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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.

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All reviewers' comments are in italics and our responses below each comment.

First we would like to thank the reviewer for insightful comments:

Reviewer 2.

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.

The following parts were added in the introduction section addressing the suggestions of the reviewer:

"Although there is relatively strong evidence that the growth rates and composition of larger than 50-nm particles are tied to the photo-oxidation of monoterpenes (Laaksonen et al., 2008; Tunved et al., 2006), evidence for the presence of these organic vapours in freshly nucleated smaller particles is scarce. This is mainly due to the lack of online analytical methods capable of assessing the composition of particles smaller than 30 nm in diameter. Until now, the main evidence has come from indirect methods that have measured the growth rates of newly formed particles when exposed to organic vapours (butanol (O'Dowd et al., 2002) and ethanol (Laaksonen et al., 2008)). Laaksonen et al. (2008) show evidence of a correlation between the gas-phase monoterpene oxidation product concentration and the growth rate of 10-nm particles in ethanol vapour. This correlation only exists during nucleation events. A similar approach has been used in the recently developed condensation particle counter battery (Kulmala et al., 2007a) where the composition of particles as small as 3 nm can be inferred through their activation properties in different vapours, namely butanol and water. Applying this technique at a rural background site (Hyytiala), the authors show that the freshly formed particles at 3 and 11nm contain water-soluble material. They further show (Riipinen et al., 2009) that at the smallest sizes (2–4 nm) the particles ac-

tivate for growth at clearly smaller sizes in water than in butanol vapour, however less than would be expected from ammonium sulphate or sulphuric acid. This indicates a presence of other less hygroscopic components in freshly nucleated particles.

A more direct evidence of the presence of organics and sulfates in freshly nucleated aerosols comes from measurements conducted using a Thermal Desorption Chemical Ionisation Mass Spectrometer (TDCIMS) (Smith et al 2004). This method has been applied mainly in urban environments and has shown that the composition of nucleation mode aerosols (10-30nm) can significantly vary from mostly composed of mainly ammonium sulphates (Smith et al 2005) to an aerosol dominated by 85

Other direct methods such as the Aerosol Mass Spectrometry (AMS) are capable of measuring the aerosol composition with a lower limit of 30nm (Zhang et al 2004). In urban environments Zhang et al (2004) have shown that the composition of growing particles was predominately sulphuric acid in the early stages with ammonia and organics appearing at a later stage of growth. In the rural background environment of Hyyutiala Allan et al (2006) found that during the non-polluted cases the grown aerosol, several hours after an event, were principally organic in composition with a mass spectral fingerprint independent of the particle diameter."

We have added a discussion on the previously measured VOC emissions from Eucalypt forest in section 3.1.1 instead of in the introduction. The second paragraph of section 3.1.1 has been modified:

"However, the question remains, what are these two components? Organic... These two curves show an excellent agreement which indicates that the more volatile but less hygroscopic particle component observed in the field measurements is of organic origin and the product of photo-oxidation of either α-pinene or some similar monoterpene. Terpenese are actually abundant in the emissions from eucalypts. Although a small number of studies have been conducted, compared to northern hemisphere tree species, relatively high isoprene and monoterpene emission rates for some species of

eucalypts were measured (Winters 2009, He 2000a, He2000b)."

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.

We agree with the reviewer and have changed the title to: "The role of sulphates and organic vapours in growth of newly formed particles in a eucalypt forest".

We have further changed the last 2 sentences from the abstract (see response bellow this one).

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.

We are addressing this comment later in the response to P17796 line 28-P17797 line 1.

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.

First we would like to point out that not only the volatility of the SOA has been used as an argument that the organic is "most likely a photooxidaiton product of a monoterpene" but also the values of the hygroscopic growth factors of the organic that were used for

the fitting of the HGF data were from the chamber measurements of α-pinene. Further the HGF was not taken to be constant but its change with thermodenuder temperature (again obtained from the chamber measurements) was used for the fitting of the HGF data. This by our opinion is reasonably convincing evidence.

The comment on the volatilities being different from different precursors has been addressed before (see response to the first reviewer on page C6). Nevertheless we have made changes in the abstract to reflect the above to comments. The last 2 sentences in the abstract have been changed to:

"It is shown that the particles are composed of both sulphates and organics, with the amount of sulphate component strongly depending on the available gas-phase sulphuric acid, and the organic components having the same volatility and hygroscopicity as photo-oxidation products of a monoterpene such as a-pinene. Our findings agree with a two-step process through nucleation and cluster formation followed by simultaneous growth by condensation of sulphates and organics that take the particles to climatically relevant sizes."

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 VH-TDMA was a part of the intensive campaign that has gone for only 7 days. Out of the 7 days the model has been applied onto all of the nucleation events that were observed (4 out of 7). Unfortunately we do not have data for other days.

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.

The 1st reviewer has made a similar comment. We agree with both reviewer and have made changes to the document (see response to the 1st reviewer on page C4) in the 2nd paragraph of the VH-TDMA measurement section.

"The observed broad decrease in the VFR as the first component evaporates is typical of a mixture of a number of compounds with differing volatilities (Riipinen et al. 2010). Therefore the first component actually consists of a number of organic compounds. . ."

P17794 Line 9: there is a word missing.

Word added. "We present here. . ."

P17794 Line 26, a comma is necessary after (Hyytiala) to make the sentence read properly.

Added.

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. . . .

The misunderstanding comes from what is considered as a "freshly nucleated particle". To avoid that the term "freshly nucleated particle" in the above sentence has been changed to "nucleation mode particles" as it encompasses also the large (20nm) particles that we have measured.

