

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

Anonymous Referee #3

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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

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Title. This investigation focuses primarily on multiphase chemical interactions between the cycling of NH_3 and HNO_3 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.”

Page 1456, lines 23-24. The authors should specify whether this range in percentage contributions of NO_3^- to aerosol mass corresponds to dry or ambient (including water) 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 sea-salt aerosol leads to significant loss of sea-salt Cl^- via HCl volatilization. Some organic compounds also partitioning significantly between phases.

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 SO_4^{2-} or accelerate its deposition to the surface? Some clarification would be helpful here.

Page 1460, lines 1 to 5. It seems likely that the factor used to weight NH_3 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

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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?

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?

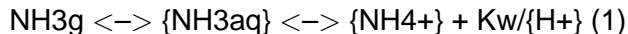
Page 1460, lines 13-14 and elsewhere in the text. Suggest changing “controlled by sulfate” and “controlled by sea salt” to “comprised of ...”

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?

Page 1461, line 3. Ammonium does not “neutralize” H₂SO₄. The text should be corrected.

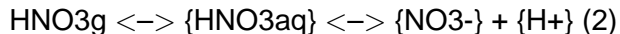
More generally, I am confused about exactly how these relationships were implemented in the model. At equilibrium, the phase partitioning of NH₃ and HNO₃ with deliquesced aerosol solutions is controlled by the thermodynamic properties of the system expressed as follows:

KH1 Kb



and

KH2 Ka



where $KH1$ and $KH2$ are the temperature-dependent Henry's Law constants in $M \text{ atm}^{-1}$ for NH_3 and HNO_3 , respectively, K_b and K_a are the corresponding dissociation constants in M , and K_w 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., H_2SO_4 or other acids) are not directly relevant to this evaluation. The phase partitionings of both NH_3 and HNO_3 are pH dependent. For a given set of conditions, as H^+ increases, relationship 1 shifts to the right (increasing particulate NH_4^+ concentration) and relationship 2 to the left (decreasing particulate NO_3^- 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 NH_3 and HNO_3 and particulate NH_4^+ , NO_3^- , 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 NH_3 preferentially "neutralizes H_2SO_4 " or that "excess NH_3 " condenses onto aerosols in association with HNO_3 . 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 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) H_2SO_4 is preferentially neutralized by available NH_3 , 2) any remaining ("excess") NH_3 reacts with HNO_3 to form "fine" particulate NH_4NO_3 in association with preexisting aerosol and, 3) in the presence of sea salt, all residual HNO_3 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 NH_3 and HNO_3 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.

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 Na_2SO_4 ...” to “This formulation ignores the formation of ...”

Page 1461, line 14. This statement is incorrect. HNO_3 partitions with acidic aerosol based on 2 above. It is evident from relationship 2 that solubility increases with decreasing acidity but “excess NH_4^+ ” is not required for significant HNO_3 to condense into acidic “fine” aerosol size fractions. This statement implies that HNO_3 will condense only into circum-neutral aerosol solutions, which is clearly not consistent with either observation or expectations based on thermodynamic properties.

Page 1461, lines 17-19. This statement is also incorrect. At equilibrium, significant HNO_3 vapor exists in association with acidified sea-salt aerosol [e.g., see papers cited above and references therein].

Page 1462, lines 3 to 14. In the preceding section (page 1461, lines 3-4), the authors imply that NH_3 and HNO_3 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 NH_4NO_3 is treated as a population of externally mixed and chemically distinct particles. The phase partitioning of HNO_3 and the degree of internal versus external mixing of particulate NO_3^- with S aerosol will substantially influence associated effects on radiative transfer. If all “fine” NO_3^- is externally mixed as apparently

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assumed in the authors' analysis, then the actual radiative effects may be substantial. Conversely, if most NO_3^- is internally mixed with S or sea-salt aerosol and/or remains in the gas phase as HNO_3 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.

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].

Figure 1. As I understand, the formation of "fine" particulate NO_3^- in the model requires that all acidity associated with "fine" S aerosol must first be completely neutralized by NH_3 , which then allows the formation of "fine" NH_4NO_3 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 NH_4^+ and non-sea-salt SO_4^{2-} are generally present in molar ratios of about 1:1 [i.e., as NH_4HSO_4 not $(\text{NH}_4)_2\text{SO}_4$] (see papers cited above). Consequently, the substantial concentrations of "fine" particulate NO_3^- 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.

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.

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

Cited Literature (not referenced in the manuscript)

Chameides, W. L., and A. W. Stelson, Aqueous-phase chemical processes in deliquescent sea-salt aerosols: A mechanism that couples the atmospheric cycles of S and sea

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