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Interactive comment on "Modelling of nitrate particles: importance of sea salt" *by* G. Myhre and A. Grini

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General Comments This is an interesting analysis and the subject matter is appropriate for publication in ACP. However, my review of the manuscript raised substantive questions about the approach for parameterizing phase partitioning, treatment of internal versus external mixing, and associated interpretation of results (detailed below). These issues should be addressed before the manuscript is reconsidered for publication. The manuscript also contains several grammatical and spelling errors that should be corrected. Specific Comments Title. This investigation focuses primarily on multiphase chemical interactions between the cycling of NH3 and HNO3 and their associated influences on radiative transfer. The effects of sea salt are interesting but seem somewhat peripheral to much of the analysis. As such, the authors may wish to consider revising the title. Title and elsewhere in the manuscript. Globally, aerosol mass is seldom dominated by nitrate. In addition, all aerosols are chemically coupled through interaction with the same gas phase and different aerosol types are mixed together during cloud processing. Consequently, virtually all individual particles in the atmosphere exist as internal mixtures of multiple components. As such, terms like “nitrate particles (or aerosols),” and “ammonium nitrate particles” seem inappropriate. I encourage the authors to consider using more representative characterizations such “particulate nitrate” or “nitrate and ammonium-containing aerosols.”

Response: We thank for the constructive and useful comments that we feel have improved the manuscript. The method for our treatment of particulate nitrate is better described in our revised manuscript and a new subsection is included in section 2. Title is changed. We have changed nitrate particles to particulate nitrate

Page 1456, lines 23-24. The authors should specify whether this range in percentage contributions of NO3- to aerosol mass corresponds to dry or ambient (including water) mass.

Response: It is now stated that this is relative to dry mass

Page 1457, line 10. The indicated classes of aerosols should not be characterized as “non volatile.” For example, as discussed later in the manuscript, acidification of seasalt aerosol leads to significant loss of sea-salt Cl- via HCl volatilization. Some organic compounds also partitioning significantly between phases.

Response: Non volatile is deleted

Page 1458, lines 16-18. The meaning of this sentence is not clear. How do “heterogeneous reactions” lead to “lower sulfate amount?” Do these processes slow production of particulate SO42- or accelerate its deposition to the surface? Some clarification would be helpful here.

Response: The sentence is clarified and extended by including. ‘The lower sulphate was a result of heterogeneous reaction that reduced SO2.’

Page 1460, lines 1 to 5. It seems likely that the factor used to weight NH3 emissions would significantly influence simulated results. What is the basis for characterizing this weighting factor as “tuning”? Do observations support the authors’ implication that the weighting factor of 4 used by Adams et al. substantially overestimates the seasonal cycle or, alternatively, that a weighting factor of 1 as used by the authors is more representative? How sensitive are the simulated results to this factor?

Response: The word tuning is deleted and we have included the following sentence. “The choice of seasonal cycle largely influences the results since in our model nitrate mostly forms in winter when it is cold, and therefore more emissions in winter gives more aerosol nitrate. To our knowledge, no global emission dataset with NH3 with a seasonal cycle exist.”

Page 1460, lines 9 through 23. The characteristics of the “fine” and “coarse” modes should be described. For instance, what is the size discrimination between modes?

Response: The following sentence is added. The fine mode particles have a standard accumulation size (section 2.3) whereas the coarse mode follows the size distribution of sea salt with most of the mass above radius of 1 m.

Page 1460, lines 13-14 and elsewhere in the text. Suggest changing “controlled by sulfate” and “controlled by sea salt” to “comprised of ...”

Response: The comment is taken into account

Page 1460, lines 24-25. This point should be clarified. It appears that the approach is based on the assumption that all H2SO4 produced via photochemistry condenses into the preexisting accumulation mode aerosol. If so, it should be pointed out that, under some conditions, this approximation overestimates the amount of fine-mode H2SO4, substantially. For example, the dry-deposition flux of non-sea-salt SO42- in marine regions is dominated by the “coarse”, short-lived, sea-salt size fractions [e.g., Huebert et al., 1996]. How sensitive are the simulated results to this apparent overestimate in the source of fine-mode H2SO4?