The sentence is changed to:

"Applying the above technique we show experimental evidence that, in a forest environment, the nucleation mode particles . . ."

. . .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.

We have addressed this comment before. We strongly believe that we have shown evidence (volatility, hygroscopicity, etc.) that the second component is very similar to the photoxodiation product of a monoterpene and disagree that we have not shown strong evidence.

To incorporate both comments the sentence on p17796 has been changed to:

"Applying the above technique we show experimental evidence that, in a forest environment, the nucleation mode particles most likely consist of both sulphates and an organic component with the same hygroscopic and volatile properties as a photo-oxidation products of a monoterpene, such as α-pinene."

Similar changes have been made in the second last sentence in the abstract.

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.

The campaign had been going for several weeks. The intensive part with the VH-TDMA present had been for one week.

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.

The limit of detection for a 5 min. averaging time for the gas analyzers used were as

follows: SO2: 60 pptv. These were determined from calibrations prior to and following the EUCAP campaign under similar experimental conditions (Temperature, flow rate, pressure). These values agree with the factory-stated limits of detection for each analyzer. We have added a sentence giving these detection limits in the text. The zero on the SO2 instrument was obtained by sampling zero grade air under conditions similar to field experiments. In experiments prior just prior to EUCAP with the same instrument (and under similar environmental conditions), we found that this analyzer had a slow zero drift of -13 pptv/day with a daily variability of $\pm$30 pptv (most likely due to temperature changes).

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.

During the intensive part of the campaign the nucleation events were observed on 4 out of 7 days. A sentence and a reference has been added in this paragraph:

"During the campaign, we observed new particle formation events almost on a daily basis. Just during the intensive part of the campaign nucleation events were observed on 4 out of 7 days. More details on the frequencies and types of nucleation events observed at this site were presented previously by Suni et al. (2008)..."

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.

The 4 days presented on figures 1 and 2 are part of the intensive campaign when the nucleation events were observed. As mentioned in the text these are typical events.

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.

A similar issue was raised by the previous reviewer and addressed. See the response on page C4 for the 1st reviewer. As mentioned before we have clarified that the first component is a mixture of a number of compounds of differing volatilities.

2nd paragraph of the VH-TDMA measurement section: "The observed broad decrease in the VFR as the first component evaporates is typical of a mixture of a number of compounds with differing volatilities (Riipinen et al. 2010). Therefore the first component actually consists of a number of organic compounds..."

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.

We have addressed this comment previously. To stress again the reviewer ignores the fact that not only volatility but also the HGF matches with the ones observed in the chamber measurements.

Further we do not claim that this material is involved in the nucleation we only said that the volatility of particles observed during the nucleation event agree with the chamber experiments. To avoid the confusion that α-pinene is involved in the nucleation the sentence has been changed to:

"As further evidence that the first component could be a product of photo-oxidation of a monoterpene such as α-pinene, Fig. 4 presents the volatilization of particles from the nucleation mode observed on 9 November..."

We do not understand the comment why would relatively high volatility suggests that

this may be unlikely, when the volatility was the same as the chamber one.

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

The sentence has been changed to:

"During the event on the 10November, the observed. . ."

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.

As mentioned already above under point P17798, line 17 we were unable to perform calibrations in the field during EUCAP, the analyzers were only calibrated before and after the experiment. These were in very good agreement. We can only provide an estimate of the zero drift effect during EUCAP based on a field campaign which ended 2 months prior to EUCAP using the same SO2 analyzer. In that study, the SO2 analyzer was automatically calibrated every 4 hours for nearly 2 months. We would also note that environmental conditions (such as diurnal temperature variations within the field trailer) were similar to those encountered at EUCAP. These results showed that the analyzer had a slow zero drift of -13 pptv/day with a daily variability of ±30 pptv (most likely due to temperature changes). Therefore, over the 3 day period described in this paper (Nov. 8-10), we conservatively estimate the error due to a drifting zero to be ±80 pptv (or ±40% for a 200 pptv measurement). Uncertainty within the gain coefficient of the instrument and accuracy of our SO2 standard is estimated to contribute an additional 10-15%. The reviewer is correct that there is considerable absolute uncertainty in the SO2 measurements not too much above the detection limits which could be

propagated into the model calculations. The modelled H2SO4 includes significant uncertainty from both unmeasured species as well as those we measured (most notably SO2); but the precision of the SO2 measurements also at the 200 pptv level (uncertainty ±55%) was easily able to tell us that its concentration more than tripled between the 2 days in question, which led to a significant increase in H2SO4 (factor of 2).

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

The sentence has been changed to:

"The calculated concentration of sulphuric acid on. . ."

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.

The last sentence in the pragaraph starting with: "This observation further points out to ammonium bisulphate as one of the candidates for neutral cluster formation. . ." was removed.

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.

A similar comment has been raised by the first reviewer (his/her first comment) and addressed previously. In short, the model has been tested on all 4 events and the results from the fitting procedure (the fraction of sulphates) are presented in Table 2 for

all 3 days. Sentence has been changed.

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.

We agree that the sample is small and have limited our conclusion on the events observed in our campaign. The sentence has been changed to:

"Our calculations further show that sulphates in most of the observed cases are responsible for a reasonably small fraction. . ."

P17802 line 26 and 27 "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.

Although we have addressed this comment previously in several places we agree to change the statement so it does not sound so strong. The sentence has been changed

to:

"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 eucalypt forest environment, we have shown to be most likely the gas-phase oxidation products of monoterpenes."

As mentioned previously the references on the presence of monoterpenes in the eucalypt forest have been added.

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