Atmos. Chem. Phys. Discuss., 9, C8481–C8498, 2009
www.atmos-chem-phys-discuss.net/9/C8481/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Changes in the production rate of secondary aerosol particles in central Europe in view of decreasing SO_2 emissions between 1996 and 2006" *by* A. Hamed et al.

A. Hamed et al.

amar.hamed@uku.fi

Received and published: 15 December 2009

We thank Jeffrey Pierce for useful comments. Our response to the comments is below.

General comment:

During the exploration of the impact of SO2 and nucleation changes on CCN, a major assumption in both the calculation of CCN generation during the nucleation events as

well as the calculation of the contribution of primary emissions to CCN is that growth of ultrafine primary particles to CCN sizes is ignored. To the extent that ultrafine primary particles are contributing to CCN in Melpitz (this may be small, but I'm not sure), the contribution of nucleation to CCN will be overestimated. This is not thoroughly addressed until the end of the paper (page 15103,

lines 8-13). It would be good to also discuss this in Sections 2.3 and 2.4. Uncertainties in the size distribution of primary particles are also important here. More importantly, the size distribution of primary particles may have changed between the time periods as the source of SO2 has changed, thus changing the number of primary CCN even without a change of mass emissions. This is a significant source of uncertainty in the CCN estimates and should be mentioned in Sections 2.4 and 3.3

Agreed, and we have added discussion based on average size distributions from event and nonevent days and on box model simulations of "average" events from both periods.

Specific comments:

1. Page 15090, line 14: Is the 4-day lifetime the lifetime of CCN number or CCN mass? These lifetimes may be different if the timescale of coagulation of the smaller CCN with other CCN is 4 days or less. The timescale of CCN number is the correct one to use here.

The aerosol lifetime has been determined by Balkanski (1991) who followed a 210Pb -tracer in a transport model. In the atmosphere, the radon-daughter 210Pb condenses rapidly onto pre-existing aerosol, and thus the lifetime corresponds to that of the particles at the peak of the condensation sink distribution. We

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agree that different scavenging processes influence the lifetimes of particles differently depending on particle size, which should be taken into account in more sophisticated approaches than our simple SS-model.

2. Page 15090, line 25: Please define EMEP.

Done.

3. Page 15091: The EMEP sector numbers are in some places preceded by a capital "S", and in other places they are not. This should be changed so that it is consistent.

Done.

4. Page 15091, lines 23 and 27: I do not understand the meaning of "(22f)" and "(22g)"

Accidental, have been removed.

5. Page 15091, line 20- and Table 2: There are many differences between the text and table 2. 420 nm vs. 430 nm. 1 mode vs. 2 modes for "other" particles. Sectors 2-6 vs. 2-8 for "Manufacture" particles. There may be others too, so please check this carefully.

Done.

6. Table 2 caption: Dp1 should be dp1. Mention if number mean or mass mean diameters. Define m% and EMEP sectors. EMEP sector 8 is listed as belonging to both the "Manufacture" and "Other" categories.

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Done.

7. Page 15092, line 2: 5 m particles?

Sorry, micron was missing now it's corrected to 5 μm.

8. Page 15092, line 12-14: Is this decrease of 50-70% the decrease for Europe as a whole? EU? Western Europe? Please be specific.

The decrease of 50-70% was in the United Kingdom, France and Germany.

We rephrase the sentence to be more clear "In the United Kingdom, France and Germany between 1980 and 2000 particulate sulfate mass concentrations decreased by 50-70% in response to 90% reductions in emissions and measured concentrations of SO_2"

9. Page 15093, line 6: What does "ca." mean here? It is an abbreviation for circa, but that doesn't seem like the right word for that sentence. Also, you've listed 3 locations, given two values for the locations and used the word "respectively". This is confusing because I don't know if Halle gets grouped with Leipzig or Cottbus? Please clarify.

The "respectively" refers to SO2 and PM, the locations are all grouped together. We have rewritten the sentence as "In the late 1980's, average SO2 and PM mass concentrations of more than 150 gm-3 could be measured around Leipzig, Halle and Cottbus. After 1990, the SO2 levels at these locations decreased to ca. 5 gm-3 and PM levels to 20-30 gm-3.