Response: A new paragraph is included on this aspect

Page 1461, line 3. Ammonium does not “neutralize” H2SO4. The text should be corrected. More generally, I am confused about exactly how these relationships were implemented in the model. At equilibrium, the phase partitioning of NH3 and HNO3 with deliquesced aerosol solutions is controlled by the thermodynamic properties of the system expressed as follows: KH1 Kb NH3g <-> {NH3aq} <-> {NH4+} + Kw/{H+} (1) and KH2 Ka HNO3g <-> {HNO3aq} <-> {NO3-} + {H+} (2)

where KH1 and KH2 are the temperature-dependent Henry’s Law constants in M atm-1 for NH3 and HNO3, respectively, Kb and Ka are the corresponding dissociation constants in M, and Kw is the ion product of water in M. (Note that the constants in the above expressions should appear above the equilibria arrows; they changed when the file was uploaded.) The sources of H+ (e.g., H2SO4 or other acids) are not directly relevant to this evaluation. The phase partitionings of both NH3 and HNO3 are pH dependent. For a given set of conditions, as H+ increases, relationship 1 shifts to the right (increasing particulate NH4+ concentration) and relationship 2 to the left (decreasing particulate NO3- concentration). In addition, aerosol solutions equilibrate with both gases simultaneously. Available evidence based on observations and thermodynamic considerations indicates that under most conditions in the planetary boundary layer 1) aerosols are acidic (or rapidly acidified) and 2) at equilibrium, finite amounts of gaseous NH3 and HNO3 and particulate NH4+, NO3-, and H+ exist simultaneously [e.g., Chameides and Stelson, 1992; Dennis, 1997; Erickson et al., 1999; Lefer et al., 1999; Lefer and Talbot, 2001; Keene et al., 2004; and references therein]. As such, I do not understand the statements (lines 3-4) suggesting that NH3 preferentially “neutralizes H2SO4” or that “excess NH3” condenses onto aerosols in association with HNO3. These statements should be clarified, the actual mechanism for evaluating the equilibria described more explicitly, and the associated assumptions justified. As written, it does not appear that the approach used to simulated phase partitioning in the model

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was based on thermodynamic equilibria as suggested earlier in the manuscript (page 1456, line 2 and page 1459, lines 19-26). Rather the text implies that partitioning was simply prescribed based the assumptions that 1) H2SO4 is preferentially neutralized by available NH3, 2) any remaining ("excess") NH3 reacts with HNO3 to form "fine" particulate NH4NO3 in association with preexisting aerosol and, 3) in the presence of sea salt, all residual HNO3 is scavenged. None of these assumptions are valid. Since this parameterization is central to the analysis but apparently not based on thermodynamic relationships, the representativeness of simulated phase partitioning should be assessed explicitly over a range of conditions. I would encourage the authors to add a multi-panel figure that depicts the simulated phase partitioning of NH3 and HNO3 in near-surface air at several regionally representative locations (e.g., remote terrestrial, polluted terrestrial - both industrial and agricultural, remote marine, polluted marine) at which multi-phase measurements are available for comparison/validation. If phase partitioning is not representative, which based on the above seems likely, then the related implications for the reliability of the global simulations and associated interpretations should be addressed.

Response: A new subsection is included to better describe the method and a new figure with comparison to observations is included.

Page 1461, lines 7-9. This relationship should be expressed as an equilibrium not a directional reaction. Also, the second sentence starting on line 8 should be changed from "This formulation avoids the formation of stable Na2SO4 ..." to "This formulation ignores the formation of ..."

Response: Comment taken into account

Page 1461, line 14. This statement is incorrect. HNO3 partitions with acidic aerosol based on 2 above. It is evident from relationship 2 that solubility increases with decreasing acidity but "excess NH4+" is not required for significant HNO3 to condense into acidic "fine" aerosol size fractions. This statement implies that HNO3 will condense only into circum-neutral aerosol solutions, which is clearly not consistent with either observation or expectations based on thermodynamic properties.

