

Interactive comment on “SO₂ oxidation products other than H₂SO₄ as a trigger of new particle formation – Part 2: Comparison of ambient and laboratory measurements, and atmospheric implications” by et al.

et al.

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We thank referee 2 for the constructive comments.

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

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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.

Answer. We respectfully disagree with referee 2 here. First, parts 1 and 2 are distinctly separate papers; in fact they were originally written quite independently of each other. However, as both papers are "attacking the same problem" from different angles, and as the papers share some of the coauthors, we decided to submit them to ACPD as part 1 and 2. In short, both papers seek evidence for a long ago suggested chemical mechanism that would explain nucleation from oxidized SO₂. Part 1 presents indirect

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evidence from specifically designed laboratory experiments involving NO_x to quench the hypothesized reaction. Part 2 shows that the hypothetical mechanism could resolve apparent paradoxes between existing laboratory and atmospheric datasets. Furthermore, there is the question of authorship: parts 1 and 2 have only partially overlapping groups of coauthors, and different lead authors. We believe that in such a case it is quite customary to publish as parts 1 and 2.

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 1 there is no mention of a temperature dependence.

Answer. This is a separate dataset from those presented in Part 1.

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 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), Vehkamäki 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 Vehkamäki 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.

Answer. Referee 2 is right about the uncertainty in the extrapolation, and about the mechanisms. We will add a linear extrapolation in Fig. 1, and a corresponding extrapolation in Fig. 2. (But we will also keep the exponential fit; note that our hypothesis is

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that the nucleation is specifically not binary homogeneous nucleation which Vehkamäki et al. discussed.)

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).

Answer. This extrapolation is based on data of Berndt et al (2005) as mentioned in the figure caption.

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.

Answer. The first order wall loss with $k = 0.017 \text{ s}^{-1}$ represents a parameterization of the diffusion controlled wall loss of H₂SO₄ for our tube and is in line with measurements of Hanson and Eisele, 2000, performed under similar conditions. Neglecting totally the wall loss, i.e. setting $k = 0 \text{ s}^{-1}$, the modeling shows a continuous increase of "H₂SO₄" with time resulting in a ca. 5-fold "H₂SO₄" end concentration for our lowest flow velocity of 3.33 sl min⁻¹ (the highest residence time), see also Berndt et al., GRL, 2006. With increasing flow velocity (lowering of the residence time) wall loss becomes of less importance. For a flow velocity of 30 sl min⁻¹ modeling with and without H₂SO₄ wall loss yields roughly the same result. In summary: neglecting wall loss, the extrapolated curve would shift to the right edge of the atmospheric dataset, however, neglecting H₂SO₄ losses would be physically very questionable, to say the least.

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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 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.

Answer. Scaling of atmospheric data would be much more difficult than scaling the lab data, due to variation in RH, and in concentrations of organics or other species possibly participating in the nucleation process, as readily demonstrated by the large scatter in the ambient data. A plot of the ambient data with a colourscale for temperature shows both low and high temperatures scattered quite randomly all over the datapoints, and does not really bring any new information beside the multivariate analysis presented in the paper.

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?

Answer. We will change "somewhat steeper" to "steeper". The slopes in our papers are overestimated, see the statements in Science, 2005, p.699, because of lower detection efficiency for lower "H₂SO₄" (lower "H₂SO₄" stands for smaller particles!). Our

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particles are in the range of 1.5 to 4 nm. For particles >3 nm the detection efficiency is about 1, Below 3 nm, detection efficiency is decreasing with decreasing diameter resulting in an overestimation of the slope N vs. " H_2SO_4 ". Attempts to calibrate with H_2SO_4 particles in this size range were without success. We will add discussion in the revised paper. The differences between Friend et al. and Berndt et al. slopes (as related to water content of critical nuclei) are discussed on p. 9685, line 20 ff.