10. Figures 1b, 2, 3, 4, 5: Please switch the order so that the 1990s time period comes first, both in the legends and in the order in which the bars appear in the bar chart.

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It increases the chance of confusion when you put the later time period first. This is particularly problematic in the bar graphs.

Done.

11. Figure 3b: For the 2000s period, the CS drops by about a factor of 2 during the morning for every season. This is much less apparent in the 1990s (in the winter and autumn it doesn't appear to happen at all!). Is there different boundary-layer growth during the two decades? Is the decrease in CS in the 1990s dampened by the faster nucleation rates that can replenish the CS? This is very interesting and deserves to be discussed in the text. Furthermore, in the text you mention that there is no remarkable difference between the two time periods during winter and autumn; there is a big difference before noon (with the 2000s having higher CS values), and only after noon are the CS values about the same.

We have rewritten the CS comparison more carefully. Regarding boundary layer growth, we don't see any reason that it would have changed. Rather, the explanation has to do with different pollution conditions during the two periods. In 1996-97, there were still several significant large-scale emittors (power plants, carbochemical plants) in the South-East German region (within a radius of 200 km, particularly in the Lusatia region). These plants had high stacks and emitted their SO2 and also particles into a boundary layer where the pollutants eventually covered the entire depth of the BL. At night, such pollutants could be transported across considerable distances in the form of atmospheric "low-level jets". Such movements take place above the surface inversions and happen unnoticed from the ground. When the boundary layer grows in the morning the pollutants could be entrained to the ground. This is the reason why in a rural place, SO2 and CS could eventually rise throughout the morning. It's a case of regional remote

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transport. Beyrich (Meteorologische Zeitschrift 3, 29-34, 1994) showed the existance of low-level jets, and Krautstrunk et al. (Atmos. Environ. 34, 1247-1266, 2000) gave an overview of the corresponding processes relevant at the period. They also gave a nice example of such a transport event on October 7, 1994 in Melpitz. By 2003, the emissions had been curbed, and during the 2003-06 period, boundary layer growth in the morning usually mixed down cleaner air from above, hence the drop in CS. It appears that in the winter and autumn, nighttime CS values were higher in the 2000's than in the 1990's for some reason unknown to us (increased emissions near to the surface?), however, this does not really affect our considerations and we have therefore not examined the issue further.

12. Page 15095, lines 18-20: Don't forget that water vapor is generally involved in nucleation too.

Sentence now reads "...such as water, ammonia and organics..."

13. Figure 5a: Make sure the corrected figure makes it into the text.

Done.

14. Table and Section 3.1.4: It is very good that you've done the statistical significance tests; however, I find Table 3 very hard to read, and the last column "Higher in" has many mistakes in it. At minimum fix this last column or get rid of it. However, if it makes sense to you, I suggest you get rid of the table and add the p-values to the plots themselves. This would require you moving the background of the stats test to earlier in the paper, but this way you can more freely discuss the statistical significance throughout the discussions of each parameter.

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We removed the last column, and now indicate significant p-values with bold font.

The background of the tests was moved into Methods-section, and the results are now discussed in Results and Discussion.

15. Page 15101, lines 9-12: I disagree that you should call this estimate "conservative". While you do make assumptions that may cause an underestimate in the number of CCN from nucleated particles, you also make a large assumption that would cause an overestimate of the number of CCN from nucleated particles (ultrafine primary particles may also be growing to CCN sizes with your nucleated particles). Since it would be very hard to quantify all of these errors, I suggest that you do not refer to the estimate as conservative.

Agreed, "conservative" removed.

16. Page 15102, lines 1-3: Also, growth of ultrafine primary emissions to CCN.

We now discuss that based on box model simulations of aerosol size distribution evolution..

17. Page 15102, lines 21-24: Probably good to mention here that primary emissions size distributions may have changed.

We now discuss these changes with the help of average non-event size distributions. We have also included some discussion on the range of potential errors of primary source contributions

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We thank Referee 2 for useful comments. Our response to the comments is below.