Response: We explain the thermodynamical principles used in EQSAM in a new section 2.2

Page 1461, lines 17-19. This statement is also incorrect. At equilibrium, significant HNO3 vapor exists in association with acidified sea-salt aerosol [e.g., see papers cited above and references therein].

Response: We corrected the statement to: NaNO3 is assumed to be more stable than NaCl so that any excess HNO3 after the fine mode equilibrium is available for equilibrium partitioning to the coarse mode containing sea salt

Page 1462, lines 3 to 14. In the preceding section (page 1461, lines 3-4), the authors imply that NH3 and HNO3 condense "on the small particles," which would be consistent with expectations under most ambient conditions. However, in this (and subsequent) section(s) it appears that NH4NO3 is treated as a population of externally mixed and chemically distinct particles. The phase partitioning of HNO3 and the degree of internal versus external mixing of particulate NO3- with S aerosol will substantially influence associated effects on radiative transfer. If all "fine" NO3- is externally mixed as apparently assumed in the authors' analysis, then the actual radiative effects may be substantial. Conversely, if most NO3- is internally mixed with S or sea-salt aerosol and/or remains in the gas phase as HNO3 until deposition (which is typical of many regions, see papers cited above), then the influence will likely range from minor to negligible. This important issue should be addressed.

Response: The following sentences are included: We assume in the optical property calculations that the fine mode nitrate particles are external mixtures. However, the more realistic situation with internal mixture with other scattering aerosol components in the fine mode would only to a small extent influence the optical properties. Such an internal mixture would impact the hygroscopic growth and could impact the size of the particles, where the latter is shown to be a small effect as long as the particles are fine mode (Myhre et al., 2004). Our approach with distinct classes for fine and coarse mode particulate nitrate is important with respect to that we can distinguish their optical properties which are quite different for fine mode nitrate and sea salt containing nitrate particles.

Page 1462, lines 13-14. It would be helpful for the authors to briefly compare hygroscopic properties inferred from the rather dated formulations of Fitzgerald [1975] (as implemented in their model) with those based on more recent work [e.g., Tang and Mulkelwitz, 1994; Tang, 1997].

Response: It is earlier shown that the hygroscopic growth described for sulphate in (Fitzgerald, 1975) is within 2-3% of using the Köhler equation with respect to radiative forcing due to sulphate (Myhre et al., 2004).

Figure 1. As I understand, the formation of “fine” particulate NO3- in the model requires that all acidity associated with “fine” S aerosol must first be completely neutralized by NH3, which then allows the formation of “fine” NH4NO3 to proceed. However, a large body of information indicates that sub-μm aerosol size fractions over most of the eastern US are highly acidic most of the time and that sub-μm particulate NH4+ and non-sea-salt SO42- are generally present in molar ratios of about 1:1 [i.e., as NH4HSO4 not (NH4)2SO4] (see papers cited above). Consequently, the substantial concentrations of “fine” particulate NO3- simulated over the eastern US as depicted in Figure 1 would appear to be inconsistent with the production pathway used in the model. This important inconsistency should be addressed.

Response: We have added the following text to respond to this: We obtain annual average concentrations of approximately 1-2 ug/m3 nitrate close to the surface in the eastern US. Measurements (e.g. Lefer and Talbot, 2001) indicate that this area mostly contains acidic aerosols and therefore, fine mode nitrate should not be important in our model in this region. We explain this by noting that this is annual average concentrations. Even though on average, the aerosols in the eastern US are acidic, there are probably days where total ammonia concentrations are high. We also note that aerosol nitrate can form in our model even though the aerosols are not completely partitioned to (NH4)2SO4, in particular at cold temperature (see section 2.2)

Page 1465, lines 13-14. Units used elsewhere in the text are based on mass per unit volume. This relationship corresponds to molar ratios. The text should so indicate.

Response: It is stated that ’molar units’ are used

Page 1465, lines 15-18. Presumably the authors are referring here to particulate ammonium not particulate ammonia. The text should be clarified.

Response: Corrected

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 1455, 2006.