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

Answer. We prefer not to show the rates converted from the SO_2 oxidation experiments from Part 1 because in those experiments, the residence time was about 1/9 of that applied by Berndt et al. (2005, 2006). This produces artificially low observed nucleation rates, since a large fraction of nucleated particles doesn't have enough time to grow past the detection limit of the aerosol instrument. We will discuss this in the revised paper. We will also add a figure that compares nucleation rates from Part 1 obtained for H_2SO_4 from the saturator to the rates measured by Ball et al. (1999).

P 9681. Temperature is not included in the regression analysis, presumably because no improvement in statistical significance was found from including it

Answer. Note that temperature is in fact included in the analysis as the data is divided into two temperature classes. The reason why it is not included in the regression model as an independent variable is that it correlates strongly with H_2SO_4 activity.

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)?

Answer. We agree that temperature has an effect on and/or correlation with many different variables possibly contributing to the nucleation, and some of these temperature effects (real or apparent) might cancel each other. We will add discussion to the revised paper.

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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).

Answer. Three of the four numbers given for H₂SO₄ in Tables 1 and 2 are a little above unity (1.23-1.46). These numbers are well in line with the general notion that the slope of log(J) vs log(H₂SO₄) in the atmosphere is between 1 and 2, indicating the presence of one to two sulfuric acids in the critical cluster. Admittedly the low-temperature number for H₂SO₄ in Table 1 is smaller (0.33). However, Table 1 also indicates that the statistical significance in this case is worse than with the other numbers. We will add discussion in the revised paper.

Sihto et al (p 9682, line 19) is based on the same data as discussed here, so should be omitted from the list.

Answer. Sihto et al. is based on the same data, but they used a different method. We will however, add a note on this to the revised paper.

P 9685/6, sections 3.2 and 4. I find 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)?

Answer. To reiterate, we assume (1) that HSO₅ is created in SO₂ oxidation process; (2) that HSO₅ reacts with an unknown species and creates a potential nucleus on which (3) H₂SO₄ can nucleate heterogeneously. The heterogeneous nucleation is a stochastic process, and at a given H₂SO₄ activity, only a certain fraction of the potential nuclei will actually be nucleated. If both H₂SO₄ concentration and the concentration of potential nuclei is kept constant, and temperature is decreased, H₂SO₄ activity increases, and the fraction of potential nuclei that actually nucleate increases as well. Thus, observed nucleation rate increases as temperature decreases. As temperature is further decreased, a threshold temperature will be found at which all of the potential nuclei do nucleate, and the temperature dependence of nucleation rate disappears. When the nucleated fraction of potential nuclei equals unity, we call the heterogeneous nucleation process "activation" (as in cloud drop activation). Of course, in our calculation, we have to assume that the production of the potential nuclei in the chemical reactions is essentially independent of temperature. Regarding the lab experiments, we assume that the threshold temperature for activation is to be found at colder conditions. We will clarify all of this in the revised paper.

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.

Answer. Will be done.

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

Answer. The phrase we use is "potential solution". Which implies a hypothesis.

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

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Answer. Ok.

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).

Answer. Note that it is actually used also when discussing the RH dependences of lab data of Friend et al. and Berndt et al.

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).

Answer. We will add cross-references in the revised papers.

P 9683 line 25: HSO5 is said to nucleate better than HSO3. Isn't the comparison under consideration between HSO5 and H2SO4?

Answer. This sentence refers to initial hypothesis of Friend et al. who suggested that either HSO3 or HSO5 could initiate the nucleation process. The given estimation shows that atmospheric steady state HSO3 concentration is about 0.05 cm⁻³. This concentration seems to be too low to initiate the nucleation process. Therefore, HSO5 is probably the better precursor, better than HSO3.

P 9684, lines 1-3: "higher concentration of HSO5": presumably compared with HSO3? How does its concentration compare with H2SO4?

Answer. Yes, compared with HSO3. The kinetics of HSO5 is not clear, so direct comparison with H2SO4 is not feasible. But HSO5 concentration should be higher than that of HSO3, see above.

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

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of $\text{In}(\text{H}_2\text{SO}_4)$.

Answer. Ok.

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

Answer. Ok.

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.

Answer. Will be done.

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

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