

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 reviewers for insightful comments:

Reviewer 1.

Certainly, the experimental approach of using a VH-TDMA, which measures volatility and hygroscopicity simultaneously is unique enough and a good way to indirectly study aerosol composition. However, it is unclear what the unique or novel atmospheric science result is. By the authors own admission, the results here only “add” to already existing evidence that terpenes cause condensational growth. What new/unique evidence or scientific result can come from this study in particular? It would seem that the

C10858

data from this study exists to dig somewhat deeper into the limiting factors for growth, and yet only two cases are analyzed in detail. If nucleation events happen almost every day then are these two cases representative of every day? Do particles grow via the same mechanism every time? The paper is almost too concise. The results and discussion section is at most 1.5 pages long, and it would be nice if some of the remaining data could be incorporated, and conclusions drawn from the entire data set as a wholep.

First we would like to point out to the reviewer that not only 2 cases were analysed in detail but all of the nucleation events that were observed during the intensive 1 week measurement period of the campaign and shown on Figures 1 and 2. The data from the analysis of other nucleation events, such as growth rates and initial volume of sulphates, is presented in Tables 1 and 2. We have chosen to present and discuss the VH-TDMA spectra from only 2 days in Figure 3 as they are most illustrative of the differences in the VH-TDMA spectra for days with different SO₂ concentrations. VH-TDMA spectra for the other days are similar to the spectra observed on the 8.11. as the concentration of SO₂ was similar and adding them will just increase the length of the paper without adding any new information. To more strongly point out to the reader that other events have been analysed the sentence on p.17802, l.4 has been changed from:

“Analyses of other events. . . “ to

“Other nucleation events observed during the intensive part of the campaign (8 and 10 November) with similar concentrations of SO₂ as on 9 November were also analysed and led to similar values of ϵ (see Table 2).”

As all of the nucleation events that we have observed during the 1 week campaign were analysed and they all show correlation between the H₂SO₄ concentration as well as good correlation with smog chamber measurements we do believe that the data is typical for the environment where we have conducted the measurements. As

C10859

similar precursors are available elsewhere our results can be generalised to other environments. We have observed a very similar situation where an increase in the HGF of freshly nucleated particles upon heating by the thermodenuder was also observed (Modini et al., Atmos. Chem. Phys., 9, 7607-7621, 2009). In that case we concluded that the condensation of sulphate and/or organic vapours was most likely responsible for driving particle growth at sizes greater than 10 nm during the nucleation events. Unfortunately we did not have any measurements of SO₂ at that campaign and could not show a link between the more hygroscopic component (sulphates) and sulphuric acid concentration. What is of importance is that these observations were made in a coastal marine environment confirming that our findings could be generalized for other environments.

To highlight this we have added a sentence in the last paragraph in the conclusion section as well as one more reference.

“...coastal and remote marine environments. In coastal environments Modini et al. (2009) have observed a similar situation with sulphates and organics both driving particle growth at sizes greater than 10 nm during the nucleation events. Further, photo-oxidation products of other secondary organic aerosol precursors, such as isoprene produced by phytoplankton, have been proposed as major...”

I would agree that sulphuric acid alone cannot account for the growth rate of nucleated particles. I also would agree that condensation of organics is likely to account for the remaining rate. However, it is not clear in this paper why the condensation of organics from terpene oxidation should be any different in the <20nm particles compared to the larger ones (>50 nm). If it is purely a condensational process that occurs, then why should the nature of the organics in the small particles be different than the big ones? In that case, one could make the argument that studying the bigger particles which are easier to deal with, should be sufficient since the same species condense in either case. In fact, the first component described in this paper seems to illustrate just this. It is possible that from the perspective of the very small particles, the nature

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of the organic composition is related to (1) the Kelvin effect and (2) potential reactive chemistry in the small particles, perhaps due to the high acidity. If certain organics have a low enough vapour pressure to overcome the Kelvin effect they will condense, which could perhaps exclude some species which may only condense on the larger particles where the Kelvin effect is negligible. Of course chemistry which may occur only on the small particles could also result in differences in composition from the larger particles. It is likely that the Kelvin effect becomes very important below about 20 nm. However this study only looks at particles greater than 20 nm. None of these scenarios are discussed in the paper (perhaps in the introduction). Simply stating why one expects there to be a difference in the first place would be a good start.

We first thank the reviewer for this insightful comment and observation. To address this we have added a discussion 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. The composition of the organics that are condensing on the particles should first of all depend on the ability of the specific compound to overcome the Kelvin effect. Compounds with smaller vapour pressure will more readily condense on smaller particles while other compounds will condense on the particles only once they reach a certain size. Modeling studies (Anttila and Kerminen 2003) showed that for organic components the Kelvin effect becomes dominant for particles with diameters smaller than 10 nm. The particles that we have analysed, both in the field and in the chamber studies, are significantly larger therefore the Kelvin effect should not have a significant influence on which compounds from the photooxidation of terpenes condense on the particles. An almost constant growth rate in the range larger than 10nm and the good agreement with the chamber studies points out that the condensation of organics for particles larger than 10nm should be the same. One could then be tempted to analyse

C10861

larger particles (>50nm), which are easier to manage, in order to obtain the composition of smaller ones. This approach should be taken with caution. If the particles need a significant amount of time to grow to the analysed sizes (beyond the growth purely due to condensation) other processes such as polymerisation and oxidation can change the particle composition (Kalberer et al. 2004, Jimenez et al. 2009)."

