentration on the 8th and 9th of November did not exceed 200 pptv while on the 10th of November the maximum concentration was around 800 pptv. If we take the SO_2 levels as

a proxy for the presence of gaseous sulphuric acid than one can assume that the concentration of sulphuric acid on the 10th was much higher than on the other two days. This is in clear agreement with the observed increase in the G_h and furthermore supports the idea that the less volatile but more hygroscopic compound observed in the core of the particles is ammonia neutralized sulphuric acid.

Figure 2 presents VH-TDMA spectra of a nucleation event observed on the 9th of November and from chamber measurements conducted at the smog chamber at LAC, PSI in August 2006. In the smog chamber experiments particles were generated via the photooxidation of α -pinene at a concentration of 5ppm, in a 27-m³ Teflon chamber at 20°C [5]. The relative humidity for the hygroscopic growth measurements in both field and chamber experiments was kept constant at 90±0.2%. There is an excellent agreement for both the volatility curves and the hygroscopic growth data up to around 80°C which corresponds to the first step volatilisation. At temperatures above 80°C the hygroscopic growth factors start to deviate as the particles measured in the field start to lose the more hydrophilic organic coating. In chamber experiments care has been taken not to introduce any gaseous sulphuric acid and therefore the particles do not have a hygroscopic sulphate core which would cause an increase in the G_h at higher thermodenuder temperatures. In addition the chamber measurements do not exhibit a two step volatilisation. This clearly indicates that the more volatile but less hygroscopic particle coating observed in the field measurements is of organic origin and the product of photooxidation of either α -pinene or some similar monoterpene.

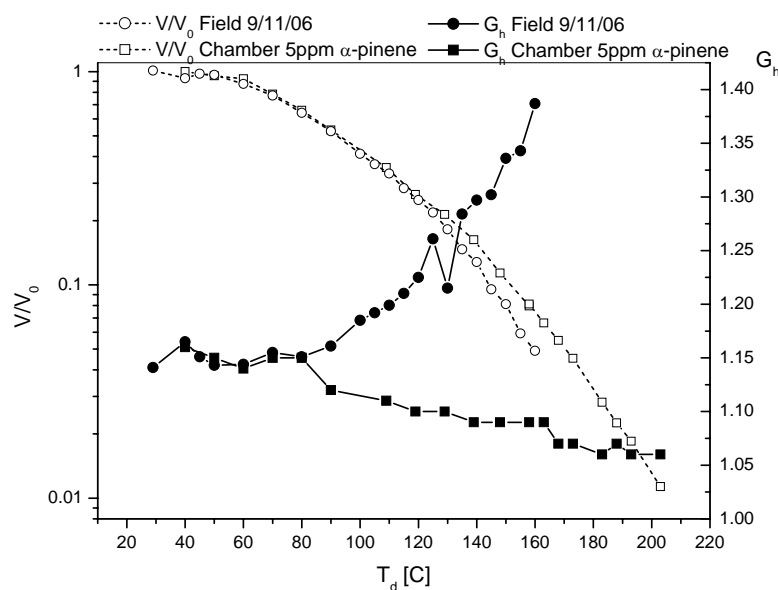


Figure 2. VH-TDMA spectra of the nucleation event observed on the 9th November (circles) and smog chamber measurements with 5ppm α -pinene (squares). The volume fraction remaining is presented with open symbols on the left axis, while the hygroscopic growth factors with full symbols on the right axis. In both measurements the relative humidity in the VH_TDMA was kept constant at RH~90%.

Acknowledgments

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