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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Organic nitrogen in $\mathrm{PM}_{2.5}$ aerosol at a forest site in the Southeast US" *by* M. Lin et al.

M. Lin et al.

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We greatly appreciate the comments by both reviewers, which brought up important points and helped us improve the manuscript.

Overall Comments: The first overall problem deals with the LOD determined for the (organo-nitrogen) ON measurement. The authors define the LOD as two times the standard deviation of the blank, giving an LOD value of 0.14 ug/m3. It seems from the figures and tables that many of the measurements were below the LOD value, but it is unclear how the LOD points were treated from a statistical standpoint (i.e., in calculating means, diurnal profiles, wind roses, etc.). This is important since it likely impacts conclusions drawn about potential ON sources (and all of the data presented

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– for example, Figure 4 presents data with many ON values below the LOD). Also, the establishment and treatment of the LOD is important in this study since it is describing a novel measurement technique.

We have revised and expanded the discussion of treatment of LOD and uncertainties. In the original manuscript all points, including those below LOD, were included into the calculations. However, we have discovered that, inadvertently, the negative observations were discarded. This is corrected now, and all points, including those below LOD and negative ones, are used to calculate descriptive statistics. This has lead to a small reduction in average concentrations, but the overall conclusions remain.

As discussed in the answer to specific comments below, the concept of LOD relates to *individual* observations, not their averages. When calculating average properties from a large number of points, the uncertainty decreases. Therefore, even though a significant fraction of observations may be below LOD, their average still may be statistically significant (which is in our case, see below).

The other big-picture issue is with the analyses of ON sources. Overall, these analyses have no detail and come off as highly speculative. The authors present many possibilities for ON sources, but none are supported with any substantial evidence, and some of the proposed sources/explanations are contradictory to one another. The authors could do a much more detailed analysis than has been presented. For example, there is not a single correlation given in the entire paper. What was the correlation between ON and OC in winter, summer, overall? How about the correlation between ON and EC, NOx, Temp., NO3-, NH4+, etc.? I think some basic analyses like these could yield some interesting results that would give the authors more insight into ON sources than they have presented.

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We have added two figures showing correlations between different components during the two months of the study and expanded the discussion of inter-dependences between different parameters measured in this study. These correlations along with the other evidence indicates a very complex picture of ON sources. It is clear that ON at the site of the measurements did not have a single well-defined source. The evidence presented in our paper, indicates that a variety of sources, both primary and secondary, influence ON concentrations. For example, as discussed below, both local and long-range sources appear to have a strong influence. We can not definitely attribute ON to particular sources and given the available information. We have emphasized the need to combine measurements of the total ON concentration with chemical speciation measurements to be able to make source attribution.

The following are specific comments that should also be addressed. In many cases, the specific comments are related to the two broad comments above.

- Last sentence of the abstract is vague.

We have modified the sentence to state that (1) higher ON concentrations tend to originate from continental U.S. and (2) that the data collected in this study suggests a wide variety of potential sources of ON, which are difficult to quantify without chemical speciation data.

- Pg.17160, ln. 13-14: “exhibits photochemical activity” is awkward as written.

We have re-phrased the sentence to: “Back-trajectories and correlation with wind direction indicate that higher concentrations of ON occur in air masses originating over the continental U.S., while marine air masses are characterized by lower ON concentrations. The data presented in this study suggests that ON has a variety of sources, which are very difficult to quantify without information on chemical composition of this important aerosol fraction."

- Pg.17160, ln. 17: "...atmosphere at sizes ranging from nanometers to millimeters." Citation is needed here.

Citation to Baron and Willeke 2005 is added.

- Pg.17160, ln. 27-29: a bit clumsy, it reads, "...and temporal variability of ON were investigated... to elucidate its temporal variability..."

The sentence is re-phrased to: "Absolute concentrations and temporal variability of ON were investigated to assess the importance of this aerosol component relative to total $PM_{2.5}$ nitrogen and to elucidate its potential sources."

- Experimental section (pg. 17161, ln. 17) lists the summer study period as "31 May – 30 June" however later in the manuscript, (e.g., page 17169) the authors give results for July. This should be clarified and presented consistently.

The typo is corrected, June was meant.

- Pg.17162, ln.7-16: transmission of insoluble particles was 85% efficient, despite 2 liquid particle filters employed to remove insoluble particles? This should be clarified. Also, do the authors have any idea what the water solubility is of ON compounds expected in the aerosol? If there is a significant fraction of ON that is insoluble (as

operationally-defined by the SJAC), then the 15% not transmitted could be significant. If the liquid filters remove insoluble particles, then the ON should be defined as 'watersoluble ON'.

