PARTICLE FORMATION PROCESSES IN EUCALYPT FORESTS – THE ROLE OF SULPHATES AND ORGANICS

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No particles no fog!!!

Introduction

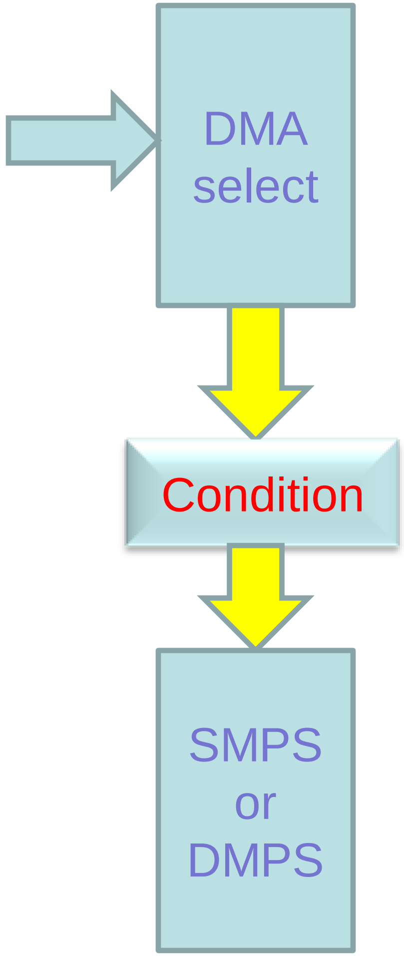
- A number of recent studies have shown that formation of new particles from biogenic sources is a frequent phenomenon in the atmosphere.
- In order to understand the mechanisms underlying these new particle formation events it is of utmost importance to estimate the chemical composition of the particles.
- One of the open questions is still the exact composition and formation mechanism of freshly formed 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.

Introduction

- The two major components of the freshly formed particles are:
  - sulphates and
  - organics
- Although sulphuric acid has been identified as one of the key components in aerosol formation and growth (Riipinen et al., 2007).
- Strong evidence that the growth rates and composition of > 50-nm particles are tied to the photo-oxidation of monoterpenes (Laaksonen et al., 2008; Tunved et al., 2006).

Riipinen et al., Atmos. Chem. Phys., 7, 1899–1914, 2007
Tunved et al., *Science* **312**, 261 (2006);
Laaksonen et al, *ACP,* 7, 2657 (2008)

