

Response to referee comments on “Overview of the LADCO winter nitrate study: hourly ammonia, nitric acid and PM_{2.5} composition at an urban and rural site pair during PM_{2.5} episodes in the US Great Lakes region” by C. O. Stanier et al.

Response to comments of anonymous referee #1

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 SO₂, sulfuric acid, and PM_{2.5} 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.

Figure 8 included a 1 week time series of particle ammonium, nitrate, nitric acid, and PM_{2.5} sulfate. Figure 5-4 of Baek et al. (2010) has daily time series of O₃, PM_{2.5}, sulfate, nitrate, ammonium, and NO_y, but the reviewer is correct – we have not plotted hourly time series for the publication. A large number of hourly time series have been added to the supplemental material. Figures S5-S8.

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 SO₂, H₂SO₄, and PM_{2.5} sulfate ion?

Additional explanation has been inserted. These are on a molar basis. H₂SO₄ is negligible and TS is the reading from the SO₄²⁻ channel.

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? 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.

Both HNO₃ and NH₃ are very reactive and very sticky, such that they even "stick" to pretty inert things like PFA Teflon tubing. Ambient HNO₃ is always tricky because concentrations are always a couple of ppb, or less, and positive or negative biases can be non-negligible. Ambient NH₃ at hundreds of ppb (e.g., near feedlots) is not problematic, but when concentrations are down in the several ppb range, then it's just as tricky as HNO₃ and for the same reasons.

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.

Response: the review is correct. This has been corrected to S3.

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.

Response: the hypothesis is for the release of NO_x from snow is not connected with melting and was inserted to show what is available in the literature, to our knowledge, on NO_x or nitrate and snow. The more interesting hypothesis for the Great Lakes is the release of HNO₃ from melting snow. The following clarification has been added. “Detailed analysis of correlation snowmelt and TNO₃ and snowmelt has not been conducted, but may be a promising area for future work; it is complicated by the fact that chemical production, phase partitioning, deposition, and release from the snowpack all occur simultaneously.”

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.

The following clarifying language has been inserted. They are from Bondville, IL, which is the closest SURFRAD station but is 326 km from Southern Wisconsin. The sunny periods occurred during large high pressure systems that affected multiple states.

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 PM_{2.5} 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.

The plots themselves can be found in Baek et al. (2010). To conserve space and keep the article more focused, the plots have not been included in the ACP article. The text has been changed to reflect this.

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 period modeled, etc.

Hourly modeled OH concentrations were taken from local surface-level gridcell values in a regional simulation with CMAQ 4.6 for January - March 2002, as described and evaluated by Grabow et al. (2012). The text and citation have been inserted.

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.

We plan on addressing this in future papers in a considerable amount of detail. The threshold of a value of 1 for ammonia rich is mentioned in the paper and the fact that the observed ratios are greater than 1 is also mentioned.

The reviewer comments on negative minimum PM2.5 concentrations

The large negative concentrations of PM2.5 (-6.3 and -2.7) sometimes occur with the TEOM method, particularly when there are rapid drops in relative humidity. Concentrations are extracted from the derivative of the TEOM loading. Although the instrument attempts to control sample relative humidity, rapid changes in ambient RH can sometimes still show in the data as spurious mass increases or decreases. Only 18 hours out of 2148 at Mayville had less than 0 $\mu\text{g}/\text{m}^3$ on the "A" TEOM. The B TEOM which recorded the negative 6.3 value was thought less reliable than the "A" TEOM due to inferior agreement with the FRM mass filters, more missing hours, and more common negative values (82 hours out of 1979). The A TEOM at Mayville was used for all analysis. Only one TEOM operated at Milwaukee, and it had only 5 out of 2142 hours as negative.

The reviewer commented on zero minimum concentrations for NH3, SO2, and HNO3.

The Illinois State Water Survey data used in this work is only for NH3 and HNO3. The denuder reported as capturing SO2 in Baek et al. (2010) likely only captured sulfuric and sulfurous acid. SO2 row should not have appeared in tables S1 and S2 and has been deleted. See Figure A2-7 of Baek et al. (2010).

The remaining "0" values are for 24 hour denuder-based ammonia and HNO3 and they occurred on February 18, 2009. A review of the original data file from the ISWS shows that there was an error on Feb 18 and the samples were invalid. The blank cells were

read by the import script as zero. The appropriate changes to Table S2 has been made. A check was made regarding the original regression of continuous versus integrated measurements and the Feb 18 sample was NOT used for the regression (see Figure A2-17 of Baek et al. 2010).

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

The scale is m/s and this is now indicated in the Figures.