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Atmospheric
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Interactive comment on “The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales” *by* D. V. Spracklen et al.

D. V. Spracklen et al.

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We appreciate the helpful comments of the referee. The issues raised are well taken and we have responded to every comment made by the referee.

Detailed comments

1. *While the basic interactions between sulfuric acid and pre-existing aerosol surfaces are accounted for, all condensable organic species are lumped together as a single compound whose emissions are associated with that of terpenes and are monthly av-eraged without regard to temperature or light. The reaction of this model compound is assumed to be that of a-pinene, and 13secondary products are assumed to be condensable vapors. Clearly an experimental validation of*

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this approach would be preferable. Were monoterpenes measured at Hyytiälä?

The referee points out that we make some simplifying assumptions regarding our treatment of gas phase organics and secondary organic aerosol (SOA). This is partly necessary due to the uncertainties in our knowledge of the relevant processes and partly because of the need to simplify processes before inclusion in a global model. Clearly further work is needed in the future to improve the model representation of these processes. Where possible we have tried to use observations made at Hyytiälä to validate our simplified treatment of organics.

Monoterpenes were measured at Hyytiälä and we make a comparison between observed and modelled monoterpenes (see P7339, l27). In April the model agrees with observed monoterpene concentrations but in March the model is about a factor of 10 too low. The model daily cycle of monoterpenes agrees with observations. However, the observed daily cycle may be caused by a daily cycle in emissions (which is not inlcuded in the model) or by differences between nighttime and daytime oxidant concentrations (which is included in the model).

Condensable organic concentrations are difficult to directly measure but have been infered by various groups using a variety of different techniques. These techniques estimate that condensable vapour concentrations at Hyytiälä are between 2 and 10 times the value in our model. We add the following text to P7340, L9:

‘Condensable vapour concentrations at Hyytiälä have been determined by a variety of techniques to be between 2.0x10^7-1.3x10^8 cm^{-3} (Kulmala et al., 2001; Dal Maso et al., 2002; Lehtinen et al., 2004; Korhonen et al., 2005). Model condensable vapour concentrations are about 0.5-2.0x10^7 cm^{-3}. This is a factor of 2-10 lower than observed.’

We also find that with standard monoterpene emissions the model growth rates are too slow. This also indicates that condensable vapour concentrations in the model are too low. Increasing monoterpene emissions by a factor of 10 (a sensitivity study that represents a wide range of uncertainies in the model) results in newly formed particles reaching sizes similar to that observed.

We add the following text (p7335, l5):

‘There are also uncertainties regarding the conversion to condensable organic species and the potential for organic species other than monoterpenes to produce SOA. We explore the effect of changing the monoterpene emission rate by a factor of 10 to take account of uncertainties in secondary organic aerosol yields and precursor emissions.’

2. *Sulfuric acid is primarily produced by cloud processing, thus the parameterization of cloud formation is key to accurately determining ambient levels of this compound. One assumption of cloud droplet formation relates to the criterion for droplet activation (a specific question relating to this issue is presented below). Another assumes that particle scavenging by clouds occurs only by nucleation, and not wet deposition. This latter assumption may result in a less accurate depiction of cloud droplet number.*

   Gas-phase sulfuric acid is produced through the gas phase reaction of SO_2 with OH. Particulate sulfate is produced in cloud processing. The main impact of cloud processing will be altering the surface area of existing aerosol and reducing SO_2 concentrations which will indirectly impact gas-phase sulfuric acid. In Spracklen et al. (2005b) we found that varying the activation diameter of aerosol particles into cloud droplets cauesed a change in CCN concentrations but had very little impact on total particle number concentrations.

   We clarify by replacing ‘In these clouds, the aerosol is processed (SO_2 reacted to form condensed sulfuric acid)’ with ‘In these clouds, the aerosol is processed (SO_2 reacted to form particulate sulfate)’.

3. *The centerpiece of this study is a data set consisting of 22 days of measurements at Hyytiälä, Finland. Some additional insights are provided by average particle*

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concentra-tion data from Melpitz and Heidelberg. Certainly other datasets are also available with high quality measurements of sulfur containing gases and aerosol. Can the authors comment on why they considered only this data set interpreting their model results?

The particle formation mechanism that we include in the model has been determined empirically (Kulmala et al., 2006; Sihto et al., 2006) based on observations at Hyytiälä. We therefore feel that it is best to interpret our model results based on the observations made at this site. A full comparison of the model against other surface sites is a major task. This is currently being undertaken but is beyod the scope of this first study.

4. *I find that the days in which the model does not capture the observed nucleation events are the most interesting. A closer look at these days (e.g., days 78 and 82), might provide insights that may lead to model improvements.*

   We do discuss days where the model disagrees with observations (see P7339, L10-26).

