

Anonymous Referee #2

Received and published: 12 May 2020

Hrdina et al. present an interesting, although circumstantial, case for the importance of coarse particles as a sink of HNO_3 in the wintertime in the Salt Lake Valley (SLV). The authors do not have direct measurements of coarse particle composition, but make use of $\text{PM}_{2.5}$ composition measurements, coarse particle size distributions, and snowpack chemistry to make a case for reactive uptake of HNO_3 on coarse particles influencing the budget of HNO_3 in the SLV and associated implications for fine particle chemistry. The manuscript is overall well written and most of the analyses presented sound. Some of the authors' planned measurements have missing data (e.g., the $\text{PM}_{2.5}$ an-ions during the main PM episode studied). This, along with the absence of any coarse particle PM composition measurements, however, makes it difficult to constrain the problem well. This is compounded by issues with how snowpack chemistry is used (incorrectly, I believe) to quantify the amount of total nitrate in the atmosphere and the impacts of coarse particle reactive uptake of HNO_3 on submicron NH_4NO_3 formation.

My specific comments follow:

1. p.2, line 27: I think it is fairer to say that automotive and industrial processes have increasingly been recognized as important ammonia sources in urban areas.

The role of these sources in urban areas has been added to the manuscript.

2. p. 5, line 31: the authors need to justify their choice of a density of 1.0 g/cm^3 for coarse particles in calculating mass concentrations from APS measurements. This is quite low for typical coarse particle types, including the sea salt and dust considered in this manuscript.

The reviewer is correct. Typically, you would assume a density of approximately 2.0 g cm^{-3} . For example, Peters (2006) applied simple assumptions of shape factor and density (shape factor = 1.4, density = 2.0 g cm^{-3}) to estimate the mass concentration of ambient coarse mode particulate ($\text{PM}_{10-2.5}$) with data from the Model 3321 APS. These estimates compared well with collocated, time- integrated filter based federal reference method (FRM) samplers in Phoenix (AZ) and Riverside (CA).

For this study, a constant density of 1.0 g cm^{-3} was assumed in the Stokes number calculation, as a standard commonly used. The universal APS response function is applicable in most cases. However, if the particle density is greater than 2.0 g cm^{-3} , Wang and John (1987) found particle density affected the APS measurement. We believe thus, this assumption is valid for a surface area calculation.

In the later part of the analysis in which we make a mass balance estimate of the total amount of calcium nitrate that could be present in the coarse mode, we have modified the calculation to take into account the actual density of calcium nitrate (2.5 g cm^{-3}). As this was only an illustrative calculation, it does not change the interpretation presented in the manuscript.

References:

Peters T.M. (2006). "Use of the Aerodynamic Particle Sizer to measure ambient PM_{10-2.5}: The coarse fraction of PM₁₀." *Journal of Air and Waste Management Association* 56:411-416.

Wang, H.-C., and John, W. (1987). Particle Density Correction for Aerodynamic Particle Sizer, *Aerosol Sci. Technol.* 6:191–198.

3. p. 8, lines 16-18: the authors should provide information about the types of road de-icers used in the area surrounding their measurement site and whether they change as a function of forecast temperature. Many liquid de-icers commonly used in parts of the Rocky Mountain west include Ca or Mg. Are these used in Salt Lake City, on the UU campus? Do they change between conventional salt and liquid de-icers depending on temperature?

According to the state department, brine solution is often used before snow events as a preventative measure and solid road de-icers are generally used after, however, we could not obtain specific information about the de-icers used by the city and the UU campus. Local media reports suggest that over the last few years, ammonium nitrate deicer has been replaced with sodium acetate and sodium formate salts. In the absence of official information, we are not adding any details to the manuscript.

4. The analysis of reactive uptake lifetimes for HNO₃ on p. 10 is quite interesting. The authors should extend this analysis to consider the relative HNO₃ sink rates for NH₄NO₃ formation vs. reactive coarse particle uptake.

The rate at which HNO₃ collides with fine mode particles (predominantly composed of NH₄NO₃) is certainly faster than with the coarse mode particles, but the HNO₃-NH₃-NH₄NO₃ system is assumed to be in equilibrium, so the net uptake, or loss, of HNO₃ to NH₄NO₃ is zero. In the case of coarse particles, the loss of HNO₃ to reactive salts is permanent. Therefore it makes more sense to limit this loss rate analysis to the coarse mode particles.