Indirect methods – Tandem DMA

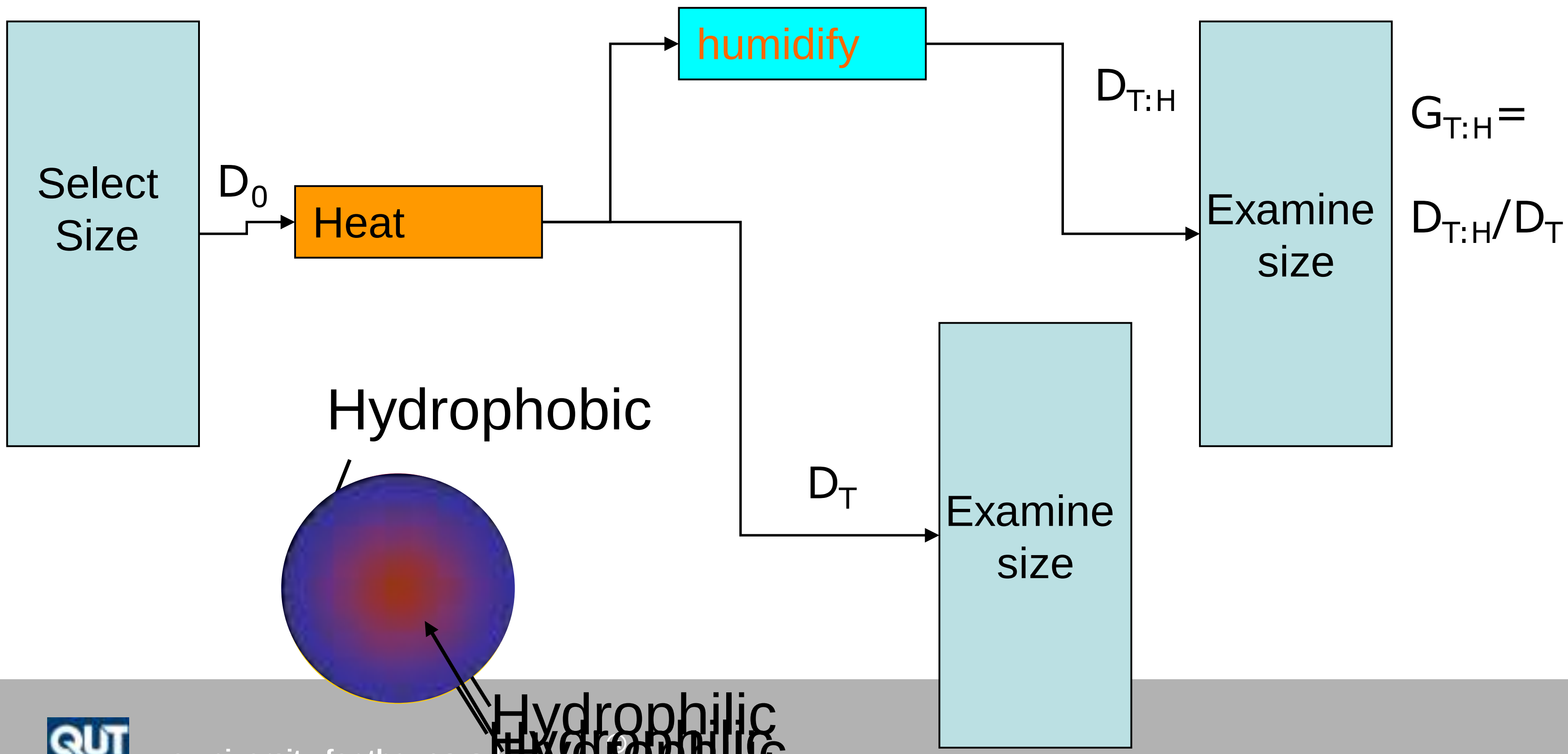


- Measurements of particle volatile properties
  - Volatile-TDMA
- Measurements of particle hygroscopic properties
  - Hygroscopic-TDMA
- Measurements of particle ability to absorb ethanol vapour ~ to organic content
  - Organic-TDMA

See review by Park et al. Aerosol Sci, Tech. 42(10), p. 801 (2008)

VH-TDMA

- Look in situ at particle hygroscopicity before during and after volatilisation.



G. R. Johnson, Z. Ristovski, et al, J. Aerosol Sci., 35 (4), 443-455 (2004)

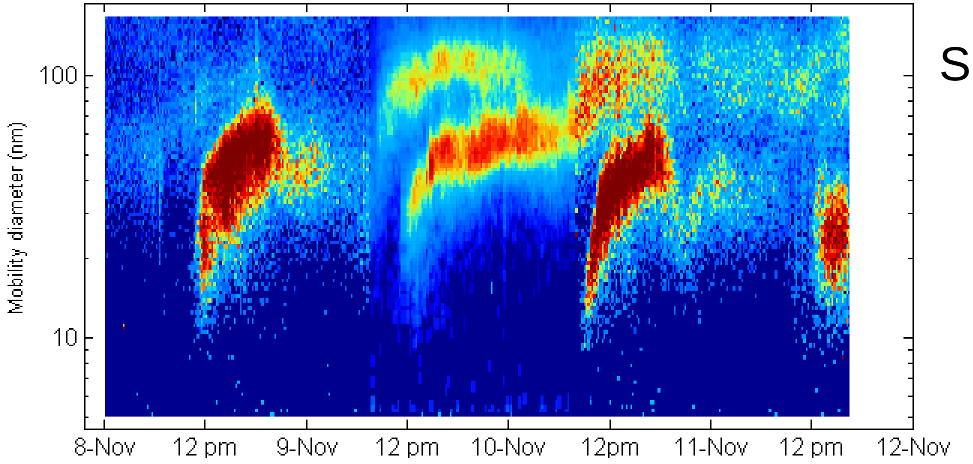
EUCAP

- Measurements were conducted as part of the Eucalypt Forest Aerosols and Precursors (EUCAP) campaign in November 2006.
- Tumbarumba flux station located in a tall open Eucalypt forest in south eastern New South Wales.
- The dominant species are *E. delegatensis* (Alpine Ash) and *E. dalrympleana* (Mountain Gum), and the average tree height is 40 m.
- Particle sizing instruments were located in a shed on the ground with inlet at 2 m height.

