

## ***Interactive comment on “Overview of the LADCO winter nitrate study: hourly ammonia, nitric acid and PM<sub>2.5</sub> composition at an urban and rural site pair during PM<sub>2.5</sub> episodes in the US Great Lakes region” by C. O. Stanier et al.***

**Anonymous Referee #1**

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The authors provide an overview of the motivation behind a field campaign designed to better understand elevated PM<sub>2.5</sub> ammonium nitrate in the upper midwest region. They review the types of special measurements taken at the urban and rural focus sites. In addition, routine measurements taken at nearby locations augment the data collected at the 2 intensive sites. The authors present the meteorological conditions associated with these episodes of elevated PM<sub>2.5</sub> ammonium nitrate. Largely, this paper is a summary of the motivation for the field study and presents some initial measurements results and data analysis.

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### General Comments:

The authors are correct in that better understanding periods of elevated PM<sub>2.5</sub> in the upper midwest are important for regulators to design effective control strategies. In addition, understanding these periods of elevated PM<sub>2.5</sub> ammonium nitrate that are associated with periods of wintertime stagnant air masses may provide insight into other areas with wintertime periods of elevated PM<sub>2.5</sub> ammonium nitrate.

In general, this is a well written paper and does a good job of providing an overview of the issue and the measurements taken. I appreciate that this is the first of many papers, but I feel a few areas need more emphasis in this paper to make it a stronger manuscript. The title of the paper includes "...hourly ammonia, nitric acid, and PM<sub>2.5</sub> composition.." but does not ever show the hourly ammonia measurements in time series form that would be useful for the reader when trying to match up to the time series information provided for nitrate related gases and meteorological variables. A time series of hourly total ammonium (gas+particle phase) and ammonia gas and hourly total nitrate (gas+particle phase) and nitric acid would be worthwhile additions to this paper. While not as critical to the paper, it appears SO<sub>2</sub>, sulfuric acid, and PM<sub>2.5</sub> sulfate ion are measured during this period and the inclusion of time series information for these species would complete the scope of the paper since it looks at inorganic chemistry. The sulfur related content may be best in the supplemental section for brevity.

### Specific Comments:

The presentation of gas ratio information is very useful and appropriate. The equation for GR in section 4 needs additional explanation. It is not clear what the units of the terms are or how these terms are operationally defined since TA, TS, and TN are not universally known. For instance, is TS the sum of SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, and PM<sub>2.5</sub> sulfate ion?

Page 14125 describes some previous measurement intercomparisons by specie. This section is interesting, but is there more recent or additional work related to nitric acid?

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I am very surprised that given the information provided it seems that measuring ammonia is more problematic than nitric acid. I had always had the view that nitric acid is the most difficult inorganic gas (or one of them) to measure. If this is a misconception then perhaps this section could be slightly modified to specifically speak to the idea of nitric acid being a chemical specie that is very problematic to measure.

Section 5.2 makes reference to a Table S-5. There does not seem to be a Table S-4 or S-5 as part of the supplemental section submitted.

In section 5.7, the authors note that in other studies NOX release from snow has been documented during the melting period. There are measurements of NOX and snow melt for this study so do the authors see this in the data collected for this field campaign? I tried to determine the answer by looking at a few of the submitted Figures but I could not come up with a conclusive answer. Since the authors have this data in hand, they should be a little more clear if this happened as part of this study or if the data was inconclusive for some reason.

In section 5.7, the authors provide some discussion about actinic flux. I assume this is based on data taken at Bondville, Illinois. Are the authors comfortable that this site provides a reasonable characterization of what is happening in central Wisconsin? At a minimum, an acknowledgement of the spatial disparity would be nice since the station is not shown in Figure 1 with the other monitor data used for this paper.

In section 5.10, the authors describe the generation of conditional probability plots, pollution roses, and bivariate polar plots but I don't see any of these in the paper or supplemental section. Many areas with elevated PM2.5 ammonium nitrate in the winter struggle to identify the sources of ammonia and any plots that may help elucidate this would be very worthwhile for this paper.

In section 5.11, the authors introduce CMAQ modeled OH concentrations. I think this is probably ok but the authors should reference CMAQ and provide a minimal description of the CMAQ simulation where OH concentrations were extracted; the version, time

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period modeled, etc.

It is worth providing more emphasis in the paper of the fact that both sites seem to be ammonia rich based on the gas ratio during these episodes and during non-episodes. Gas ratio numbers are provided in the manuscript but there isn't a strong conclusion to what the numbers mean for ammonium nitrate chemistry and which chemical component is typically limiting formation.

Technical Corrections:

Page 14120 line 13 change to "...using larger datasets"

Page 14128, the GR equation, in the numerator "assumption" is misspelled.

Page 14129, line 6 change to "...as meeting either of"

Page 14136 line 1, not sure what "snow cover leading" means here

Page 14136 line 4-5 change to "...inspection of the time series of upswelling..."

Table S-2. It is hard to imagine a minimum wind speed of -49.6 ms. I can understand small negative concentrations but a -6.3 ug/m3 of PM2.5 and -2.7 ug/m3 of PM2.5 seems rather large. I am also surprised there was a day where the 24-hr average NH3, SO2, and HNO3 were exactly 0. What was the meteorology like on those days?

Figure S-4. What are the units of these plots?

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