5. p. 11, lines 8-17: The authors here focus discussion on prior work concerning coarse particle uptake of HNO₃ in coastal environments. This is interesting and relevant, but they should also cite observations of uptake in more continental environments which might be better models for the SLV. Lee et al. (doi:10.1016/j.atmosenv.2007.05.016), for example, examine the importance of coarse particle nitrate at both interior and coastal U.S. environments.

We have incorporated the suggested reference into the text commenting on the few studies that have speciated coarse nitrate. Lee et al. identify that coarse mode nitrate particles, formed from acid displacement, were more important in national parks areas in Arizona and Tennessee. Measurements at both sites were during Spring and Summer, respectively, so did not have competing NH₄NO₃, but they do highlight the fact coarse particle nitrate extend into the PM_{2.5} size regime and not all nitrate in this regime is associated with NH₄.

6. I have serious reservations about how the authors use snowpack chemistry observations to constrain atmospheric levels of total nitrate. As discussed in the manuscript, falling snow composition reflects some combination of in-cloud and below-cloud scavenging processes. The composition of snowpack on the ground is further affected, over time, by accumulated

dry deposition. If one hypothesizes that significant nitrate is present in reacted coarse dust or salt particles, this coarse particle nitrate can be effectively scavenged by falling snow (coarse particle scavenging efficiencies are much higher than scavenging efficiencies for accumulation mode particles) and is also very effectively deposited to snowpack on the ground by dry deposition via sedimentation of these large particles. NH_4^+ particles, on the other hand, are submicron and thus have both lower scavenging efficiencies by falling snow crystals and much lower dry deposition rates to the surface than coarse nitrate particles. What this means is that a comparison of snowpack $\text{NO}_3^-/\text{NH}_4^+$ ratios is not at all representative of atmospheric concentration ratios of total nitrate/ammonium. The snowpack ratio, in the presence of coarse mode nitrate, will be significantly higher than is found in the ambient atmosphere. For this reason, the author's use of this snowpack ratio as a surrogate for what was in the atmosphere is incorrect and certainly biased high. Using this ratio to estimate the impact that eliminating coarse nitrate would have on $\text{PM}_{2.5}$ NH_4NO_3 formation will, therefore, lead to a significant overestimate. I honestly don't see how the authors can get around this limitation on the utility of the snowpack composition data. I think the fact that the $\text{NO}_3^-/\text{NH}_4^+$ ratio is elevated in the snowpack does help the authors make the case that coarse particle nitrate is present, but I do not see how they can properly extend the comparison to argue what the total nitrate/ammonia ratio is in the ambient atmosphere.

The reviewer raises some of the same concerns identified by referee #1 regarding the interpretation of the snowpack data. The reviewer is correct that the composition of the snowpack does not precisely and quantitatively reflect the relative abundance of the components in the atmosphere. It is true that the dry deposition and scavenging of coarse particles is faster than for fine particles, but not necessarily much faster than for the gas phase constituents. Also, during a snowfall event, the *efficiency* of scavenging may not be important if the scavenging is nearly complete.

In the absence of the ability to directly quantify coarse mode nitrate in the atmosphere, we use an approach that allows us to infer how much nitrate may be present as Ca or Na salts in the coarse mode. We agree with the reviewer that this approach likely reflects an upper estimate of its importance to the atmospheric burden (though not to the overall nitrate budget, since the deposition rate matters). Our subsequent simple analysis then examines how much additional NH_4NO_3 could have been formed if no reactive coarse particles had been present. We have amended the text to clarify this sensitivity test and to explain how this reflects an upper estimate, as pointed out by the reviewer.

7. Fig. 1: Suggest changing $\text{NH}_3(\text{g})$ and associated flux arrows to another color. The orange color used could be misinterpreted by the reader as related to daytime pathways per the description in the caption. 8. Panels (a) and (b) of Figure 2. I personally found it somewhat unhelpful to see the PM concentrations presented in mass units while the gas concentrations are given as mixing ratios. This makes it hard, for example, to compare relative amounts of gaseous and particulate NH_x in panel (a).

We have updated the figures as suggested.