As is described in the text (p.17162, lines 9 - 16), the liquid sample collected in the SJAC is split into two lines: one for the IC analysis, the other for the TN analysis. The inline filters are installed only in the IC line. Therefore, they do not affect the transmission in the TN line. Since the inorganic N species are water-soluble (both NH_4^+ and NO_3^-), the removal of insoluble material in the IC line should not affect the inorganic N reading. On the other hand, the TN line does not have filters installed. Insoluble particle losses originate mostly due to deposition in the transfer lines. We have modified the text to make it explicit that the liquid filters are installed only in the inorganic (IC) line. The part now reads: "Two inline filters in series (one 2 µm, the other 0.5 µm pore size; Upchurch Scientific) were installed in the IC line to protect the ICs from suspended insoluble particles. No filters were used in the line to the TOC/TN instrument, which measured both soluble and insoluble material".

The reviewer is correct that the 15% loss of insoluble material could be significant, if the insoluble fraction dominates the ON. However, the maximum possible underestimation is 15%, which will happen only if all of the ON is water-insoluble.

- Pg.17162, ln. 25: If the OC measurements by the SJAC-Shimadzu were not used due to high blanks, then details about the carbon measurement ("...carbon in the aqueous sample from the SJAC is dominated by dissolved CO2...") should be omitted.

We have removed this sentence.

- Pg. 17164, ln.14-23: If the average blank value of the ON measurement was 0.14 ug/m3 (ON blank = TN - IN = 0.31-0.17 ug/m3, right?), this value is almost equal to the average ON concentration measured for the entire study: 0.18 ug/m3. This raises the question of uncertainty. How do the authors come up with an uncertainty estimate for the ON measurement of only 22%? It seems likely to be much higher than this. Especially if the TN uncertainty is 25% and the IN uncertainty is 16%, because the values are subtracted from one another to calculate ON, shouldn't the uncertainties be additive, making the ON uncertainty at least 40%?

In the revised manuscript we have added a detailed discussion of how uncertainty is calculated. We have also revised these calculations. In the original manuscript we used 95% confidence intervals of the fit parameters of the calibration curves and did not take into account that more than one measurement was used to calculate hourly-averaged concentrations. Thus, the original estimate of the uncertainty was overestimated. Further, the calibration curves from the two months were combined into one composite. Since different separation columns were used in the two months, a more correct approach is to use separate calibration curves for each month. Even though the calibration curves were very close to each other, this has also contributed to the reduction of the uncertainty. Further, the absolute value of the blank is not as important as the magnitude of its variability. Also, one should keep in mind that the uncertainties in the TN and IN air concentrations both include uncertainties of the flow rates. If one calculates the ON uncertainty from the uncertainties of air concentrations of IN and TN, the uncertainty due to the flow rates will be included twice. We calculate ON concentration in air by first calculating its concentration in the liquid collected by the SJAC (as the difference in IN and TN concentrations in the liquid) and only then convert it to the concentration in air. Therefore, the uncertainty of ON air concentrations is not equal to the square root of the sum of squares of the uncertainties of air concentration of IN and TN. We have added a detailed discussion of the uncertainty analysis to the revised manuscript.

- Pg. 17164, ln. 23-24: What is the basis for using two times the standard deviation of blanks to define the LOD? Often analytical chemists define the LOD as 3 times the standard deviation of blanks? A citation justifying the defined LOD here should be given. This seems to be an important point for the study, as 3 times the standard deviation of the blank would put the LOD at 0.21 ug/m3, which would mean the LOD value was nominally above the average ON value calculated for the study.

The definition of LOD as 2 or 3 times the standard deviation of the blank relates to the probability of a *single* observation being distinct from the blank. Assuming the noise is normally distributed and that negative values are not set equal to zero (both of which is true in our measurements), the probability of an observation being higher than the mean of the blank by more than 2 standard deviations of the noise of the blank is 97.5%. The LOD defined as 3 std of the blank noise corresponds to the probability of 99.9%. For ambient observations, the LOD defined as 2 times STD, provides a very robust probability that an *individual* observation is above the blank and is, therefore, very common.

