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Interactive comment on "Simulating emission and chemical evolution of coarse sea-salt particles in the Community Multiscale Air Quality (CMAQ) model" *by* J. T. Kelly et al.

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We thank Referee#3 for constructive comments and a positive assessment of our study. The manuscript has been strengthened by revisions made in response to the referee's comments. In particular, these comments prompted us to find a more complete explanation for predictions of accumulation-mode nitrate at Sydney and to provide further evidence of the soundness of our model development with a supplementary table that compares results from all model versions. Below, we have copied the referee comments in italics and inserted our responses in standard font where appropriate. Note that the line and page numbers in our responses refer to those of the article published

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in GMDD.

General Comments
The paper is well written and clear and may be published with minor to medium
modifications. The developed modules are on a sound scientific basis within the
limitations beeing necessary for a computationally efficient approach.

Specific Comments
Three versions of CMAQ are used: v4.6 is a standard release version which is used
to provide a reference run. v4.6b is identical to v4.6 except that it incorporates a surf
zone emission parameterization for sea salt particles. v4.6c is identical to v4.6b except
that the GSD of the coarse mode is variable and a dynamic transfer of HNO3, H2SO4,
HCl, and NH3 between coarse particles and the gas phase is introduced. Results of
v4.6c are compared with those of v4.6b, i.e. results from a model (v4.6c) with two
modifications with respect to v4.6b are discussed.

It is not completely clear to what extend contribute the two modifications in each
case to the differences between the model results of v4.6b and v4.6c. The inclusion
of a further version with only one of the two modifications could be helpful to explain
well-founded the individual phenomena.

Actually, calculations of coarse-mode GSDs and dynamic mass transfer are coupled
and do not correspond to individual phenomena as suggested by the referee. The
modal condensation rate used in the dynamic mass transfer equations is obtained by
integrating over the particle size distribution, which is defined in terms of modal GSDs
(e.g., see equations A9 and A10 of Binkowski and Shankar, 1995). Since modal GSDs
influence dynamic mass transfer, and dynamic mass transfer influences modal GSDs,
separating the effects of these updates is not straightforward. Moreover, knowledge of
the individual effects of these modifications would not be of obvious value, because the
variable GSDs and dynamic mass transfer updates both clearly provide a more realistic
representation of aerosol processes than the previous approach. Note, however, that

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additional studies of CMAQ's aerosol representation are underway. As mentioned in the response to Referee#1, we are currently comparing results of CMAQv4.6c simulations with those of CMAQ-UCD. Since the CMAQ-UCD model uses a sectional representation of particle size distributions and a fully dynamic mass transfer approach, this comparison should provide insights on the impact of different aerosol representations in CMAQ.

In the discussion of differences between predicted and measured particle size distributions (Section 4.2) the authors well demonstrate the importance of aerosol dynamics modelling. The authors note differences in coarse mode sodium concentrations predicted by v4.6b and v4.6c with the same emission parameterization which can only be explained due to size dependent processes.
Page 1352, line 8/9: "... under-prediction of sodium ... leads to under-prediction of coarse nitrate." This is not the case at the Azalea Park site. There is coarse nitrate under-predicted by v4.6c but sodium is over-predicted.

Actually, sodium is under-predicted at the Azalea Park site (e.g., see Table 2 and Fig. S1), and so our original statement is valid. However, results for Azalea Park are a bit different than those for the other two sites because Azalea Park is located in a grid cell with coastal surf-zone emissions of sea salt. This issue is discussed in Section 4.3 (p. 1355, lines 18-20).

Page 1352, line 9-11: "At the Sydney side, the under-prediction of sodium in the coarse mode appears to cause the over-prediction of nitrate in the accumulation mode by CMAQv4.6c." The over-prediction of accumulation mode nitrate at the Sydney site may also be attributed to the fact that this station is farer away from the coast as the other two sites and therefore, depending on wind direction, may be more influenced by anthropogenic emissions.

