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Atmospheric
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Discussions

Interactive comment on “The role of sea-salt emissions and heterogeneous chemistry in theair quality of polluted coastal areas” *by* E. Athanasopoulou et al.

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(1) Page 3812: line 18:"The threshold diameter in the hybrid model of 2.5 um seems too high, which could introduce appreciable errors in the predicted distribution of nitrate. This diameter was typically set at 1 um in some of the previous studies. A discussion on the sensitivity of the results to the threshold diameter is warranted to ensure that the errors due to this assumption are acceptable."

We do agree with this point. Reducing the equilibrium threshold does not affect significantly the PM10 aerosol nitrate levels over the urban area of interest (similar to Capaldo et al., 2000) but changes the nitrate size distribution shifting it to larger sizes. At the same time it increases the computational cost of the model by approximately a factor

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of 3-4. Given the problems with the ammonia emission inventory and the resulting significant underprediction of ammonium nitrate we do not think that a detailed discussion of the size distribution of nitrate is worthwhile (at least at this stage). We have added the following text making this point about the use of a lower threshold for equilibrium in future applications (after improvement of the ammonia emissions): "Previous studies have recommended 1 um as the cut-off diameter between the equilibrium and dynamic approach (Capaldo et al., 2000; Koo et al., 2003; Gaydos et al., 2003). Our base-case results use an increased threshold (2.5 um), in order to reduce the computational cost of the model. A sensitivity test using of lower cut-off (1 um) resulted in small (less than 0.5 ug m-3) changes in average nitrate concentrations. This effect of the cut-off diameter is expected to be different when ammonia emissions are increased, and therefore future applications of the model should probably use the recommended lower threshold diameter."

(2) Page 3816, line 14: "Mg+ should be Mg2+, Ca+ should be Ca2+ and K-; should be K+. Also, what are the percentages of Ca2+, K+, and Br-. Finally, give Na+ also in percentage to be consistent."

We have corrected the typos and also added the requested information.

(3) Page 3821, line 4: "The equilibrium constant is a function of temperature only. I am not sure I understand how the presence of additional salts could reduce it?"

The ammonium nitrate equilibrium constant for aqueous particles depends not only on temperature and relative humidity but also on the concentrations of other ions in the solution (Atmospheric Chemistry and Physics, Seinfeld and Pandis (2006), fig. 10.21, page 477). For a fixed T and RH, this constant (equal to the product of the gas-phase concentrations of nitric acid and ammonia) in general decreases when other ions are present in the solution.

To better explain this rather fine point we have rephrased this section to: "Inclusion of SSA can also impact the formation of ammonium nitrate when liquid aerosol is present.

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Over Thessaloniki, in the early morning during rush hour, significantly more ammonium nitrate is predicted to be formed when SSA is included, because the presence of additional ions in the solution reduces the ammonium nitrate equilibrium constant, shifts its' partitioning towards the particulate phase and increases the ammonium and nitrate concentrations in the liquid particles. The phenomenon is especially pronounced in the Thessaloniki area due to the stably high RH over Thesaloniki gulf (around 90%) during the simulation period."

(4) Page 3821, section 5.3: "This section is very confusing.

Line 14: If chloride is mainly displaced by H2SO4 in the bulk equilibrium approach, then why is there little production of sulfates? All H2SO4 that is condensed would lead to production of sulfates, whether it is calculated by dynamic mass transfer or by equilibrium approach.

Line 15: Why does the rest of the NaCl remain inert? Why doesn't some if it react with HNO3 to produce NaNO3 and HCl(g) as dictated by thermodynamic equilibrium?

Line 16: I fail to understand how low concentrations of HCl(g) in the bulk equilibrium solution leads to large underprediction in nitrate. It should the other way around: less displacement of chloride by nitrate leads to low concentration of HCl(g)."

These three sentences were confusing and have been rewritten as follows:

"The instant equilibration dictated by the equilibrium approach fails to accurately represent the competition between the fine and coarse particles for the condensing sulphuric and nitric acid especially in the marine areas of the modelling domain. In the bulk equilibrium approach the sulphuric acid reacts with the larger NaCl particles forming sodium sulphate. This reaction leaves only small amounts of alkaline NaCl available to react with the nitric acid vapour and therefore the equilibrium approach predicts relatively small amounts of coarse nitrate. In the marine areas, the concentrations of ammonia are low, so there is also little ammonium nitrate formed in the fine particles.

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Therefore, in the marine areas the bulk equilibrium approach predicts significantly less nitrate than the hybrid approach. This leads to large differences (up to 90%) in inorganic PM10 nitrate concentrations between the base-case simulation and that with the bulk-equilibrium approach over most of the marine-affected domain (not shown). In the urban parts of the domain the bulk-equilibrium approach continues to seriously under predict the coarse nitrate concentration (Fig. 10)."

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 3807, 2008.

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