

Interactive comment on “Interferences on Aerosol Acidity Quantification due to Gas-phase Ammonia Uptake onto Acidic Sulfate Filter Samples” by Benjamin A. Nault et al.

Anonymous Referee #1

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Nault et al. identify and characterize apparent artifacts associated with NH₃ uptake onto acidic aerosols collected on filters during aircraft campaigns. This is important work and certainly relevant and useful for readers of AMT. It should be pointed out, however, that their results are not terribly surprising. It has long been recognized that filter samples of acidic aerosol need to be protected from human breath and other sources of ammonia during handling and storage. The fact that some practitioners of aerosol sampling by filters in aircraft campaigns (where acidic aerosols are even more likely to be encountered than at the typically more ammonia-rich surface) have ignored these lessons outlined in the literature is unfortunate.

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I have several comments for the authors to consider in preparing a revised manuscript.

1. Abstract lines 45-47 and manuscript lines 376-379: the authors need to more fully specify the LOD they provide for filter sampling. This depends on a variety of factors, including sampled air volume and (depending on the stage where contamination occurs) filter extraction volume. At a minimum they should state their LOD estimate is appropriate for typical SAGA filter collection and extraction protocols.
2. Line 92: Please change “cations” to “anions.” Sulfate and nitrate are anions.
3. Lines 178-181: Can the authors exclude loss of NH₄⁺ volatiles from the warming/drying of the AMS sample stream as a cause of some of the difference vs. filter NH₄⁺ levels?
4. Lines 223-224: Plastics are common sources of NH₄⁺ contamination vs. offgassing of NH₃ adsorbed onto the plastic surface. Many researchers who are worried about artifact neutralization of acidity on aerosol filter samples use acid-coated substrates as NH₃ sinks inside bags or other containers used for sample storage. Did the authors evaluate the polyethylene bags as a potential source of contamination? Were acid scrubbers inserted into the bags to prevent such an artifact from offgassed NH₃?
5. Lines 225-226: I was shocked to see that collected filter samples were extracted with 20 mL of water. This represents a huge dilution when extracting a sample that has collected only 2-3 m³ of air. By diluting aqueous concentrations to low levels, any background NH₄⁺ in the extract solution has an outsize effect on raising calculated aerosol ammonium concentrations and the uncertainty associated with measuring low extract ion concentrations is also magnified. Can the authors justify this large extraction volume and assess possible contributions to the concluded artifacts in the filter samples? A modern conventional IC analysis needs only 20-100 μ L of injected volume (some capillary systems use far less) and even an autosampler can easily work with a total extract volume of several hundred μ L.

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6. Section 2.2.3. I am puzzled why the authors rely on PALMS data to get an independent (of AMS) estimate of online particle ammonium balance. The PALMS sulfate acidity indicator, as pointed out by the authors, is calibrated by comparison to PILS ion concentration ratios. The WINTER campaign flew with a PILS onboard. The authors should use that PILS ion balance directly rather than the PILS-calibrated PALMS data, which the authors point out can be influenced by changes in laser power. By its design and reliance on direct IC measurements of ion concentrations in aerosol extracts, the PILS should provide the most definitive measure of ratios of NH₄⁺ to SO₄²⁻.

7. Section 2.3.1. The FIREX campaign targeted smoke plumes. Biomass burning smoke can be very rich in NH₃. How much might penetration of smoky air into the aircraft cabin influenced the NH₃ concentrations measured there? The authors' air exchange measurements and calculated concentrations with assumed human NH₃ emission rates suggest that smoke NH₃ might not have been a major factor in determining cabin NH₃ concentrations. That surprised me!

8. Line 393: The filter storage bag here is specified to be Teflon vs. the polyethylene bag referred to earlier in the manuscript.

9. I like that the authors consider the timescale for diffusion to the collected aerosol particles in the filter. I do want to be sure they are calculating the timescale correctly. Can the authors please verify that the timescale expression they used (Eqn. 1) applies to a porous membrane? I am surprised that there is no dependence on pore size included. Also, what is the relevant timescale for NH₃ to diffuse into an acidic particle itself? It needs to do more than just reach the surface.

10. Pp. 26-27. The discussion of CSN and CASTNet NH₄⁺ differences is interesting, although other factors beyond those discussed are likely at play. Both filter sampling systems can lose volatile NH₄⁺ (e.g., NH₄NO₃). The degree of loss will increase in the denuded system as the equilibrium with the gas phase is strongly perturbed. Differences in sample handling, shipping, and storage may also be important.

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11. Lines 589-592: The authors' computed $0.2 \mu\text{g}/\text{m}^3$ threshold is relevant for the SAGA system as used here but should not be more generally claimed for other filter-based sampling approaches with different sample volumes. Post-collection NH₃ uptake will yield different impacts on ambient aerosol LODs in other systems.

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