

Atmos. Meas. Tech. Discuss., referee comment RC2  
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## Comment on amt-2021-263

Anonymous Referee #2

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Referee comment on "A systematic re-evaluation of methods for quantification of bulk particle-phase organic nitrates using real-time aerosol mass spectrometry" by Douglas A. Day et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-263-RC2>, 2021

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Day et al. provide a comprehensive, and likely exhaustive, review of studies which have used AMS measurements to derive the relative concentrations of organic and inorganic nitrate aerosols from a suite of laboratory-based, ground-based, and aircraft-based research campaigns. This paper appears to be very carefully researched and written and will become an important resource for future investigators wishing to use AMS data to quantify organic nitrates.

Day et al. first review and evaluate the existing datasets that can offer insight into the capabilities of AMS data for distinguishing organic and inorganic nitrates. This leads to the primary conclusion that a reasonably simple analysis using the AMS data (so-called "RoR" analysis) can usefully differentiate these chemically distinct classes of nitrate aerosols. Further, the RoR analysis is applied to data from a suite of previous campaigns and then used to argue that organic nitrates are an increasingly important fraction of aerosol nitrate in cleaner environments, almost everywhere where AMS measurements have occurred. This is a significant conclusion that may direct future research.

There is no question to me that this paper deserves publication in AMT and I recommend publication following very minor revisions and consideration for a few points.

The primary question that I have for the authors to consider is whether they have sufficiently demonstrated that variations in the  $\text{NO}_x^+$  ratios are overwhelmingly due to the relative importance of inorganic and organic nitrates. For example, the result in Figure 5 could in principle be explained by a simple variation in the  $\text{NO}_x^+$  ratio from pure  $\text{NH}_4\text{NO}_3$  as a function of the  $\text{NH}_4\text{NO}_3$  concentration. Or perhaps a matrix effect could play a role where the relative ion signals changes depending on the fraction of total aerosol mass that is  $\text{NH}_4\text{NO}_3$  relative to e.g. organics. I did not see it sufficiently argued here that one of these could not be the explanation. It would be nice for example to see a laboratory measurement of the  $\text{NO}_x^+$  ratio as a function of  $\text{NH}_4\text{NO}_3$ , both from pure or internally

mixed aerosols. I expect that in one of the cited papers this has already been shown, and I would suggest drawing some attention to that and clearly stating it in this work.

Specific points:

Line 252: The idea that a mechanism for variability in the  $\text{NO}_x^+$  ratio might be understood by studying it systematically with the same instrument is somewhat refuted by the FIREX observations (Fig S5) where a wide range was observed for both  $\text{NO}_x^+$  ratios with no known variability in instrument operation.

Fig S5 actually shows a lot of instability in the *RoR*, and that the  $\text{NO}_x^+$  ratios from 4-nitrocatechol and  $\text{NH}_4\text{NO}_3$  are poorly correlated from day-to-day, or that there may be some anti-correlation. One thing I find problematic here is that the uncertainties indicated for each measurement do not represent the range of all the values measured. That is, the precision of the *RoR* measurement from any short period of time seems a lot better than the day-to-day variability in the measurement of this parameter, meaning that significant variability in ambient  $\text{NO}_x^+$  ratio might be observed without a change in the real ratio of  $\text{RONO}_2 / \text{NO}_3^-$ . I realize that these measurements were performed on a nitro compound rather than an organic nitrate, but it's not made clear that this would matter. My expectation also is that since this experimental group is probably the most experienced and meticulous of those who use AMS, this represents the best-case scenario for AMS  $\text{NO}_x^+$  ratio stability. Overall, it would be nice to have some comment here or elsewhere on what this tells us about the uncertainty in the derived  $\text{RONO}_2$  and  $\text{NO}_3^-$  concentrations.

Line 293: "was" -> "were"

Line 458: FPEAK appears here for the first time and is not well explained. Please define this.

Section 7 / figure 5: It may make sense to remind the reader of the method used here to quantify pRONO2 and the pRONO2 / pNO3 ratio, after all the discussion of RoR vs. PMF methods.