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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The role of sulphates and organic vapours in new particle formation in a eucalypt forest" *by* Z. D. Ristovski et al.

Anonymous Referee #2

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Summary The paper describes a study conducted in a subtropical eucalypt forest to investigate the properties of freshly produced particles. An air ion spectrometer and an SMPS are used to define when new particle formation events occur and when this leads to growth of new particles. This is used to target measurements of 20-50 nm particles by a volatility-hygroscopicity tandem differential mobility analyser. The VHTDMA is used to explore the relative roles of organic and sulphate on the growth of freshly formed particles to sizes that may be CCN active. The analysis is sound, and the findings are interesting and add to the new observations of the control of growth of new particles. However, the paper is rather short. It focuses on only four days and is very cursory in its summary of the project and the data set as a whole. This context would be very useful. I am also concerned that the authors make too many definitive conclusions when they do not substantiate their findings (see below). Finally, I do not think that the title represents the paper. It would be better if it said "The role of sulphates and organic vapours in growth of newly formed particles in a eucalypt forest" or similar. Overall then I think that this paper can make a good contribution to the field and is worthy of publication, however, I would very much like to see improvements in the above areas that are outlined in more detail below.

General Comments

The introduction discusses nucleation at Hyytiala in some detail. However, this paper does not deal with nucleation nor does it deal with a boreal forest. Rather the investigation is focussed on what controls the subsequent growth of new particles towards CCN sizes in a sub tropical eucalypt forest. I recommend that far less space is given to a discussion of all aspects of particle formation at Hyytiala and instead the introduction considers both previous studies of growth of new particles and links to composition both at Hyytiala and other locations. I am surprised that the authors do not review previous work on chemical influences of particle growth at these sizes as it does exist in the literature and some of the authors were involved in those studies. A further omission is a review of precursor concentrations, particle formation and SOA at eucalypt forest sites. Central suppositions in this work are that terpene concentrations dominate the VOC profile at this type of location, and terpenes are important sources of SOA. However none of this is introduced earlier in the paper and it is assumed that the reader takes this for granted in the discussion. Given that the discussion relies on previous knowledge it is important to present this in the introduction.

I feel that in a few places the conclusions of the paper are too strong. i) The abstract states that "Our findings confirm a two-step process through nucleation and cluster formation followed by simultaneous growth by condensation of sulphates and organics that take particles to climatically relevant sizes". I agree that the AIS see ions associated with nucleation and the SMPS clearly shows new particle growth. These findings are used to define periods of new particle growth so that targeted measurements of this mode are made by the VHTDMA. However, the VHTDMA measurements are made at sizes above 20 nm. The investigation therefore focuses on the role of sulphate and organic vapours on the growth of newly formed particles. The title does not reflect this and when coupled with the line from the abstract above implies that the paper can say something about the composition during formation – it cannot in my view do this. I suggest changing the title to make it clear that the focus of the paper is on the composition necessary for growth to CCN sizes and not the role of composition in new particle formation.

ii) The VHTDMA is a very powerful instrument but it cannot measure composition directly – rather it infers this from the volatility and hygroscopicity profiles. On this basis, the authors make a convincing case that the bulk of the sulphate in the observed particles is not sulphuric acid but either ammonium bisulphate or ammonium sulphate. This is an interesting and novel finding. However, given that the measurements are made on particles of 20 nm or larger the authors cannot conclude that this provides evidence for ammonium bisulphate being involved in nucleation as they suggest. A 20 nm particle that is composed of 5% sulphate contains 12.5 times as much sulphate as a 2 nm particle composed of 100% sulphate. It is not possible to probe what form the sulphate involved in nucleation takes compared to the large bulk of the particle measured at 20 nm.

iii) The papers states in the abstract that “the organic components being photochemical products of most likely monoterpenes”. This is a very strong and unsubstantiated statement. The results do show a large fraction of the particles are composed of material that has a range of relatively high volatilities and is only weakly hygroscopic – consistent with organic material. The correlation between the volume fraction of organic material as a function of denuder temperature as measured in the field is consistent with that measured when studying particle formation experiments from a-pinene oxidation in a chamber study. However, this is not conclusive proof as SOA from other precursors may show similar behaviour within the measured uncertainties. Has this been explored? Do SOA from other types of VOC precursor give very different volatility

and hygroscopicity profiles? If so then the authors do have a good tool for discriminating different types of organic precursor. If not then figures 4 and A1 are really only generically representative. However, if the latter is the case then it means their model approach is likely to be very successful across a wide range of environments. Probing this would be a very instructive thing to do, yet is brushed over and used to make a strong conclusion, when this may not be possible. Without this evidence the data are merely consistent with the picture that the high volatility component is consistent with organic aerosol from monoterpene oxidation. The authors must then discuss their results more fully together with other results from the literature to support their arguments.

Detailed comments

Only four days of data are analysed from the project. Does the model work on other days? The application of the model to other days would be very useful in understanding the general applicability of the model approach in this environment.