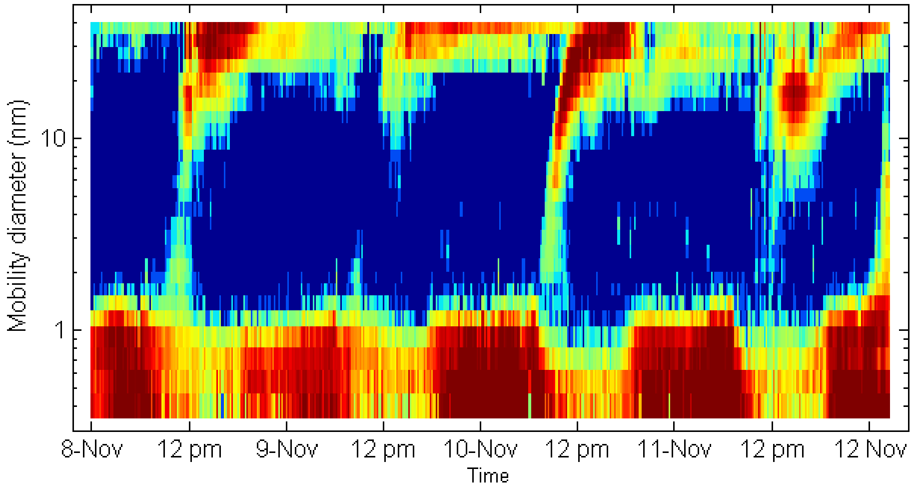
EUCAP

- Size distribution measurements
  - Air Ion Spectrometer (AIS; Airel LTD, Estonia) (0.34 to 40 nm)
  - SMPS (TSI 3936) (5 to 160 nm).
  - The volatile and hygroscopic properties were measured using the VH-TDMA
- Additional measurements of gas phase particle precursors were also conducted (PTR-MS, SO_2, tenax tubes, etc.)

