

# ***Interactive comment on “Evaluating Secondary Inorganic Aerosols in 3-Dimensions” by K. Mezuman et al.***

**K. Mezuman et al.**

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We would like to thank the referees for the comments and review of our paper.

Response to Referee #1:

General comments The authors reported a comprehensive comparison of secondary inorganic aerosols between the model results and measurements. The sensitivities to aerosol configurations and agricultural ammonia emissions were explored. The results shown in this paper are interesting. However, the treatment of the NH<sub>3</sub>/NH<sub>4</sub> partitioning is too simplified in the model, and more advanced techniques have been applied in global models. Even though the authors confirm that the heterogeneous chemistry on dust is important sink for nitric acid, this is ignored for the simulations with the microphysical scheme. Consequently, the simulations with the microphysical scheme

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worsen the agreement of nitric acid. I think that the paper needs substantial work to be published in ACP. 1. ‘... the treatment of the NH<sub>3</sub>/NH<sub>4</sub> partitioning is too simplified in the model, and more advanced techniques have been applied in global models.’

EQSAM (Metzger et al., 2002a, 2002b) and ISORROPIA-II (Fountoukis and Nenes, 2007) are widely used thermodynamic schemes, both as modules in other models (Pletier et al., 2007, Aan de Brugh et al., 2012 Athanasopoulou et al., 2013, Metzger et al., 2015, Weber et al., 2016, to name a few) and as reference models for newly developed thermodynamic modules (e.g. Hauglustaine et al., 2014, Snider et al., 2016). They are considered state-of-the-art, and are among the most advanced techniques applied in global models to date, the opposite of simplified.

2. ‘Even though the authors confirm that the heterogeneous chemistry on dust is important sink for nitric acid, this is ignored for the simulations with the microphysical scheme.’

As seen in Figures 7 and A2 (third column), the difference in the vertical profile of nitric acid between MATRIX and OMA is mostly apparent at the higher levels of the atmosphere at the ATCTAS, ARCPAC (ARC) and CALNEX, INTEX-B (WUSA) campaigns. The difference equals the sum of nitric acid and nitrate on dust. OMA appears to be closer to measurements, partially because of the heterogeneous loss of HNO<sub>3</sub>. However, this loss is insufficient to explain the discrepancy between the model and measurements. Of course, heterogeneous uptake on mineral dust, and other surfaces is an important pathway, and thus we have included it in the OMA model many years ago Bauer et al, 2005. A later version of MATRIX might include these processes as well, but this is not the focus of this paper, as it evaluates the schemes as they are and investigates the differences between OMA and MATRIX and EQSAM and ISORROPIA. Currently we further develop volatile organics in the MATRIX scheme, after that we will decide how much more detail we will include in the nitrate simulation. This study clearly showed that more development is necessary. We added the following sentence to line 324: “However, this loss is insufficient to explain the discrepancy between the

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model and measurements.” And to line 409: “A more complex version of MATRIX, that currently does not exist, should include heterogeneous uptake on dust.”

Specific comments 3. p.1, l.19: ‘The higher mass concentration of sulfate with the microphysical scheme improved the agreement in summer when underestimated, but not in winter. It is not clear whether this scheme can improve mass concentration of sulfate significantly. Please clarify if the improvement is statistically significant.’

As discussed in the paper, in all of the sulfate profiles except for ACE-ASIA and MILAGRO-MIRAGE, regardless of season, the microphysical scheme agrees better with the measurements (Figure 7, Figure A2, and Figure A3). The same is observed at surface (Figure 4), with higher concentrations simulated by the microphysical scheme. As shown in the manuscript, the correlation coefficient calculated from all available data improves the results for EUSA from 0.63 (OMA) to 0.76 (MATRIX). The points the reviewer makes regarding the sulfate seasonality refers to EUSA sulfate in Figure 6, where MATRIX does not improve the winter overestimation of OMA, which might depend more strongly on precursor levels but significantly improves the summer underestimation (by about  $1 \mu\text{g m}^{-3}$ ).

4. p.1., l.24: ‘Why do you ignore the heterogeneous chemistry on dust with the microphysical scheme, even though this is important sink for nitric acid? ‘

MATRIX does represent the mixing state of aerosols population, but it does not track the  $\text{NO}_3$  and  $\text{NH}_4$  tracers for the aerosol populations. In that sense it is a simplified representation of nitrate mixing state. However in a future version of the model we might integrate that pathway, but the current setup of the model does not allow that. Also please refer to answer #2.

5. p.l., l.25: ‘The model overestimated ammonia concentration. Please rephrase this (see comment on p.16, l.338).’

Please refer to answer #11. We decide to stick to our current phrasing in p.1 l.25.

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Overestimating ammonia does not mean that the area can't be ammonia limited, which that depends on other factors such as sulfate concentration.

Model description 6. p.4, l.81: 'Please explain the correction clearly. ' This was essentially a bug fix, related with the effective solubility of ammonia. In short we were using the Henry value for ammonia, not the effective Henry value, which resulted in large abundances of ammonia, hence ammonium, hence nitrate. We added to p.4, l.82 the following: "The model was using the Henry value of ammonia instead of the effective Henry value, which resulted in large abundances of ammonia, hence ammonium, hence nitrate."

7. p.4, l.88: 'In Bauer et al. (2007), the heterogeneous uptake is taken place on the four size bins. Please describe the five size bins and the reason of the changes.'