We are not sure which emissions the referee is citing. Direct emissions of particle nitrate are low in the model (Reff et al., 2009) and do not account for the over-

prediction of accumulation-mode nitrate at the Sydney site. In any case, this comment prompted us to find a more complete explanation for the accumulation-mode nitrate predictions at Sydney. Considering that direct emissions of nitrate are small, the modeled accumulation-mode nitrate must have resulted from nitric acid condensation on particles. Since there is little sodium chloride in the accumulation mode to enable replacement reactions, significant nitric acid condensation would be favorable in the model only if sufficient ammonia were available to neutralize the acidity resulting from the dissociation of aqueous nitric acid. This requirement arises because the vapor pressure of nitric acid is proportional to the hydrogen ion concentration in the particles. Ammonia concentrations in excess of those necessary to neutralize the acidity resulting from aqueous sulfuric-acid dissociation are necessary for significant neutralization of nitric acid, because sulfuric acid is non-volatile in the model, whereas nitric acid is semi-volatile. To determine if sufficient ammonia was available to neutralize aqueous nitric acid, we calculated the average predicted ratios of the total number moles of ammonia (i.e., $NH_3+NH_4^+$) to moles of non-sea-salt sulfate at the BRACE sites. At the Azalea Park and Gandy Bridge sites, this ratio is about two, and so just enough ammonia is present to match the stoichiometry of neutral ammonium sulfate, $(NH_4)_2SO_4$. However, the average ratio at the Sydney site is greater than four, and so ample ammonia was present at Sydney to neutralize a significant amount of aqueous nitric acid in addition to aqueous sulfuric acid. Therefore the prediction of significant accumulation-mode nitrate at Sydney (but not the other sites) is largely explained by the higher ammonia-to-sulfate ratio for the Sydney site than the other sites. However, the lower accumulation-mode nitrate predictions for CMAQv4.6c than CMAQv4.6b indicate that the association of nitrate with sodium in coarse particles can reduce accumulation-mode nitrate slightly, even in the presence of excess ammonia. This behavior suggests that increasing coarse-mode sodium concentrations in CMAQv4.6c would slightly lower its accumulation-mode nitrate predictions. This explanation for the accumulation-mode nitrate predictions for the Sydney site is briefly summarized in Section 4.2 of the revised manuscript.

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Page 1352, line 18: "... differences in sodium predictions are attributable to differences in advective transport and deposition." Dry deposition (and sedimentation) is in fact size dependent, but is particle size significant for the parameterization of advective transport?

As the referee correctly points out, advective transport of particles is not directly dependent on particle size in the model. However, advective transport and deposition are linked in the sense that the total deposition of particles in a given location for a given deposition rate is proportional to the residence time of particles in that location. And the residence time is determined by characteristics of advective transport. Our intention in the sentence was to refer to the combined effects of transport and deposition. This issue is clarified in Section 4.2 of the revised manuscript.

Technical Corrections:
The allocation of CMAQ version numbers is somewhat confusing. Is v4.7 the same as v4.6c ?

Sorry for the confusion. As mentioned on p. 1341 (lines 2-4), CMAQv4.7 contained numerous model updates in addition to those that are the focus of this study. Since isolating the impacts of the model updates under consideration is not possible with CMAQv4.7, two non-standard versions of CMAQ (CMAQv4.6b and CMAQv4.6c) were developed and used here. This issue is clarified in the "CMAQ model versions" section (Section 2.4) of the revised manuscript.

An additional column with model results (no skill scores) from v4.6 in Table 2 would be useful.

Good point. Actually, a column with CMAQv4.6 results would be misleading in Table 2, because the CMAQv4.6 simulation only covered 1-15 May 2002, whereas the v4.6b and v4.6c simulations covered all of May. However, a table comparing results of all models with observations for 2-15 May 2002 has been included in the article supplement. This table highlights the improved performance of v4.6c and v4.6b compared

with v4.6. The table is cited in the revised manuscript in Section 4.1.

References:

Binkowski, F., and Shankar, U.: The Regional Particulate Matter Model 1. Model description and preliminary results, J. Geophys. Res., 100(D12), 26191-26209, 1995.

Reff, A., Bhave, P. V., Simon, H., Pace, T. G., Pouliot, G. A., Mobley, J. D., and Houyoux, M.: Emissions Inventory of PM2.5 Trace Elements across the United States, Environ. Sci. Technol., 43(15), 5790–5796, 2009.

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