

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.

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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. *The manuscript never explain how boundary layer is defined in the model. What is the vertical resolution of the model near the surface? Does the boundary layer height extends above the first model layer? Are there measurements of boundary layer height at Hyytiälä; if so, how does model PBL heights compare to the measurements? Is it possible that PBL height contributes significantly to the discrepancies in modeled and observed concentrations?*

We include a more detailed description of the model boundary layer (BL) height and the model treatment of sub-grid transport in the BL. We add the following text (p7330, l6):

‘Tracer advection is performed using the scheme of Prather et al. (1986). Sub-grid transport is calculated using the convection scheme of Tiedtke et al. (1989). Turbulent mixing in the BL and BL height are calculated using the parameterization of Holtslag et al. (1993). A comparison of model BL height with observations is given by Wang et al. (1999). They show that calculated BL height is in good agreement with Holtslag et al. (1993) and that including the scheme results in an improved seasonal cycle of model tracers.’

and (P7338, l27):

‘Maximum mixed BL height at Hyytiälä during August 2001 was calculated as between 1000 and 2200 m (Spirig et al., 2004). Radio soundings launched at Hyytiälä on 4 April 1999 recorded maximum BL height of 2180 m (Nilsson et al., 2001). At Hyytiälä model mean BL height in March and April 2003 is 550 m and maximum BL height is about 2000 m.’

Differences between model and observed BL height at Hyytiälä are unlikely to be the main cause for discrepancies between model and observed particle concentrations.

We describe vertical model resolution near the surface by adding the following text (p7330,l5):

‘with the lowest layers centered at about 30 m, 140 m, 340 m, 600 m, 930 m, 1300m, 1710 m above the surface.’

- The calculation of particle formation rate is not explained in enough detail in section 2.2. The parameterization for the apparent new particle formation rate J_m in Equation (2) assumes that the condensation sink term CS is constant, which*

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requires a small time step. What time step is used for calculating J_m ? How is the growth rate GR determined? Does GR also include organics or just sulfate?

We add information on the growth rate and the condensation sink. We add information on the timestep length. We add the following text (P7333, L8):

‘Growth rate is calculated using the following approximation from Kerminen and Kulmala (2002):

$$GR = \frac{3.0 \times 10^{-9}}{\rho_{nuc}} \sum \bar{c}_i M_i C_i, \quad (1)$$

where index i goes over condensible vapours and C_i is gas-phase concentration (molecules cm^{-3}), \bar{c}_i is molecular speed of condensing vapour (m s^{-1}) and M_i is its molecular weight and ρ_{nuc} is nuclei density (kg m^{-3}).

We assume that only sulfuric acid contributes to the growth of nuclei between 1 nm and 3 nm diameter but that both condensible organics and sulfuric acid contribute to the growth of particles larger than 3 nm. We discuss a sensitivity study where we let both organics and sulfuric acid be allowed to contribute to sub-3 nm growth.

We add a definition for condensation sink adding the following line (P7333, L8):

‘The reduced condensation sink (CS’) is calculated by summing over the aerosol size bins j :

$$CS' = \sum_j \beta_j r_j N_j \quad (2)$$

where β_j is the transitional correction for the condensational mass flux (Fuchs et al., 1971), r_j is the particle radius, N_j is the particle number. The condensation sink (CS) has units of s^{-1} and is calculated from the reduced condensation sink by

$$CS = 4\pi DCS', \quad (3)$$

where D is the vapour diffusion coefficient. ’

The time step for calculation of nucleation (and calculation of J_m) is 3 minutes. On page 7333, 114 we have added:

‘The timestep in the model for this process is 3 minutes.’