   On days 78 and 96 the model predicts a particle formation event when none is observed. Both these are caused by model H_2SO_4 being higher than observed. The main cause for this is likely to be that the model using monthly mean OH fields (specified at 6 hour intervals) interpolated onto the model timestep. In reality OH will be impacted by cloudiness and solar radiation.

5. *It is not at all clear to me that CN are not affected by new particle formation in urban areas, although the authors state this as a main result of their model (ref page 7344, lines 20 - 23). Examples of recent observations in the Po Valley and Mexico City have shown that areas of high primary emissions can still regularly host new particle formation events. This could be merely an phenomenon related to vertical mixing, e.g., the breakup of the planetary boundary layer. These high sources of condensable material, which may or may not be adequately repre-*

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sented in the model, make these important areas to explore (as in point 4, worthy of more careful inspection).

The model does simulate nucleation events in polluted continental condidtions with a similar frequency to that observed. For details see P7344, L14-L24. We show here that these events only lead to relatively small enhancements to total particle number concentrations (generally less than a factor of 2) whereas over remote continental areas enhancements up to a factor of 8 are modelled. Further work is required to fully test the model against observations in urban areas.

To clarify we change (P7344, L22):

‘There is little evidence that the formation events have a lasting impact on CN in regions with such high primary emissions’

to:

‘The model suggests that although particle formation does occur in polluted regions, particle concentrations in such regions are dominated by primary emissions.’

Specific comments

1. *Page 7330, line 10: Please clarify your criterion for cloud droplet formation. As it currently reads, all particles larger than 50 nm activate to form droplets regardless of supersaturation.*

   All particles larger than 50 nm dry diameter activate to from droplets when low clouds are present.

2. *Page 7330, line 19: Please clarify what is meant by the new boundary layer formation mechanisms.*

   We change ‘Secondary sulfate particles are formed through homogeneous nucleation as well as through new boundary layer formation mechanisms, while sea salt, BC and OC are added as primary particles.' to 'Secondary sulfate particles are formed through binary homogeneous nucleation above the boundary layer (Kulmala et al., 1998; Spracklen et al., 2005a) as well as through particle formation within the boundary layer. For a description of the particle formation mechanisms used in the model see section 2.2. Sea salt, BC and OC are emitted as primary particles.'

3. *Page 7332, paragraph starting at line 19: Please correct all statements in this para-graph that refer to SO2 emitted as particulates, as this implies that SO2 can exist inparticles. From the abstract of the Adams and Seinfeld paper: Both analyses show that the few percent of anthropogenic sulfur emitted as particulate sulfate results in an increase in CCN concentrations comparable to that resulting from much larger emis-sions of gas-phase sulfur dioxide. Thus the correct statement should be 'industrial sulfur emitted as particulates'*

   We change all instances of 'SO_2 emitted as particulates' to 'anthropogenic sulfur emitted as particulates'.

4. *Page 7334, paragraph starting at line 17: In this paragraph discussing the competing effects of condensate production and scavenging due to particulate surfaces it seems appropriate to mention the work of P. McMurry, who developed a simple parameter that predicts whether new particle formation will occur based on the ratio of the rate of formation of the thermodynamically stable clusters to the rate at which they are lost to pre-existing particles (McMurry et al., JGR, 2005).*

   We add reference to McMurry et al. (2005)

5. *Page 7336, line 12: Although this paper focuses primarily on the prediction of CN concentrations, their formulation for cloud production (i.e., any particle greater than 50 nm forms a cloud droplet) will be greatly influence by disparities between both the growth rates and CCN activities of biogenic SOA versus those of sulfate. For example, VanReken et al. (JGR, 2005) studied a variety of biogenic*

compounds in chamber studies and found that CCN activity differed from that of pure ammonium sulfate in all cases (lower), and that particles became significantly less hygroscopic as they aged. I suggest a sentence or two that convey the implications of your simplification regarding SOA formation.

We add the following line after describing our aerosol activation scheme:

‘This simple scheme does not take into account aerosol activation that depends on aerosol size distribution (Dusek et al., 2006), aerosol composition (Van Reken et al., 2005) or cloud updraught velocity.’

6. *Page 7339, line 27: correct the Figure reference. It should be 1d.*

   ’Figure 1c’ changed to ‘Figure 1d’.

7. *Page 7348, line 10: correct the word Increases*

   ‘Increase’ changed to ’Increase in’

8. *Table 1: should there be an entry for the source strength of sea salt?*

   We have added the source strength of sea salt as 13 500 Tg NaCl / yr^{-1}.

9. *Figure 1: caption for plot 1c: blue should be the color of the modeled data.*

   ‘Red’ changed to ‘blue’.

References

[Dal Maso et al.(2002)Dal Maso, Kulmala, Lehtinen, Mäkelä, and Aalto] Dal Maso, M., Kulmala, M., Lehtinen, K., Mäkelä, J., and Aalto, P.: Condensation and coagulation sinks and formation of nucleation mode particles in coastal and boreal forest boundary layers, J. Geophys. Res. - Atmos., 107, 8097, doi:10.1029/2001JD001 053, 2002.