General comments:

1) As the authors also point out themselves, the "primary CCN" numbers they estimate from aerosol mass emissions are highly uncertain. As pointed out by Jeff Pierce in his report too, it is, for instance, likely that the emission sources and thus typical number-mass size distributions have changed over the years (the improvement of air quality being in the core of this study too!). Taking this into account, I would be quite sceptical about drawing any conclusions about the change in primary vs. secondary CCN numbers over the investigated period - particularly since the change in the secondary source is not, according to the authors' estimates extremely clear either (and has high uncertainties). In general, I would not enphasize the possible implications on CCN numbers too much in the paper, since these results do not seem scientifically extremely sound.

We have now improved our consideration of the primary emissions by examining the average non-event day size distributions, and using them to represent the pre-existing aerosol in box model simulations of nucleation events.. We should point out here, that calculation of the increase in CCN number after nucleation events is in fact not as uncertain as the primary CCN and total (steady-state) estimates. Our calculation method is quite similar as employed by Kerminen at al. (2005) and Kuang et al. (2009).

2) Interestingly, there seems to be a reduction in the 100-750 and 200-750 nm particle numbers, but such a clear effect is not seen in the smaller 50-750 nm size bin. The authors speculate that the increased growth rates might be a reason for this. I do not

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fully understand this logic. If the differences were caused by nucleation events, should not all the nucleation-originated particles in the > 100 nm size classes have grown through the sub-100 nm sizes and thus contribute to the concenration?

There is an increase in the 100-750 and 200-750nm particle numbers, not a reduction. An increase can clearly be explained by increased GR, whereby the survival probability of particles to a given size range increases. Of course the 100-750 nm particles contribute to 50-750 nm particle concentrations and yields. During both periods, the average 50-100 nm particle concentrations were almost the same as 100-750 nm particle concentrations. However, if we look at the CCN yields (per nucleation event), in 1996-97 only 27% of the 50-750 nm particles survived to the 100-750 nm size range, whereas 2003-06 the corresponding percentage was 47. We have added discussion on these findings based on box model simulations of nucleation events.

3) Taken into account the high uncertainties in the predicted CCN numbers (which the authors acknowledge themselves too), it would be very helpful for the reader if some - even rough - sensitivity analysis would be provided. Now, since almost all the parameters used in the CCN calculations are more or less uncertain, it is quite difficult to form an opinion about how conclusive the results are.

We have now discussed the error sources based on average size distributions and box model simulations. There is now some estimate of potential range of error of primary emissions based on differing source parameters.

4) The authors report that nucleation event frequencies and particle formation rates have decreased over the investigated decade. However, simultaneously the condensation (and coagulation) sink and particle growth rate values have increased. The

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authors also acknowledge that there is a possible bias to this - following from the effect that the sink and growth rates have on the survival probability of the freshly-nucleated particles: the increasing sink values are likely to contribute to the decrease in the NPF event frequencies. Also, is it possible that the same reason is in fact causing the observed increase in the particle growth rates? That is, since the authors are only looking at days that have been classified as particle formation event days according to the criteria by Hamed et al. (2007) (and thus need to show signs of both nucleation AND growth), is it possible that due to the increase in the sink, only days with high enough vapor concenrations (and thus high enough growth rates and survival proabilities) are classifiable as NPF events in 2003-2006 as compared with 1996-1997?

In spring and summer – when most nucleation events take place – the CS has decreased, not increased. We have reworded the discussion concerning the CS in section 3.1.2 to make this clearer.

5) Related to the last comment, it would be helpful if the authors could give an estimate on how much the increased sink is likely to affect the results. In light of this, I think it would make sense to also compare nucleation mode particle numbers (maybe with the influence of traffic somehow filtered away) directly to the reduced SO2 instead of only particle formation frequencies and formation rates determined for days when also growth was observed?

We now show and discuss 3-10 nm particle concentrations from the same times that the J3-values have been determined. Similar decrease can be seen as in nucleation rates and frequencies. The 3-10 nm size range was chosen, because in this size range, influence from other sources than nucleation should be minimal, whereas at larger sizes, error sources due to primary particles increase.

6) The manuscript seems to have been written in a rush. I would recommend going

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the manuscript text and figures through once again, paying special attention to using consistent units and labeling them consistently, removing all unnecessary repetition from the text and checking spelling one more time.