Particle and Ion Size Distributions



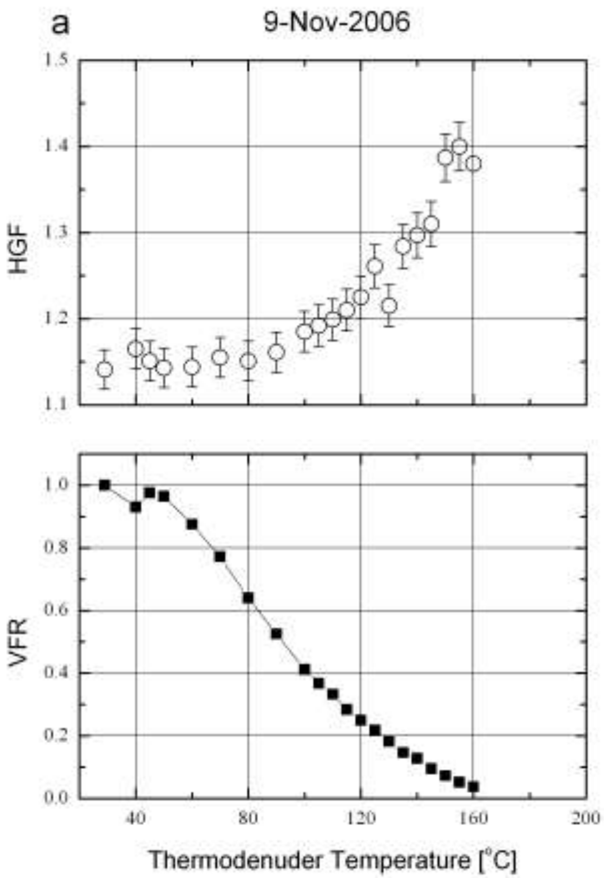
SMPS



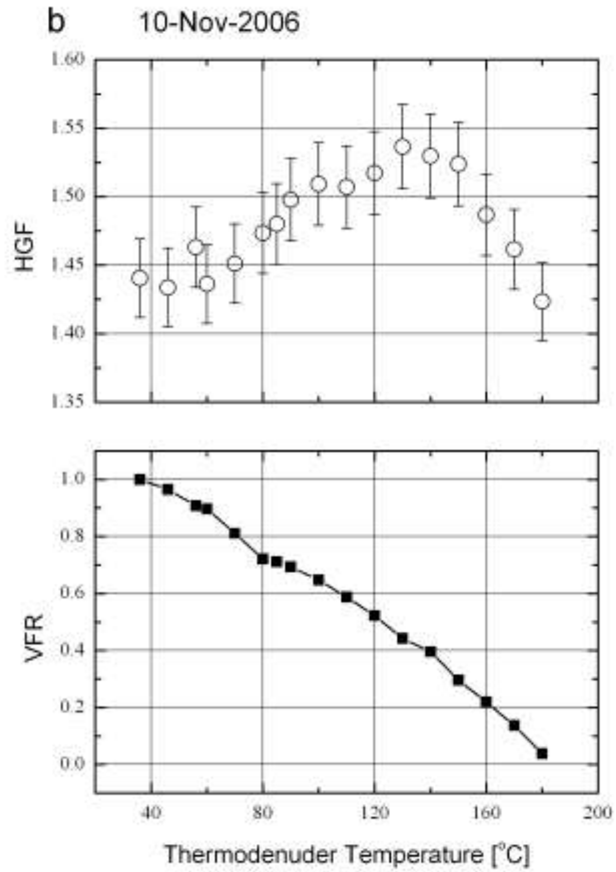
AIS

Day	Growth rate (7-20 nm (nmh^{-1})	Growth rate (ions) (7-20nm) [nm h^{-1}]	Form. rate J2 (ions) [cm^{-3}s^{-1}]
8.11.	9.93	9.06	0.26
9.11.	6.08	8.49	0.055
10.11	8.69	6.48	0.23
11.11 .	7.31	3.51	0.054