The VHTDMA shows a large fraction of the particles are composed of material that has a range of relatively high volatilities and is only weakly hygroscopic. However, that is not how the authors choose to convey the data. They describe a high volatility, low hygroscopic fraction. This nomenclature does not capture what they are really observing. I suggest the authors describe their observation and that it is consistent with a range of components with a range of volatilities all having low hygroscopicity suggesting an organic fraction.

P17794 Line 9: there is a word missing. P17794 Line 26, a comma is necessary after (Hyytiala) to make the sentence read properly. P17796 line 28-P17797 line 1: There is no evidence presented that demonstrates that the freshly nucleated particles consist of both sulphate and organics. The VHTDMA measures 20 nm particles and shows up to 95% of the material of the material is consistent with organic material. This does not mean that the composition of 2-5 nm particles is the same. The ratio of sulphate to organic may be very different during formation. Furthermore, whilst the presence of semi-volatile material can be measured by the HVTDMA and this can be used to show it is consistent with organic material. There is no convincing evidence presented in this paper to demonstrate that this material is derived from products of monoterpene oxidation, only that the measurements are consistent with other VHTDMA measurements of monoterpene products. More work needs to be done and presented before a sentence as strong as this can be used.

P17797 line 8: How long did the campaign last? Only 3-4 days of data are shown in the plots. I get no sense of the representativeness of the measurements in the paper.

P17798, line 17: what is the detection limit and uncertainty levels of the different gas analysers? These are used in the calculation of sulphuric acid formation so it is important to state them. It is often difficult to obtain a good zero for the SO2 instrument. As the levels are low and close to detection for this instrument, the way the calibration was performed needs to be discussed.

P17799 line 7: On how many days and what fraction of the total number of days were new particle formation events observed? I get no sense of the statistics in this environment and there is no other paper for reference.

P17799 line 12 Only 3 days are shown. Are the event days referred to special or typical, the reader cannot get any feel for this from what is presented.

P17799 line 24-P17800 line 1: (and elsewhere). The authors misleading state that the particles are made up of two components. This is very unlikely to be the case. Whilst it is true that a fraction of the particles are more volatile, the measurements in figure 3 show material with a wide range of volatilities is measured. This is indicative of a range of components with a range of properties. This needs to be reflected in the discussion as it is an important property of the organic fraction.

P17800 line 13-14: The data shows that the volatility of atmospheric particles is consistent with those produced by a-pinene oxidation in a chamber no more. There is no conclusive proof in this paper that a-pinene oxidation products are responsible for the high volatility, low hygroscopicity fraction nor is there any evidence to suggest that it is this material that is involved in the nucleation of particles. In fact the relatively high volatility suggests that this may be unlikely – yet this is not mentioned in the discussion.

.P17800 line 20: “During this event” change to “The event on the 10 November“ to clarify.

P17800 line 23-P17801 line 2: The measurements of SO2 were made with a Teco SO2 analyser which has a rather high detection limit, low accuracy and suffers from zero drift at the levels stated by the authors in the paper. The numbers stated here are very close to the lower detection limit here. It would be good to see the actual errors stated and the paper to lay out the full error propagation. I suspect that the overall error in the calculation uncertainty from the measurements will be more like 200% at 200 ppt.

P17801 lines 2 and 3. The concentrations are calculated and this should be stated explicitly.

P17801 lines 18-20: The measured data provides convincing evidence that the bulk of the sulphate in particles of 20 nm and greater size is not sulphuric acid but it provides no evidence at all of whether ammonium bisulphate takes part in neutral cluster formation. A simple calculation shows that if 5% of the 20 nm particles are composed of sulphate then the sulphate is over ten times that required to form a pure sulphate particle of 2 nm. The measurements cannot therefore shed any light on the chemical state of sulphate at nucleation sizes and this implication must be removed from the paper.

P17802 line 4: Other events are alluded to here but are not discussed at all in the paper. It would be good to show other cases and to test the model developed on these other cases to demonstrate its robustness.

P17802 line 15: “Our calculations show that in most cases sulphates are responsible for a reasonably small fraction of the growth”. Only 4 cases are presented and of these 3 show this to be true. The sample statistics are rather more to be making such a statement. Whilst I believe that it may be true many more cases are required to show this to be the case.

P179802 line 26027 “we have shown to be the gas-phase oxidation products of monoterpenes” Again, whilst monoterpene oxidation is a strong contender to be the supplier of condensable organic material, the data in the paper do not show this to be the case. One can make a good case that the continuous volatility profile of the VHTDMA is consistent with organic material being dominant in the particles, the only evidence that monoterpene oxidation is the precursor is provided by the associative similarity between the volatility of atmospheric particles and those from a-pinene photo-oxidation studies in a chamber (fig 4). However, if other organic precursors also produce particles with similar hygroscopic behaviour and volatility profile then this is not in any way conclusive and is not as convincing as is made out here. The reader is left with her/his own knowledge from the literature that monoterpene concentrations are high over eucalypt forest and monoterpenes are efficient at producing SOA. The paper does not lay any of these arguments out and it needs to support the case. The definitive statements in the paper are really too strong to be justified given the data and arguments presented.

P17803 line 25: You cannot say that there are no solute-solute interactions but that no solute-solute interactions were observed within the uncertainties when studying this system.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 17793, 2009.