Specific comments:

Pg 17799, line 24: The use of the term "component" is somewhat misleading. It implies that there are only two species, when we know that the organics are composed of very many species. That is why you see the slow decrease in the VFR rather than a step change. The authors should try and use some other terminology. Did the authors try doing this experiment with larger particles as well during the same time? It would be interesting to see if the VFR and GF were any different. If such experiments were done then they should be included and compared in this paper.

We agree with the reviewer that there are not only two "species" of organics involved but actually many organic species or compounds exist in the particle phase. This has been highlighted in the text (see the above comment). Unfortunately it is not possible with our setup of the VH-TDMA to simultaneously measure different sizes. We can only measure the whole VH-TDMA spectra at one size by ramping the temperature from room temperature upwards. As such we do not have experiments conducted at different sizes for the same nucleation event.

Pg 17800, line 15-16: Although the two curves are in excellent agreement, how different are these curves from any other curve generated from any number of species, including anthropogenic ones? How sensitive is the VFR to the type of organic aerosol? This is not really definitive proof of where the organics originated, and the authors should be careful not to extrapolate too far.

The second reviewer has also had a similar comment. The volatilization curves are significantly different depending on the source of the aerosols. See for example our

C10862

recent publications:

For Diesel exhaust:

1. Meyer, N. K. and Z. D. Ristovski (2007). "Ternary nucleation as a mechanism for the production of diesel nanoparticles: Experimental analysis of the volatile and hygroscopic properties of diesel exhaust using the volatilization and humidification tandem differential mobility analyzer." *Environ Sci Technol* 41(21): 7309-7314.
2. Surawski, N. C., B. Miljevic, et al. (2009). "Particle emissions, volatility and toxicity from an ethanol fumigated compression ignition engine." *Environmental Science Technology* 44(1): 229-235.

Marine Aerosols:

1. Fletcher, C. A., G. R. Johnson, et al. (2007). "Hygroscopic and volatile properties of marine aerosol observed at Cape Grim during the P2P campaign." *Environ Chem* 4(3): 162-171.
2. Modini, R. L., Z. D. Ristovski, et al. (2009). "New particle formation and growth at a remote, sub-tropical coastal location." *Atmos Chem Phys* 9(19): 7607-7621.

It is important to stress that due to the short residence time in our thermodenuder (0.3 s) particles did not reach equilibrium. As such our volatilization curves cannot be compared with other thermodenuders. There is a good discussion on the residence time and its influence on the VFR (or MFR) in Riipinen et al 2010 (cited in the paper). With a short residence time a number of compound parameters will influence the evaporation rate and therefore produce a different volatilization curve. If equilibrium is achieved in the thermodenuder the differences between different compounds becomes less obvious. For example Greishop et al 2009 (EST, v.43, p.4750) observe for large thermodenuder residence times (16s), where they assume that they have almost reached the equilibrium, similar volatilisation curves for diesel and oil (Graph 3b). For shorter residence times volatilisation curves from different aerosols can be clearly

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distinguished (Figure 3c).

Pg 17801, line 4-6: This paragraph is not clear. If there was more SO₂ which resulted in higher sulphuric acid vapour, does this mean more initial particles or the same number of nucleated particles which are bigger? Assuming that the available organic vapors were about the same in both cases, then why would the GF's be different at room temperature? Unless the amount of sulphate per given nucleated particle was larger. Is that the case? The other scenario is that sulphuric acid was causing most of the growth to bigger sizes. This should be made clearer and perhaps analyzed in more detail in the paper.

A larger concentration of SO₂ will lead to a larger concentration of sulphuric acid. The SO₂ concentrations were shown in the same paragraph as the sulphuric acid concentrations. The sentence states:

"This increased concentration of sulphuric acid had led to a larger amount of sulphates present within the particles. . .". The term "amount within the particles" refers to what the reviewer calls "amount of sulphate per given nucleated particle". A larger amount of sulphate per nucleated particle leads ". . . consequently, to the higher observed HGF"

This has all been analysed later in the paper when we present the results for the initial volume fraction of sulphates within the particle (Table 2), and clearly show that it is proportional to the concentration of sulphuric acid. We would like to keep our terminology ("within the particles ") as compared to the suggested ("per given nucleated particle") and think that this sentence should stay as is.

Figure A1: Is this figure not the same as part of figure 4?

Yes it is and the only reason is that it could be compared with the HGF curve presented above.

Technical Corrections:

Pg 17794, line 9 (abstract): "We" should be replaced with "it is shown that..." Or
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something of that form.

The sentence has been changed to:

"It is shown. . ."

Pg 17794, line 20: "This way. . ." Is awkwardly written. Perhaps use "In this way" or "therefore" etc. . .

The sentence was changed to: "In this way. . ."

Pg 17799, line 11: Remove the word "have" from the sentence.

The word "Have" has been removed.

Title: Technically the authors are not studying "new particle formation", but more like the "growth of newly formed particles..." Although I am not against keeping the old title.

As the second reviewer has raised the same question in regards to the title we agree that the following new title would be more suitable:

"The role of sulphates and organic vapours in growth of newly formed particles in a eucalypt forest"

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