

Interactive comment on “Eddy covariance measurements with high-resolution time-of-flight aerosol mass spectrometry: a new approach to chemically-resolved aerosol fluxes” by D. K. Farmer et al.

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We thank the referee for his/her insightful comments. Our responses are in plain text below, with the referee's comments italicized.

1. The authors speak of PM1 concentrations, fluxes, and deposition velocities. This is an oversimplification. Transmission efficiency curves for the standard AMS aerodynamic lens show a dropoff well below 1 micrometer. This is not clear in the manuscript.

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On p. 5872 the authors state that “The HR-AMS focuses particles in the 50-1000 nm size range into a narrow beam with an aerodynamic lens.” This issue needs to be clearly discussed in a revised manuscript and any implications for the authors' conclusions clarified. For example, actual PM1 fluxes of components may well exceed values reported here as PM1 fluxes, if size distributions of the discussed species extend much above 500 nm. Likewise, if particle deposition velocities are size-dependent, actual PM1 component deposition velocities may differ from those reported here.

We respectfully disagree with the referee that using AMS measurements to describe submicron (PM1) measurements is an oversimplification or misleading. While it is true that the transmission efficiency of the AMS is not a step-function (i.e., 100% for 0-1000nm particles, and 0% for anything higher), nor is this the case for other particle measurement systems. For example, most particle measurement systems use a cyclone to isolate submicron measurements; however, all cyclones show a collection efficiency that is a function of particle diameter, and is also not a 100% to 0% step-function - i.e., all other submicron particle measurements typically include some particles over 1000 nm, and exclude some fraction below (see, for example, the technical specifications of the 16.7 Lpm 1um cyclone, <http://www.urgcorp.com/assets/pdf/2000-30EHB.pdf>). Consistent with that, comparisons between the AMS and other accepted measurements of submicron aerosol typically show good agreement. For example, DeCarlo et al. (2008) show correlations between the AMS and an SMPS with a slope of 0.98 ± 0.01 . Thus, we feel that there is sufficient evidence in the published literature to justify our use of the term “NR-PM1” to describe the total signal observed by the AMS. However, to make clear that the transmission efficiency for the AMS that is a function of size, we have added the following text to describe these effects: “The size range measured by the HR-AMS is determined by the transmission efficiency of the lens, and depends on aerodynamic lens design and operating pressure. However, comparisons between the AMS and other accepted measurements of submicron aerosol typically show good agreement. For example, DeCarlo et al. (2008) show correlations between the AMS and an SMPS with a slope of 0.98 ± 0.01 , suggesting that AMS measurement

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can be considered non-refractory PM₁.”.

2. P. 5872: *Please elaborate on the system flow control. Since the residence time in the long sample tube is critical to properly pairing concentration and velocity fluctuations, we need to know how (and how well) the sample flow rate was maintained.*

The sample flow was maintained by pumps, with flow controlled by critical orifices. The flows were monitored and recorded by digital TSI flow meters, and found to be constant through the campaign. We will add additional details regarding flow control to the manuscript.

3. *Have particle losses through the sample system been characterized? How do these affect reported fluxes or deposition velocities?*

Losses through the sample system were estimated based on flow rates and tube dimensions, and were estimated to be negligible (<5%) for the size range of the AMS for the BEARPEX conditions. We have added a sentence explaining this point to the manuscript.

4. P. 5880, line 18: *What do you mean by “particle flux measurements are LIMITED by particle counting statistics?”*

While the mass spectrometer measurements are taken rapidly, they rely on measurements of particles – which, unlike gas phase molecules, are not necessarily entering the instrument nearly continuously. This effect is typically considered to be a dominant source of error for particle flux measurements, and has been well-documented in previous publications (e.g. Nemitz et al., 2008, Pryor et al. 2008). We will reword this sentence to clarify the point.

5. P. 5884, lines 3-4: *The authors state that “: : a non-unity slope can be interpreted as the uncertainty in sulphate deposition velocity.” Please explain what you mean by uncertainty. Uncertainty is often used to imply precision, but the slope of this relationship really tells us little about measurement precision. It would seem to be more a*

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measure of bias between two methods although, given that neither method is known to give a true value, it is also unclear whether the slope necessarily implies anything about accuracy.

The reviewer is correct that by uncertainty, we are referring to potential systematic errors (i.e., bias) – we will reword this section to clarify the point.

The same comment applies to lines 14-15 of p. 5885.6. Section 5.2: Do the authors have any evidence whether ammonium oxalate is an important component of the ammonium budget at the BEARPEX site? If it is, this could affect some of the tests the authors invoke (e.g., ammonium vs. anion charge balance). Malm et al. (2005) found that summertime oxalate concentrations at another Sierra Nevada foothills site in Yosemite National Park were high enough to noticeably influence the fine particle charge balance.

This is an interesting point that we had not considered. Malm et al. (1995) observed fine aerosol composed of NH₄NO₃ (6%), NaCl (2%), (NH₄)₂SO₄ (83%), and a remaining 9% that was potentially NH₄oxalate. Ammonium oxalate is a potential component of the ion balance at BEARPEX, as the measured anion concentrations (sulphate, nitrate, chloride) are extremely close, but not identical nor without uncertainty (slope = 0.94, r² = 0.92), to the cation concentration (ammonium). This leaves room for a few percent of the measured ammonium to be associated with oxalate, which is not inconsistent with Malm et al. (2008). Positive bias of the AMS total anions from AMS inclusion of organic nitrates and organic sulphates (Farmer et al., PNAS 2010; Docherty et al., ACPD 2011) could provide some room for additional contributions of ammonium oxalate to the ion balance, again of the order of several percent. We have added the following text to discuss this point in the manuscript: “The small discrepancy between the anion and cation balance may be due to ammonium oxalate, which has been observed in a higher elevation site in the Sierra Nevada (Malm et al., 2005). ”.

7. P. 5889, lines 14-15: *The statement about ammonia concentrations being too low*

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to support ammonium nitrate formation at the site is too strong. Perhaps the authors mean to say that concentrations are too low to support very much ammonium nitrate formation. 1-2 ppb of ammonia can certainly result in some ammonium nitrate formation, depending on T, RH, and HNO₃ concentrations.

We have reworded this section in the revised manuscript to read “NH₃(g) concentrations are too low at this site (<1-2ppb) (Fischer et al., 2007) to support substantial NH₄NO₃ production with the warm daytime temperatures and low humidity present at the site”.

8. P. 5890, line 9: These are the first direct eddy covariance observations of particulate ammonium deposition over a forest.

We are unaware of other *direct* flux measurements of particulate ammonium over forests, whether by eddy covariance or other methods, and will welcome direction to appropriate references. In the absence of additional input, we will keep this text as is.

9. Fig. 2 caption: The term nitrate equivalent mass concentration is likely to confuse readers not intimately familiar with terminology used in the AMS user community. The meaning of this set of units should be briefly explained.

This change has been implemented in the revised manuscript.

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