

## ***Interactive comment on “New particle formation in the front range of the Colorado Rocky Mountains” by M. Boy et al.***

**M. Boy et al.**

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Dear Referees,

thanks for your constructive comments and your help to improve the value of this manuscript. Below I will give short statements to the different points from both of you.

Statements to comments from Referee Nr. 1:

1.) Is the condensation sink (CS) calculated using wet or dry particle diameter?

From dry particle diameter

If CS is calculated from dry diameter then how much of the observed dependence of formation events on RH might be due to swelling of particles?

As we know the growth of particles by water molecules depend mainly on the com-

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position. Without any HDTMA measurements it is difficult to say anything about the influence of RH on the CS values. However, the observations show clear new particle formation events on the selected days and a decrease of RH in the morning. The growth rates could in this way be influenced by the uptake of more water molecules through more hydrophilic composition of new formed particles but this is difficult to prove without any measurements. We will mention in the new version of the ms that the CS-values are calculated based on dry particle diameter but speculations about the dependence of formation on RH would be only hypothetical and for this reason we will not be included in this paper.

2.) Fig. 7. Are the values of sesquiterpenes shown here interpolated from the two-hour mean observations? The figure should be replotted to make the time resolution of the observations apparent.

The data plotted are 10 minutes mean values and the figure will be plotted in a way to make the start time and the time step visible.

3.) Fig. 8. Is it possible to give uncertainty ranges on the linear fit? The slope of 1.94 appears (within the likely uncertainty range) to suggest a square dependence on sulfuric acid concentrations. Is this slope significantly different from the value of 1.24 calculated by Sihto et al. (2006).

I'm very happy that the referee mentioned this point because I had to check the figure again and realized that the slope was out of an unknown reason incorrect. The new value is 1.66 and a new figure is included. I also included one sentence to mention that the higher slope at the MRS compared to Hyytiälä would involve higher contribution of sulphuric acid in the nucleation mechanism.

4. ) P15593. I think the following statement "Most of the data fit between two lines with slope 1 or 2" is possibly misleading. The presentation of the purple and red lines in Fig. 8 does suggest this is the case. But does the vertical position of the 2 lines not depend on the value chosen for the intercept of the straight line? I would have thought

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that the gradient of the linear fit suggests a square rather than linear dependence.

As pointed out above the value is now changed to 1.66 which would suggest that between 1 or 2 sulphuric acid molecules are involved in the nucleation process. In this case the start point of the fitting lines does not have any influence on the amount of sulphuric acid molecules in the nucleation only the slope.

5.) P15591, L19-20. Clarify whether you mean no other correlations with other parameters were explored or no other correlations were found. I think it is premature to claim a "clear relation" between the ratio of growth rates and sesquiterpenes from Fig. 7. How does this relationship compare with monoterpene concentrations or sulfuric acid? What about other days when both parameters are available?

All other parameters were checked concerning their relation with the ratio of the growth rates and the text will be changed to "no other correlations were found";. Although we will delete the word "clear"; concerning the observed relationship and already mentioned in the text that this results suggests that sesquiterpenes could be responsible and not that they are responsible. I believe that this interpretation of the figure is acceptable.

6.) P15595. The "activation by organic molecules" is an interesting and useful section of the paper. However, it is not clear what the "simplified" organic mechanism involves. Without a detailed description of the simplifying assumptions it is difficult to interpret the results. How do the assumptions made affect the calculated  $J_2$  rate? What measurements of organic compounds would be required to use the full mechanism of Bonn et al., (2007)? What concentrations of aldehydes have been assumed? Given the likely uncertainties in your assumptions I do not think the statement that "strong improvements" in prediction of nucleation rate is valid. This section could be improved by a more complete description of the mechanism, the necessary assumptions and the likely uncertainties.

We will include in the new version a more detailed description of the organic nucleation

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code. However, how do the assumptions affect the calculated  $J_2$  values is difficult to say without having the possibility to calculate these values. In our version of the organic nucleation code we did not use any aldehydes because only acetaldehyde was measured. With respect to the full mechanism of Bonn et al. (2007) the following measurements are needed: (i) sesquiterpene concentration and possibly height profile, (ii) ozone and water vapour concentration, (iii) temperature and condensation sink, (iv) sulphuric acid as well as (v) measurements of the carbonyl concentrations (aldehydes and ketones). Some of these requirements are easy to fulfill like (ii) and (iii) but some create difficulties like (i) and (iv). Especially the sesquiterpene height profile is critical because of its reactivity and the lacking knowledge about the emission structure within the vegetation layer. Carbonyl concentrations depend on the onset of chemical reactions of emitted VOCs. Formaldehyde will be the predominant aldehyde with smaller contributions of acetaldehyde. But acetone and larger biogenic aldehydes will provide increasing contributions with increasing time for oxidation of for instance terpenes.