- The model assumes that newly formed particles that grow to 3 nm consist of pure acidic sulfate. According to Kulmala et al. (2004), for cluster-activation nucleation represented by Eqn (1), the sulfate is likely ammonium bisulfate and organics are also involved. By not including organics in newly formed particles, the model is reducing gas-phase sulfuric acid faster than if organics were included, which could lead to decreased new particle formation rate.*

Depletion of gas-phase sulfuric acid due to sub-3nm growth is minimal compared to depletion due to condensation onto existing particles. For a typical formation rate for 3 nm particles of $1 \text{ particle cm}^{-3} \text{ s}^{-1}$ (Kulmala et al., 2001) assuming that the entire particle is made of sulfuric acid will deplete gas-phase sulfuric acid by approximately $150 \text{ molecules cm}^{-3} \text{ s}^{-1}$. Given a relatively low condensation sink of 0.002 s^{-1} loss of gas-phase sulfuric acid onto pre-existing aerosol is $2000 \text{ molecules cm}^{-3} \text{ s}^{-1}$.

- There are several competing theories on nucleation mechanism in the literature. The manuscript should provide a brief discussion on why Eqn (1) is chosen for the boundary layer and why binary homogeneous nucleation rate of sulfuric acid/water particles is used above the boundary layer. What are the fundamental differences between the boundary layer and the rest of the troposphere such that a different particle formation scheme is required? While the actual nucleation mechanism is still undetermined, it is well known that ammonia plays a role. What is the implication by not considering ammonia in the nucleation mechanism?*

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. In Spracklen et al. (2005a) we showed that a binary homogeneous nucleation scheme was capable of simulating particle number concentrations in the free troposphere and upper troposphere. We add the following text (P7334, L12):

‘In Spracklen et al. (2005a) we showed that this nucleation scheme is capable of reproducing observed particle number in the FT and UT.’

Binary homogeneous nucleation does not calculate new particle formation in the BL. We apply the new particle formation mechanism to the BL. Applying the new particle formation mechanism throughout the depth of the atmosphere does not limit particle formation events to the BL and the observed Z-shaped profile of particle number (Schroder et al., 2002) is no longer produced by the model. This suggests that J^* depends on more than sulfuric acid and that equation 1 breaks down above the BL. See P7334, L11-20.

We change the following:

‘Our limited measurements above the boundary layer at Hyytiälä suggest that this is a valid assumption. Aircraft observations showing CN enhancements in the European boundary layer and a minimum just above it (e.g., Schroder et al., 2002) are also consistent with this assumption, although primary emissions at the surface also play a role.’

to:

‘Our limited measurements above the BL at Hyytiälä and aircraft observations showing CN enhancements in the European BL and a minimum just above it (Schroder et al., (2002) suggest that new particle formation is confined to the BL. However, the reason for such behaviour is not understood.’

We do not consider ternary nucleation in this work. Gaydos et al. (2005) used their model of ternary nucleation to simulate particle formation events in the Eastern U.S. In Hyytiälä ammonia is in excess and so will not experience the same

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behaviour as in the Eastern U.S. where ammonia is the limiting species. See P7332, L8-20.

5. *In section 2.3, how is SOA distributed among to size bins?*

The condensation of condensible organics onto the aerosol size distribution is described using the modified Fuchs-Sutugin equation (Fuchs et al., 1971) and the implementation of this in GLOMAP is explained in Spracklen et al. (2005a).

6. *In paragraph 3 of section 4.2, the statement The modelled monoterpenes show the same diurnal cycle, with minima at night due to rapid reaction with NO₃ is misleading. The observed diurnal cycle is mostly like due to diurnal cycle of emissions, which is not modeled. Though not universal, monoterpene emissions tend to be high during day time and low during night time. This also means that oxidation by O₃ and OH is biased low during the day and NO₃ oxidation is biased high at night in the model.*

We agree that the observed daily cycle in monoterpenes will likely be due to daily variability in emissions as well as the differences between daytime and night time chemistry. We therefore remove the line:

'The modelled monoterpenes show the same diurnal cycle, with minima at night due to the rapid reaction with NO₃.'