It should be also noted that this concept relates to the *individual* observations. When working with averages of *multiple* observations, as in our case, the total number of observations needs to be taken into account. For example, if N measurements were used to calculate an average value, the probability that this average is higher than blank should be calculated using a corrected standard deviation of the blank. According to the central limit theorem (see any book on basic statistics), the means of N observations randomly taken from a normal distribution will also be normally distributed, with the same mean as the original distribution, but with standard deviation being square root of N smaller than the std of the original distribution. Therefore, an average of 100 blank values will have the same mean, but its standard deviation is going to be 10 times smaller.

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The monthly averages reported in this study have more than 300 hourly measurements each. The standard deviation of hourly blanks of ON is 0.08 μg/m^3. The standard deviation of a 300-point average of the blank is 4.6 ng/m^3. Therefore, the probability that the mean ON concentration measured in this study (around 0.16 μg/m^3) is higher than blank is practically indistinguishable from 100%.

- Pg. 17164, ln. 24: LOD for ON measurement is given as 0.14 ug/m3, however, for the entire study, the average ON concentration was 0.18 ug/m3. Since the average was so close to the LOD, presumably many measurement points were below the LOD. How were these points treated when average concentrations and diurnal profiles were calculated? (i.e., in other studies, 1/2 the LOD value may be used for statistical purposes). Also, since the LOD value was so close to the observed averages, the fraction of measurements above and below LOD should be given (possibly added to Table 1).

All points, including those below LOD, were included in calculations of descriptive statistics. On average, approximately 50% of the observations were below LOD. This, however, does not invalidate the means obtained with these points, because the number of individual observations is large. As discussed above, the LOD relates to *individual* observations, not averages of several observations. As the number of observations increases, the noise of the blank cancels itself out, reducing the uncertainty associated with the blank.

- Pg.17165, ln. 15-17: The concentration of OC was 2.6 times higher in June compared to January – this is probably heavily influenced by increased biogenic emissions and biogenic SOA in summer compared to winter. But the ON concentration was basically the same in January and June: does this give any insight into potential sources of ON?

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Indeed, it suggests that biogenic emissions do not contribute to ON as much as to OC. We have added discussion of this to the revised text.

- Pg.17165, ln. 21-25: the low nitrate concentration was attributed to a warmer-than normal January, however, looking at Figure 6, it appears as if the average temperature during this month fluctuated between 5-10 deg.C. This may be warmer than normal, but it is certainly cold enough to form NH_4NO_3*. Other factors (humidity, available* NH_3*, variations in* HNO_3 *concentrations, etc.) were likely responsible.*

Yes, this is certainly true. For example, the average RH during the study was 64% as compared to 74–76% in the preceding years. A lower RH does not favor formation of NH_4NO_3. This in combination with other factors, such as the availability of free NH_3 and HNO_3 could have contributed to the absence of NO_3^- in our observations. It should be also noted that the observed molar ratios of NH4 to SO4 were, on average, around 1.5, which indicate that there was not enough free ammonia to neutralize sulfate. Such conditions, in general, do not favor formation of ammonium nitrate. We have added this discussion to the text.

- Pg. 17166, ln. 10: remove "robust"

Removed.

- Pg. 17166, ln. 21-22: There is no evidence given that the organic aerosol has any characteristics of HULIS. The similar C/N ratio observed in this study to humic substances seems more coincidental than "remarkable", unless additional chemical characterization of the organic aerosol is performed.

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We agree, we modified the text to state that is probably “coinsidental”.

- Abstract: “Back-trajectories and correlation with wind direction indicate higher concentrations of ON in continental air than in marine air masses and indicate a variety of potential sources.” From Figure 3, this statement seems too broad. Not all “continental” air had high ON concentrations. It seems from the figure that air from the north and northeast had concentrations almost as low as air from the east, while only airmasses from the southwest were clearly elevated compared to others.

It should be noted that local wind directions do not necessarily indicate the origin of air masses. Back-trajectories are a better indication of the air mass origin and were used to make this statement. It should be also noted that NE wind directions are usually associated with marine air masses. The northern winds often originate over Canada and are in general associated with low concentrations. We agree, however, that a more correct statement would have been “Back-trajectories and correlation with wind direction indicate higher concentrations of ON in air masses originating over continental U.S. than in marine air masses”. We have modified the text to reflect this.

- Pg. 17167, ln. 8-11: “Back-trajectories showed that relatively high concentrations of ON, as well as of other aerosol components, tended to originate in air masses coming from the continental US, while low ON concentrations were associated with marine air masses coming from the Atlantic.” A little more detail is needed here: What distinguished “relatively high” from “low” ON concentrations? Was it daily averages? Were the back trajectories run starting at 12:00 local time, as with the other analysis?