[Dusek et al.(2006)Dusek, Frank, Hildebrandt, Curtius, Schneider, Walter, Chand, Drewnick, Hings, Jung, Borrmann
Dusek, U., Frank, G., Hildebrandt, L., Curtius, J., Schneider, J., Walter, S., Chand, D., Drewnick, F., Hings, S., Jung, D., Borrmann, S., and Andreae, M.: Size Matters More Than Chemistry for Cloud-Nucleating Ability of Aerosol Particles organics, Science, 312, 1375–1378, 2006.

[Korhonen et al.(2005)Korhonen, Kerminen, and Kulmala] Korhonen, H., Kerminen, V.-M., and Kulmala, M.: Development and application of a new analytical method to estimate the condensable vapor concentration in the atmosphere, J. Geophys. Res. - Atmos., 110, D05 201, doi:10.1029/2004JD005 458, 2005.

[Kulmala et al.(1998)Kulmala, Laaksonen, and Pirjola] Kulmala, M., Laaksonen, A., and Pirjola, L.: Parameterizations for sulfuric acid/water nucleation rates, J. Geophys. Res. - Atmos., 103, 8301–8307, 1998.

[Kulmala et al.(2001)Kulmala, Dal Maso, Mäkelä, Pirjola, Väkevä, Aalto, Miikkulainen, Hämeri, and O'Dowd]
Kulmala, M., Dal Maso, M., Mäkelä, J., Pirjola, L., Väkevä, M., Aalto, P., Miikkulainen, P., Hämeri, K., and O'Dowd, C.: On the formation, growth and composition of nucleation mode particles, Tellus, Ser. B, 53B, 479–490, 2001.

[Kulmala et al.(2006)Kulmala, Lehtinen, and Laaksonen] Kulmala, M., Lehtinen, K., and Laaksonen, A.: Cluster activation theory as an explanation of the linear dependence between formation rate of 3nm particles and sulfuric acid concentration, Atmospheric Chemistry and Physics, 6, 787–793, 2006.

[Lehtinen et al.(2004)Lehtinen, Petäjä, Kulmala, and Hari] Lehtinen, K.E.J. Rannik, U., Petäjä, T., Kulmala, M., and Hari, P.: Nucleation rates and vapour concentration estimations using a least squares aerosol dynamics method, J. Geophys. Res. - Atmos., 109, doi:10.1029/2004JD004 893, 2004.

[McMurry et al.(2005)McMurry, Fink, Sakurai, Stolzenburg, Mauldin III, Smith, Eisele, Moore, Sjostedt, Tanner, Huey
McMurry, P., Fink, M., Sakurai, H., Stolzenburg, M., Mauldin III, R., Smith,

J., Eisele, F., Moore, K., Sjostedt, S., Tanner, D., Huey, L., Nowak, J., Edgerton, E., and Voisin, D.: A criterion for new particle formation in the sulfur-rich Atlanta atmosphere, J. Geophys. Res. - Atmos., 110, doi:10.1029/2005JD005 901, 2005.

[Sihto et al.(2006)Sihto, Kulmala, Kerminen, Dal Maso, Petäjä, Riipinen, Korhonen, Arnold, Janson, Boy, Laaksonen Sihto, S.-L., Kulmala, M., Kerminen, V.-M., Dal Maso, M., Petäjä, T., Riipinen, I., Korhonen, H., Arnold, F., Janson, R., Boy, M., Laaksonen, A., and Lehtinen, K.: Atmospheric sulfuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms, Atmospheric Chemistry and Physics, 6, 3845–3882, 2006.

[Spracklen et al.(2005a)Spracklen, Pringle, Carslaw, Chipperfield, and Mann] Spracklen, D., Pringle, K., Carslaw, K., Chipperfield, M., and Mann, G.: A global off-line model of size-resolved aerosol microphysics; I. Model development and prediction of aerosol properties, Atmospheric Chemistry and Physics, 5, 2227–2252, 2005a.

[Spracklen et al.(2005b)Spracklen, Pringle, Carslaw, Chipperfield, and Mann] Spracklen, D., Pringle, K., Carslaw, K., Chipperfield, M., and Mann, G.: A global off-line model of size-resolved aerosol microphysics; II. Identification of key uncertainties, Atmospheric Chemistry and Physics, 5, 3233–3250, 2005b.

[VanReken et al.(2005)VanReken, Ng, Flagan, and Seinfeld] VanReken, T., Ng, N., Flagan, R., and Seinfeld, J.: Cloud condensation nucleus activation properties of biogenic secondary organic aerosol, J. Geophys. Res. - Atmos., 110, 2005.

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