7. *The last paragraph of section 6.1 goes better with the discussion of the first paragraph of section 6.2. A plot like Figure 6 should be made for the sensitivity runs discussed in the first paragraph of section 6.2.*

We have moved the last paragraph of section 6.1 as suggested.

8. *One of the major short-coming of this study is its modeling of aerosol-relevant gas-phase organics and secondary organic aerosol (SOA). The model uses -pinene as a surrogate of all monoterpenes and assumes 13gas-phase oxidation*

rate and aerosol yield can be very different for different monoterpenes. Furthermore, aerosol yield depends on temperature and availability of other organics. Sesquiterpenes, of which oxidation products can have high aerosol yield, is not included in the model. To some extent, the sensitivity simulation on emissions of monoterpenes incorporate all these uncertainties. The manuscript should be careful to note that the 10xGEIA emissions simulation is really only a proxy for all the uncertainties related to modeling SOA and SOA precursors.

We agree with the referee that there are many uncertainties in the treatment of gas-phase organics and secondary organic aerosol. Many of the processes are not yet at a sufficient level of understanding to include in a global model. We modify text to emphasise that our sensitivity simulation on the emission of monoterpenes is a simple attempt to include a large range of uncertainties associated with organics and SOA.

We add the following text (p7335, I5):

‘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.’

9. *In section 6.3, how does varying k affect CN over polluted regions and globally?*

Reducing k by an order of magnitude reduces mean model CN at Hyytiälä by a factor of 2. This is similar to the reduction over many remote continental locations. Over polluted regions (where the enhancement to CN number through BL nucleation is less) mean CN number is reduced by about 25% for an order of magnitude reduction in k . We add the following line to P7349, I8:

‘Over remote continental regions reducing k by an order of magnitude reduces mean model CN by a about a factor of 2 whereas over central Europe mean CN

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is reduced by about 25%.’

Minor comments

1. *Last paragraph, page 5 : Adams and Seinfeld (2003) should be Adams and Seinfeld (2002).*

We have changed ‘Adams and Seinfeld (2003)’ to ‘Adams and Seinfeld (2002)’

2. *Section 3 on page 9: All instances of BHN of sulfuric acid aerosol should be rephrased BHN of sulfuric acid aerosol above the boundary layer for clarity.*

We change all instances of ‘BHN of sulfuric acid aerosol’ to ‘BHN of sulfuric acid aerosol above the BL’ for clarity.

3. *Caption for Figure 1(c): There is no red line in the figure; red should be blue?*

Figure 1(c). We have changed ‘red’ to ‘blue’.

4. *In the caption for Figure 1(d), (blue) should be (red).*

In caption for Figure 1(d) black is observed monoterpenes, blue is model monoterpenes and orange is model condensible organics.

5. *There is an inconsistency in the units of CS: m^2 in the text and s^{-1} in Figure 1(e), which are off by a factor of diffusion coefficient.*

We have changed the symbol CS (condensation sink) in equations 2 and 3 to CS’ (reduced condensation sink).

The relationship between CS and CS’ is given by:

$$CS = 4\pi DSCS' , \quad (4)$$

where DS is the vapour diffusion coefficient. CS has units of s^{-1} and CS’ has units of m^{-2} .

6. *Page 10, second line of second paragraph of section 4.2: obvious should be obviously.*

We have changed 'obvious' to 'obviously'.

7. *In section 6.1 and Figure 6, what fractions of the emissions are considered anthropogenic?*

The fraction we refer to is the fraction of present day anthropogenic primary emissions that we include in the model run.

We change the title of section 6.1 from: 'Sensitivity to primary emissions' to 'Sensitivity to anthropogenic primary emissions'

We emphasise throughout section 6.1 and in the caption for figure 6 that we are referring to change in anthropogenic primary emissions.

8. *Table 1: What is the source strength in Tg yr⁻¹ and yr⁻¹ of sea salt?*

Table 1. We have added the source strength of sea salt as 13 500 Tg NaCl / yr⁻¹.

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