Statements to comments from Referee Nr. 2:

1.) Very little has been said about the performance of the instruments measuring trace gases and  $\text{H}_2\text{SO}_4$  during the campaign. What about the accuracy and detection limits of trace gas measurements, did that have any influence on the results? Why no  $\text{H}_2\text{SO}_4$  data were available for type A event days?

We will include in the new version one more paragraph in section 2.5 to give more details about the instruments and detection limits concerning the trace gases. There were no  $\text{H}_2\text{SO}_4$  data available on the A event days because the instrument (CIMS) had some problem.

2.) The authors could mention briefly whether and how their classification criteria for the events are related to the criteria used by other researchers in analyzing nucleation events (page 15587). In literature, quite different classification criteria have been used.

Correct and we will include this in the final version. The classification of the events was

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done in the same way as described in detail in the paper by Boy et al. (ACP 2, 1-16, 2002) and we also included one extra category for undefined days.

3.) Unlike stated in the text (page 15591, lines 24-25), there a few recent papers in which formation of larger organic molecules by oligomeration reactions have been observed in field measurements as well (e.g. Kalberer et al. 2006 EST 40, 5917-5922; Surratt et al. 2007 EST 41, 517-527; Iinuma et al. 2007 EST 41, 6678-6683).

We will mention these papers in the new version.

3.) The description of the third mechanism "nucleation by activation of organic molecules" (page 15595) is incomplete in the sense that no information is given about the functional dependence of the  $J$  on concentrations of organic compounds. Without this information, it is very difficult to get a proper idea on how this mechanisms works and how the curves related to this mechanism in Figure 10 have been created. From Figure 9 alone, such information cannot be deduced in a simple way.

As already mentioned under referee Nr. 1 point 6 we will improve this part of the ms by including a more detailed description of the organic nucleation code.

4.) One conclusion based on Figure 10 is that none of the three nucleation/activation mechanisms can be excluded in explained observed particle formation. Especially, also activation by organic vapors seems possible. Could this latter result be simply due to the combination of facts that 1) the analysis is based on measured particles number concentration in the 6-10 nm size range, not in the 3-6 nm size range, and 2) the contribution of organics to the growth nanometer-size particles is very high anyway?

If we believe that the published relationship of measured and calculated  $J$  values by Kerminen and Kulmala is correct then there is no reason to assume that the calculated  $J$  values based on particles in the size range 6-10 nm is not valid. I agree with the referee that the growth of clusters from a size around 1 nm by organic molecules has an direct influence on the calculated nucleation rates, but still the estimated amount of

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new formed particles (in our case at 2 nm) by assuming our assumptions are correct is fact. This paper and the calculated nucleation rates by different mechanisms only shows the possibility that different ways are possible and more research in this area is necessary to complete the picture and.

5.) The term "mass balance" in section 3.3.2 is slightly misleading, normally mass balance is used to when comparing the gravimetric mass of particles to the sum of measured/estimated chemical constituents. Furthermore, the lower plot of Figure 11 compares two different things: 1) the absolute mass concentration change which may be negative when particle sinks exceed their sources, and 2) contribution of sulfuric acid to condensational enhancement of particulate mass which is always positive.

I agree with the referee that the title of this sub-section should be changed (new title: Particle Mass), however I see no reason why the two different values in the lower plot of Figure 11 should be not plotted in one figure. This figures shows clear at what time sulfuric acid contributes to the particles growth concerning the mass of the particles. Although the two parameters are different as the referee mentioned the combination of both in one figure is scientific interesting &#8211; at least up to my own opinion.

Minor technical comments: 6.) I doubt that the term "trend" is correct here when analyzing the daily patterns of various variables and new particle formation (page 1558, lines 9-10)

Correct and we will change it to apparent difference.

7.) The statement, "mean growth rates of particles ... 3.96 nm/h for all 4 days", is unclear. Was the average the same for all the 4 days, or was the overall average during these three days equal to 3.96 nm/hour? (page 1559, lines 20-22).

This was the overall average and will be pointed out in the final ms.

8.) There some resemblance between the sesquiterpene concentration and the ratio of particle growth rates with/without TD (Figure 7) but the relation is definitely not clear

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as stated by the author (page 15591, lines 15-19).

Already discussed under referee nr 1 point 5.

9.) I recommend that the authors use the term "formation rate" rather than "nucleation rate" when discussing the increase in the number concentration of different-size particles. Nucleation refers to a specific process, whereas "formation" or "apparent formation" can be used for particles of all sizes.

By checking the ms again we have to agree with the referee that in certain sentences the words formation rate would be more accurate than the words nucleation rates and we will change this in the final version.

10.) Table 1 would be more readable if the days were ordered according to the strength of events (e.g A, B, undefined, non-event), not in the chronological order.

That's easy to do and an open point but I'm by myself not sure if this is really the best way. I believe it is very subjective to the reader and I know that many readers prefer a chronological order. If referee Nr. 1 would be the same opinion I will change it concerning to the suggestion of referee Nr. 2.

I will again thank both referees for their contribution and send the new version asap to the editor.

Best regards Michael

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 15581, 2007.

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