Coating takes place on three of the smallest size bins. This was changed after Bauer et al., 2007 where dust was represented in 4 size classes, and coating on all classes was tracked. We don't calculate anymore the coatings on the large particles as its amounts are negligible. We added the following to p.4, l.93: "This was changed after Bauer et al., 2007 where dust was represented in four size classes, and coating on all classes was tracked."

Results and discussion 8. p.10, l.213: 'Please explain how the changes in size distribution of sulfate lead to longer lifetime of sulfate. Please also explain why the changes in solubility do not matter.'

We have not addressed the solubility of sulfate, which does matter. We have changed that paragraph as follows, to address this comment: "... This result is due to the microphysical processes included in MATRIX (i.e. nucleation, condensation and coagulation), which allow for aerosols to spread over the entire size distribution, including the existence of smaller particles (the freshly nucleated ones). Additionally, the solubility of sulfate in MATRIX is calculated as a weighted average of the internally mixed particle component's solubility (SO<sub>4</sub> mixed with dust, BC, etc.), and is always less than the

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pure SO<sub>4</sub> solubility in OMA. The differences in both size and solubility lead to a longer lifetime of MATRIX sulfate, thus increasing the aerosol mass . . .”

9. P.11, I.235: ‘How is the existence of smaller particles with longer lifetimes related to more pronounced peak in summer? In other words, how do you explain lower sulfate with the microphysical scheme in winter?’

The variation in sulfate lifetime is more pronounced in MATRIX compared to OMA. MATRIX does include nucleation and the growth of nano-particles into accumulation sizes. Further microphysical processes like condensation and coagulation leads to the presence sulfate spread over the entire size distribution, from ultra-fine to coarse. However the presence of sulfate in smaller sizes leads to the prolonged lifetime of sulfate in MATRIX, and thus higher loads. For example for the year 2005 the lifetime in January is: 3.8 days (MATRIX configuration) and 3.1 days (OMA), but in July it is: 4.2 days (MATRIX configuration) and 3.2 days (OMA).

10. p.14, I.302: ‘Shindell et al. (2006) discussed the nitric acid simulations performed with and with- out the inclusion of heterogeneous chemistry on dust, and for a run without the use of the liquid tracer budget. They also noted, “The model’s stratosphere-troposphere exchange (STE) agrees well with values inferred from observations for both the global mean flux and the ratio of Northern (NH) to Southern Hemisphere (SH) downward fluxes”. It is not clear whether the overestimate of nitric acid is due to too strong stratosphere-troposphere exchange. Please show the flux and the sensitivity to it.’

We fixed our statements: p.15, I.317: “HNO<sub>3</sub> overestimated at high altitudes is consistent with Figure 10 from Shindell et al., 2006.” We also deleted from: p.1, I.24 the following: “influenced by strong stratosphere-troposphere exchange” p.18, I. 408 the following: “the overestimation is attributed to too strong stratosphere-troposphere exchange”

11. p.16, I.338: ‘We know that the treatment of the NH<sub>3</sub>/NH<sub>4</sub> partitioning is too simpli-

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fied in the model, and the model overestimates NH<sub>3</sub> concentrations with the standard NH<sub>3</sub> emissions. Why do you need to show the model-measurement comparison for implausible case? This should be moved to the Supplement and replaced by improved simulation, as is outlined in conclusions. ‘

Please refer to answer #1 for a discussion on the thermodynamic schemes, where we explain why our partitioning is not simplified. The sensitivity tests presented in the paper simulate the response of ammonium nitrate to changes in ammonia emissions. We study the sensitivity of the system to such changes compared to our base case of model with normal emissions, and present day measurements. Our motivation was to study whether adding more NH<sub>3</sub> in the system enhances both NH<sub>3</sub> and NH<sub>4</sub> or just NH<sub>4</sub> and conclude whether the system is NH<sub>3</sub> sensitive or saturated.

Response to Referee #2:

General Comments: In “Evaluating Secondary Inorganic Aerosols 1 in 3-Dimensions”, the authors compare surface and aircraft measurements to model predictions for the regional and vertical distribution of secondary inorganic aerosols. The NASA GISS ModelE2 model predictions used a combination of two aerosol microphysics configurations and two computationally efficient thermodynamic models (EQSAM and ISOR-ROPIA II). The paper is somewhat similar to Bauer et al. 2007 for nitrate aerosols, extending that work to include the more aerosol configurations, and the additional inorganic aerosol measurements. The results, including a systematic underestimation of ammonium and nitrate for all configurations, likely due to the simplified treatment of ammonium – ammonia partitioning, are of importance to the atmospheric science community. Overall, it is a valuable study, and publication is recommended after addressing the points below.

Specific Comments: 12. ‘Line 81 – how has the nitrate scheme been corrected? Please add more information here.’

Please refer our answer #6 to the first referee.

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13. 'Line 379-382 – please elaborate. Why would temperature and RH not be a dominant factor?'

Temperature and RH are important factors for thermodynamic calculations, however, since the simulations are nudged they exhibit similar environmental parameters, which do not play an important role in the difference between the results.

14. 'Line 397 – why was the pH examination not presented? It is important to this work, and should be included, at least in the supplement material.'

The pH examination is very important, and is not a minor supplemental material. It is a topic by itself that does not fit the scope of this paper, and will be submitted to publication soon.

Technical Corrections: 15. 'Consider use of different symbols, in addition to different colors, for Figure 4. Likewise, please use different line types, in addition to different colors, for Figures 5, 6, etc.'

We have emphasized the continental boundaries in Figures 1 and 2 and have corrected a typo in Figure 4.

16. 'Finally, there are some minor errors in the references and the in-text citations that should be addressed.'

We could not find the minor errors in the text that were not specified by the referee.

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