We have improved the writing.

Specific comments:

7) On p. 15089, line 12 the authors say "To quantify condensation processes during new particle formation, we calculated the condensation sink by using the method described by Pirjola et al. (1998) and Kulmala et al: : : (2001)". Besides looking at the sink for sulfuric acid, the CS acts as a measure of the capability of the particle size distribution to remove small particles. I think this point should be made clear.

Done.

8) What do the authors mean by visually estimating the growth rate? Why not use a more quantitative method? I think this is important since the growth rate plays such a crucial role in the survival probability of the freshly-formed particles. At least, the authors should give a more detailed explanation on how the growth rates were determined exactly.

We used a standard procedure of determining the GR which is used in almost all papers where atmospheric growth rates are determined, i.e. following the movement of the mode through time. Whether the mode size is determined by visual inspection at different times, or by an algorithm, hardly makes a difference to the result. We have now clarified the method in the text.

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9) Is the use of a residence time of 4 days in the SS calculation justified? For instance, how likely is it that the particles in the investigated size ranges have all the same life time? How does this assumption affect the results that the authors obtain for the CCN production rates (see also my comment about the sensitivity analysis)?

The aerosol lifetime has been determined by Balkanski (1991) who followed a 210Pb -tracer in a transport model. In the atmosphere, the radon-daughter 210Pb condenses rapidly onto pre-existing aerosol, and thus the lifetime corresponds to that of the particles at the peak of the condensation sink distribution. We agree that different scavenging processes influence the lifetimes of particles differently depending on particle size, which should be taken into account in more sophisticated approaches than our simple SS-model.

10) I think the authors should give the statistics of the NPF events and good quality data in the paper, i.e. how many days in total were analysed, how many event, nonevent and equivocal days were observed each year (even monthly resolution would be good), and how large fraction of the data was considered to have a good enough quality. I think this could be done in an additional table. This would help assessing the results presented in Figs. 2b and 5, when the reader could immediately tell how many events the results are actually based on.

We believe that such descriptions of data are appropriate to present in papers discussing basic nucleation event statistics, but we can't see how they would affect our discussion or conclusions in any way. The reader surely can get a sense of the number of events from Fig. 6.

11) p. 15092, line 2: There is a typo in in the CMD - it says it was 5 m.

Corrected.

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12) p. 15098, line 26: The authors state "Note, however, that with decreased nucleation, the condensable vapour will be divided among fewer particles, and average growth rates could increase even if the condensable vapour levels stay constant." Is this really relevant, i.e. is the reduction in the condensational sink due to decrease in nucleation mode number concentration enough to potentially have any effect on the growth rates of the nucleation mode? I would imagine most of the vapor sink is anyway due to the larger particles.

We believe that once nucleated particles have grown past about 100 nm in diameter, they can effect the CS. After all, nucleation usually occurs when CS from pre-existing particlesis reasonably low.

13) p. 15100, line 5. The sentence "Based on this assumption we used the growth rate (GR) from 1nm to 3nm for each nucleation day and therefore we estimated the delay time as 2nm divided by GR." is confusing: it gives the impression that the authors estimated the time delay from the GR of 1-3 nm particles when in fact, I assume, it was vice versa (if anything - I assume 1-3 nm GRs were not even used in the study)?

We have written this in a clearer form as: "Based on this assumption we used the GR to determine how long it takes for the clusters to grow from 1nm to 3nm for each nucleation day and therefore we estimated the delay time as 2nm divided by GR."

14) Figure 1a is difficult to read, and the data sets difficult to compare. It might be a good idea to plot the y-axis in a log scale? Please also label the units in the axes consistently.

The point of the figure is to show the overall decrease of SO2 in the region rather than the details. Axes have now been labeled consistently.

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15) Figure 7. Please make all the panels of the figure equal in size.

Done

16) In Table 1 "wind speed" should probably be capitalized.

Done.

17) Table 2 and its caption: Please use consistent symbols for the diameters. Now in the caption they are capitalized but in the actual table not.

Done.