VH-TDMA measurements



H_2SO_4 7.3 $10^6 cm^{-3}$



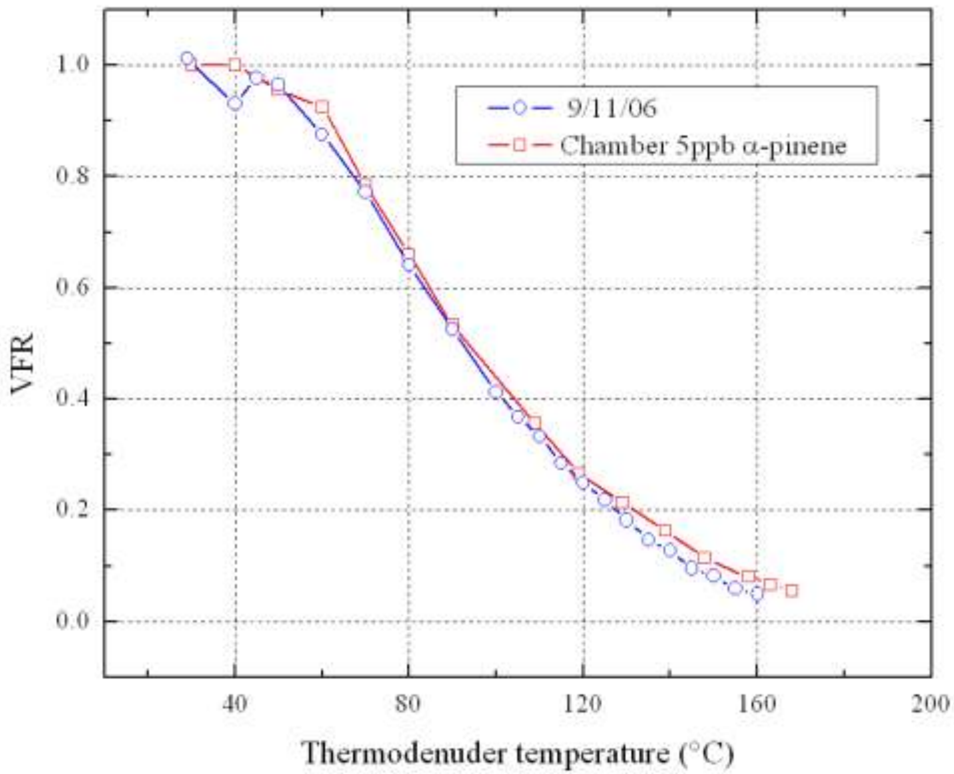
H_2SO_4 15.3 $10^6 cm^{-3}$

Chamber experiments

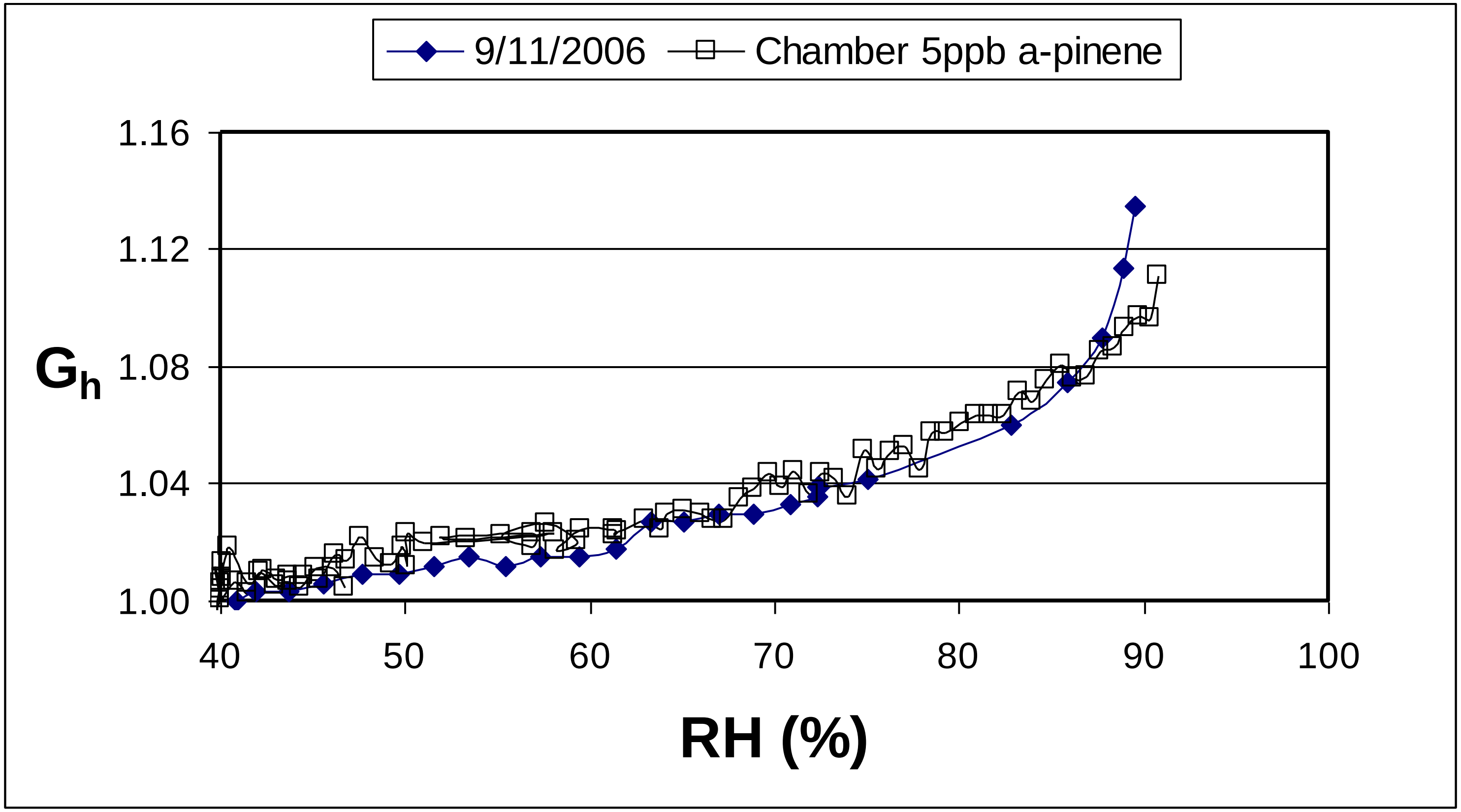
- Smog Chamber at the Laboratory of Atmospheric Chemistry, PSI, Villigen, August 2006.
- The SOA was generated via the photo-oxidation of a-pinene in a 27-m^3 Teflon chamber at 20°C and 50 % relative humidity.
- VH-TDMA measurements conducted at RH90% and temp range 20-200 C.

