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# Interactive comment on "SO<sub>2</sub> oxidation products other than $H_2SO_4$ as a trigger of new particle formation – Part 2: Comparison of ambient and laboratory measurements, and atmospheric implications" by et al.

### Anonymous Referee #2

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This manuscript gives an interesting account of how recent laboratory measurements on nucleation of SO2 oxidation products compare with atmospheric measurements made in the Finnish boreal forest. The laboratory measurements, as detailed in the accompanying manuscript (Part 1, Berndt et al, ACPD 8), provide evidence that SO2 oxidation products other than H2SO4 may be more efficient in producing particles than H2SO4 itself. This is concluded based on the lower (calculated) concentration of "H2SO4" needed to form particles when it is produced by gas phase oxidation of SO2 as compared to H2SO4 evaporated from a liquid reservoir. Corroborating evidence is





that the presence of NO inhibits particle formation via the gas-phase oxidation route, but not via the liquid reservoir route. In Part 2 it is shown that the relation between SO2 oxidation products ("H2SO4") and nucleation is similar for these laboratory measurements and for atmospheric measurements in the Boreal forest, and that the relation is very different for "real" H2SO4.

Major point:

While it is valuable to have these measurements put in the context of other laboratory and atmospheric measurements, I fail to see why this should be done in a separate paper. The full interpretation of the laboratory results, their atmospheric relevance and the providing of context is in my opinion best at its place together with the paper describing the results. The two papers right now read as if one good paper is split in two. Neither paper is very long, and a combined version will still be of very reasonable length, especially when taking into account that many redundancies can be removed. The current manuscript (Part 2) reads as if it is an integral part of the paper where the actual results are presented (Part 1); it appears incomplete by itself. It does not seem to be geared towards a different readership either. Indeed, the conclusions (4) and chemistry (3.1) sections are based to a large degree on the laboratory results and their interpretation as described in Part 1, with the addition of a comparison with atmospheric measurements. That is the kind of comparison that is very well suited to be part of the same paper, rather than a separate paper.

I suggest making one manuscript which combines the current two parts.

Other points:

Regarding the temperature dependence of the nucleation rates: P 9677 line 17-18 (Laboratory ... temperatures). This seems a strange statement since in Part I there is no mention of a temperature dependence. P 9678 line 10-18 and Fig 1. The range of measured temperatures in the lab is relatively narrow compared to the range over which the values are extrapolated. This makes the extrapolation quite uncertain. For

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example, if the point at 296 K (or at 289 K) would not have been measured, the resulting fit would be substantially different (i.e. more than one order of magnitude lower (or higher) at 273 K than the current fit). This uncertainty should be addressed. Moreover, notwithstanding the plausible reasoning behind the assumption of an exponential relationship (p 9678, line 16-18), Vehkamaki et al (2002, including some of the same authors as this manuscript) report that the relationship between J and T is less than exponential according to theory. This apparent contradiction needs explaining. Eyeballing the graph in Fig 1, a relation such as shown in Fig 11 of Vehkamaki et al, would fit the data better than an exponential relation as currently used (though, again, this depends mainly on the one datapoint at 296 K, so it is not at all a robust conclusion). It could bring the resulting extrapolated nucleation rates down by another order of magnitude or even more.

In any case, these extrapolations show that the nucleation rate is larger at low temperature. So for a given H2SO4 concentration, a lower temperature causes the nucleation rate to be larger. However, in Fig 2 the curves seem to have undergone another extrapolation: namely from high H2SO4 to lower H2SO4. This makes sense, since that way they can be better compared to the atmospheric measurements, but this extra extrapolation should be acknowledged (as well as the extra uncertainty it adds).

The assumed wall loss rate constant for H2SO4 in the flow tube (0.017 s-1) seems very high. A lower wall loss rate would cause the calculated H2SO4 concentrations to be larger; how sensitive are the resulting H2SO4 concentrations to the wall loss rate? The uncertainty in H2SO4 likely points in the same direction as the uncertainty in the extrapolation mentioned above: it would tend to move the extrapolated curve of Berndt et al (2005) in Fig 2 more to the right.