18) Table 3 is confusing. Why does it, for instance, say in the last column "No difference" for the SO2 concentrations, although (if I understand correctly) it has been significantly lower in the latter period as compared with the earlier period? I suspect there the rows in the last column have been mixed up at some point?

We have removed the last column, and now show the means with statistically significant differences with bold font. Errors have been corrected.

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We thank Michael Boy for useful comments. Our response to the comments is below.

Concerning the language I believe the paper is easy to read and to understand in is current form. However, looking at the list of co-authors and knowing their English language skills it would be worth if some of them could proofread the manuscript and improve the final version. For me the language issue is no reason not to publish this article by taking into account that the manuscript was not writer by an English native speaker and we are not writing English novels but scientific articles.

We have improved the English, aiming at good scientific style.

The results presented about the nucleation event frequency and the formation rates are very impressing and spending long time to think about it seems that no other explanation at this time beside the decrease in SO2 concentration can explain it. This results stands in contradiction to results presented by Boy et al. 2003 (ACP 108) where they could not find any correlation between SO2 concentration and new formed particles for a rural side in central Finland. It seems that in more polluted areas SO2 and following up sulfuric acid has more influence on the nucleation or formation of particles compared to cleaner environments.

We have now referenced Boy and Kulmala (2002) and Lyubovtseva et al (2005) who did not find a clear correlation between SO2 concentration and new particle formation in Hyytiälä.

One point already mentioned by referee 2 is to include the amount of nucleation mode particles (like 3-10 nm – also 10-30 nm) and not only the formation rate. As we all know calculated J-values already include assumptions which could be accomplished

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with uncertainties. So showing the real measured numbers for the smallest particles would be essential and give the reader a better overview about the total numbers.

We have now added a plot and discussed the 3-10 nm concentrations. At 10-30 nm, there clearly are primary sources that can produce much more uncertainty than in the 10-30 nm range, therefore we preferred not to show such a plot. Instead, the 10-30 nm size range is discussed in connection to average size distributions from nonevent days.

Some parts of the manuscripts are very speculative interpreted like the discussion on figure 6. In my opinion there are more non-event days hidden behind the red dots as there are event days, but a very general trend is visible.

Above the dividing line there are many more event days (red dots) than non-event days (blue dots). Below the line, vice versa.

However, the discussion about the CCN production from primary source is for me scientifically to speculative. Taking the uncertainties in interpolation backwards from 2000, assuming a fixed ABL, assuming for certain fractions size distributions, including no growth of primary particles and so on and on makes me feel that this is not anymore science at all and the value for such calculations and the following up interpretations are questionable. The manuscript without this part is already very interesting and worth to publish, so deleting this whole section would in my opinion not decrease the value of the article but shorten it.

Please see our answers to Jeffrey Pierce and to referee 2 concerning the CCN part. We have modified this part in our revised manuscript.

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The extrapolation of emissions from the 2000 backwards was necessary, as the EMEP database does not have gridded (i.e. modeled) emissions for PM before that date. The extrapolation from national averages are not on our opinion the worst source of uncertainty in this case, especially as the comparison to the gridded emissions and national trends are rather well correlating in the years 2000-2005.

We have now improved the discussion and calculations on the primary particles based on the average non-event size distributions and box model simulations. Note also that our method for calculation of the yield of CCN from nucleation events is almost similar as that of Kerminen et al. (2005) and Kuang et al. (2009), and we don't regard it being too uncertain. The result – that over 100 nm CCN have increased despite reduction in nucleation – is extremely interesting, should be pointed out, and discussed, even if the discussion is somewhat speculative. We hope others to take interest in the issue, and hopefully they will be able to use more quantitative methods. Our aim in the future is to study the CCN production using a regional model with aerosol microphysics, but that is clearly out of the scope of the present work.

Minor comments:

Page 15085 line2: I would be carefully with the statement : : : in turn forms new aerosol particles : : : it is not proven until now that sulfuric acid really forms particles by nucleation although many results show that this could be the case. At least we know that sulfuric acid only contributes a small fraction to the growth of particles - also to the small particles at 10 nm and other molecules are involved.

We have modified the statement.

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Figure 1: the b for the lower plot is missing in the text in the last line

Has been added.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 15083, 2009.

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Interactive Comment