Meyer et al, ACP (2009)

Comparison with chamber experiments



Dependence of G_h on RH



Modelling HGF change during volatilisation

- Assuming that the two components are photo-oxidation products of organics (α-pinene) and ammonium sulphate (AS), we fitted the measured HGFs using the ZSR aprox. (Meyer et al 2009).

$$HGF_m = \left(\varepsilon \cdot HGF_{AS}^3 + (1-\varepsilon) \cdot HGF_{SOA}^3\right)^{1/3}$$

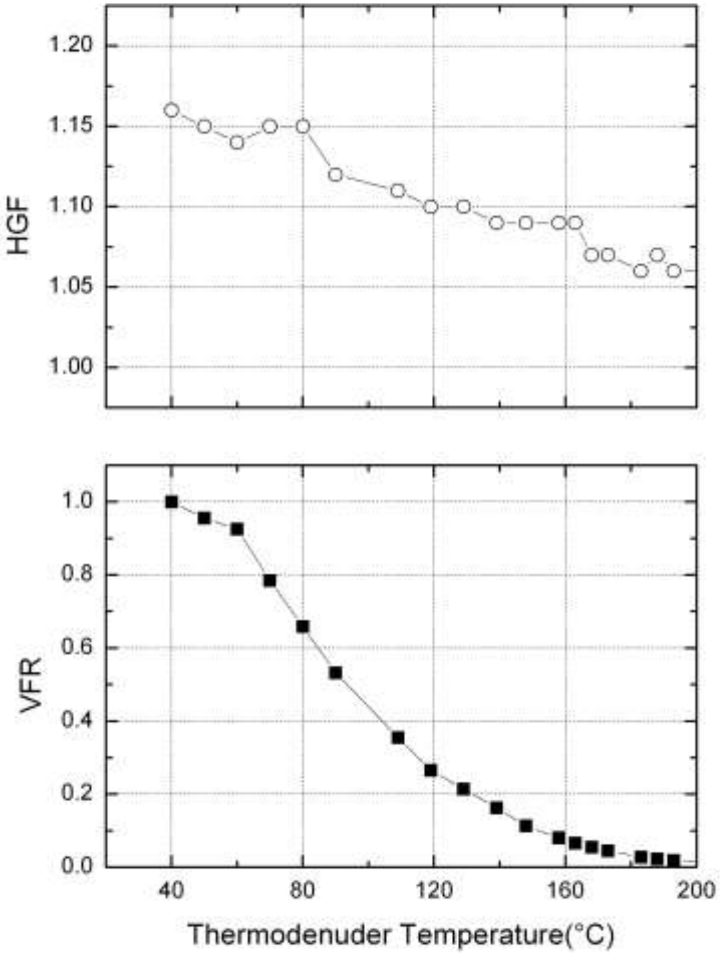
- Where ε is the volume fraction of AS.

$$\varepsilon = \frac{V_{AS}}{V} = \frac{V_{AS}}{V_0}\frac{V_0}{V} = \frac{\varepsilon_0}{VFR}$$

- ε_0 is the initial volume fraction of AS before volatilisation.

Meyer et al, ACP (2009)

HGF_{SOA} and VFR (Chamber results)