The atmospheric data were measured at temperatures between 263 and 281 K. In light of the strong dependence of the nucleation rate on temperature and the extrapolation of the lab data to 273 K, this relatively wide temperature range could substantially influence the interpretation. If the atmospheric data were also scaled to 273 K (or

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alternatively, leave all data (including lab) at their measured temperature, but include a colorscale to show the associated temperature), how would this change Fig 2? Would the slope in the atmospheric data become larger or smaller (or unchanged)? This could have a large influence on the agreement between lab and atmospheric data.

The slopes of the lab data are said to be "somewhat steeper" than the ambient data (p 9679, line 9). That seems an understatement to me, and the large difference in slopes needs to be explained/discussed. A potential reason is perhaps the temperature dependence of the ambient data, but that needs investigating. Differences and similarities with Friend et al (1980), who found a slope that is in better agreement with the ambient data presented here, could be discussed. Likewise, differences and similarities between the lab conditions (no organics) and the ambient conditions (many organics) should be discussed in more detail. How representative (and comparable to the lab data) are the ambient data shown here? Would other ambient data support or contradict the conclusions drawn here?

Why are the results from the current study (Part I) not included in Fig 2?

P 9681. Temperature is not included in the regression analysis, presumably because no improvement in statistical significance was found from including it. This would be surprising. Could it be due to the conflicting effects of temperature directly (ie negative effect on J) and indirectly, via the correlation of temperature with daylight and thus OH production (ie positive effect on J)? If so, then disentangling these two causal relationships could improve the regression analysis. The results of the regression could be quite sensitive to the specific combination of independent variables included. The different results for the slopes for H2SO4 between tables 1 and 2 indicates that one cannot equate the slope to the number of molecules in the critical cluster. The slope for one specific species depends on how many and which other variables are included in the regression analysis. This caveat should be mentioned (eg p 9681, lines 23-27 and p 9682, line 18). Sihto et al (p 9682, line 19) is based on the same data as discussed here, so should be omitted from the list. P 9685/6, sections 3.2 and 4. I find

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the discussion of the effect of temperature on nucleation confusing and incomplete. Is the absence of a temperature dependence of activation type nucleation due primarily to the assumption that all nuclei activate, and that H2SO4 is present far above its saturation value? Doesn't the production of critical clusters (of HSO5 in the hypothesis put forward here) depend on T (via its saturation vapor pressure)? Please specify the conditions and assumptions more clearly. Don't atmospheric nucleation rates often depend negatively on T? What about the stark contrast between the absence of a temperature dependence for activation nucleation (fig 3) and the strong dependence found and used in the lab data (Fig 1)?

Technical/minor points:

When discussing nucleation in the text, it should be made clearer where H2SO4 from a liquid reservoir is meant, where oxidation products (including H2SO4) from SO2 are meant, and where predictions from classical nucleation theory are meant (eg p 9675, line 6 "binary or ternary H2SO4 nucleation" sounds like the latter, but probably H2SO4 from a liquid reservoir is meant). Also p 9675 line 4, p 9676 line 14, and elsewhere.

P 9676 I suggest to use the word "hypothesis" instead of "solution".

P 9679 line5-7: omit "laboratory data regarding".

P 9680 line 14 to p 9681 line 3: The explanation of the nucleation theorem could be shortened (or perhaps omitted), since in the end it is not actually used (though indirectly it is via the log-log dependencies in the regression equation).

p 9683 line 3: "Here we provide" and p 9684 line 4: "we suggest". The explanation has already been provided in Part 1, and repeated here. This should be acknowledged (and the discussion shortened), or better yet, the two parts should be re-combined into one paper (see above).

P 9683 line 25: HSO5 is said to nucleate better than HSO3. Isn't the comparison under consideration between HSO5 and H2SO4? P 9684, lines 1-3: "higher concentration of

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HSO5": presumably compared with HSO3? How does its concentration compare with H2SO4?

Tables 1 and 2: Clarify that the estimates for ln(H2SO4, etc) are slopes, either by an explanation in the table caption, or by adapting the symbol, eg Beta1(H2SO4) instead of ln(H2SO4).

Figure 2: The source of the atmospheric data (Sihto et al) should be mentioned in the figure caption and/or legend.

Reference list is incomplete: Bonn et al (2002), Bonn and Moortgat (2002), Dal Maso et al (2005), Selegri et al (2005) are missing. Please check the complete list.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9673, 2008.

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