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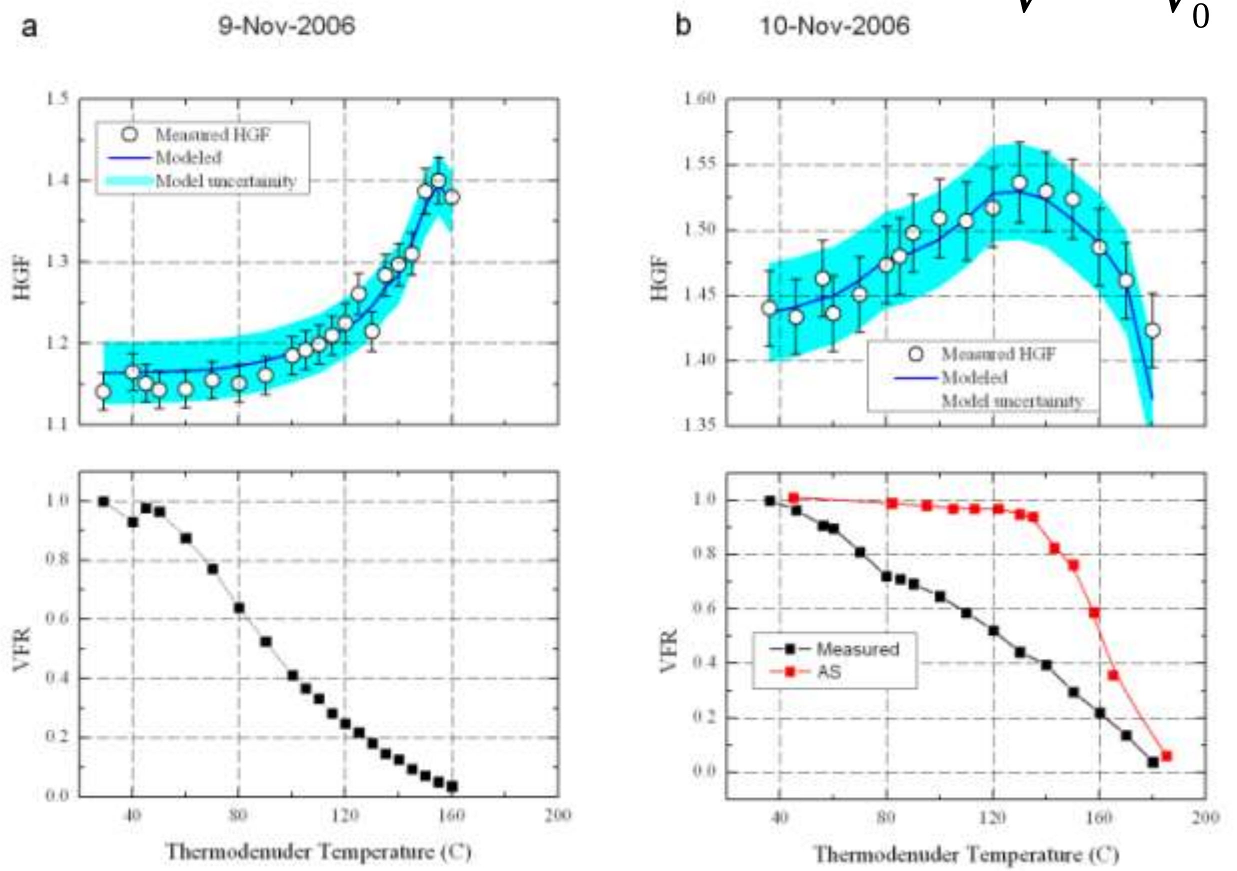
$$\varepsilon = \frac{V_{AS}}{V} = \frac{V_{AS}}{V_0}\frac{V_0}{V} = \frac{\varepsilon_0}{VFR}$$



Date	ε_0 [%]	H_2SO_4 max [10^6 cm^{-3}]
8/11/2006	3.5	9.25
9/11/2006	5.9	7.32
10/11/2006	49.2	15.3
11/11/2006	3.5	6.5

Fitted values of the initial volume fraction of ammonium sulphate for the 4 nucleation events analysed and the maximum calculated value of H_2SO_4 concentration during the nucleation events.

Conclusion

- Good agreement between chamber experiments and field - more volatile but less hygroscopic particle component observed in the field measurements is of organic origin and the product of photooxidation of either α-pinene or some similar monoterpene.
- Assuming 2nd component to be AS(ABIS) calculations show that sulphates in most cases are responsible for a reasonably small fraction (<6%) of the growth, with the organics being responsible for the remaining fraction.
- Only exception day with very high SO_2 concentrations where the sulphates were responsible for almost 50% of the growth.

Conclusion

- Our results confirm the existence of a two-step process suggested by Kulmala et al. (2000, 2007b) with nucleation and cluster formation and subsequent growth of these particles being carried out not only by one component but ***by simultaneous growth of sulphates and organics***.
- As the sulphates compromise only a small fraction of the total particle volume whether the particles will grow to climatically relevant sizes will depend on the available organic vapours, which in the forest environment, we have shown to be most likely the gas-phase ***oxidation products of monoterpenes***.
- Biogenic atmospheric particle formation is a global phenomenon and as such the observed role of sulphates together with organic vapours should be included in global climate models.

Acknowledgement

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