5% highest and 5% lowest observations were selected from each month and back-trajectories were calculated for the time of those observations. In total, 27 out of

31 (87.1%) of high ON observations originated over the continental US; 19 out of 31 (61.2%) low ON originated from the sea. We have added this information to the text.

- Figure 4: In Section 2.4, the LOD of the ON measurements is given as 0.14 ug/m3. In Figure 4, it seems that more than half the data is reported below this value. This should be corrected.

We are not sure what needs to be corrected here. As was discussed above, points below the LOD should not be discarded. LOD relates to the probability that an individual observation is distinct from the blank. The fact that practically all points (more than a 100) are above zero suggests that our estimate of the blank noise is probably exaggerated.

- Section 3.2: was wind speed measured along with wind direction? It would be interesting to see how concentrations of ON varied with wind speed as well.

Yes. We have added this information into Figures 3 and 4 together with the correlation coefficients. There was no clear correlation between ON and wind speed.

- Pg.17167 ln.24-27: "The trajectory from 5 June originates over an area of the Midwest that is heavily influenced by animal production, which suggests that the concentrations of ON on 5 June may have been influenced by primary emissions from animal manure such as urea and aliphatic amines." This seems highly speculative. The trajectory also passed over major forested regions and was likely influenced by biogenic emissions. It also passed over part of the Ohio River Valley, which has coal burning power plants and high NOx emissions. This Midwest region is not in close proximity to the measurement site: as back trajectories go farther back, the

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uncertainty increases. Also, it seems somewhat confusing to mix highly time resolved measurements with a single back trajectory per day in the hope of explaining ON sources. For example, on June 5, the ON concentration exhibited significant structure and a wide concentration range, from -the LOD value (0.14 ug/m3) to almost 0.4 ug/m3. The concentration increased and decreased rapidly on this day. The authors theorize that ON concentrations on this day were influenced by animal production. But which ON concentrations on June 5: the concentrations near LOD, or the large spike?

We used this period to illustrate general characteristic of the data, understanding, as the reviewer points out, the difficulties in using back-trajectory analysis to explain highly time-resolved measurements that exhibit large temporal variability. We have modified our description to be less speculative.

- Pg. 17168, ln. 1-2: "their ratios change dramatically, which may be an indication of a predominance of secondary compounds under this regime" This is also highly speculative, and is based on the assumption that the previous period was dominated by primary emissions. That seems far from certain.

We agree that this is somewhat speculative and have removed it from the description. Our explanation of the time series in Fig. 4 has been modified.

- Pg. 17168, ln. 3-5: "This example shows that while the concentrations of ON and other aerosol species tend to correlate in general...": See above comment – no correlation has been given for ON with other aerosol species, either for the entire study, for one month, or for even shorter periods.

We have added two new figures (for January and June) that show inter-relation between different parameters and their correlation coefficients. The discussion of these inter-correlations is added to the revised manuscript.

- Pg. 17168, ln. 5-6: "It also demonstrates the power of highly resolved measurements that can capture such transient phenomena and help locate potential sources of ON.": I agree that highly time resolved measurements can be very useful in analyzing aerosol sources, however I don't think the present study has used the highly time resolved measurements to locate potential sources of ON (see above comment).

The highly resolved measurements did help us to detect the fast changes in concentrations and relate them to changes in meteorological parameters. However, given the apparent complexity of ON sources, which is clearly influenced by both primary and secondary emissions, it is indeed very difficult to pinpoint its sources.

- Pg. 17168, ln. 9-11: "In January ON concentrations were relatively high during the night, while low concentrations were observed in the afternoon." From Figure 6, qualitative trends are visible, but it is very hard to discern any quantitative information from the figure. The figure should be made more clear, and numerical values should be given in the text when discussing diurnal profiles.

We have added quantitative values of night and day ON concentrations to the text. We have also extended the vertical size of the figure. Part of the problem probably arises from the landscape orientation of the discussion paper. The figure should be more readable in the portrait format.

- Pg. 17168, ln. 11-12: "ON concentration anti-correlation with ambient temperature, which could indicate some volatility of some fraction of ON." The correlation between

temperature and ON for January should be given. Also, it seems that the anticorrelation is only for a short period (9am-12pm). And, as is stated by the authors later in the same section, the ON diurnal profile in this time is similar to that of NOx. This seems to indicate a dilution effect from an expanding BL, not necessarily volatility (though dilution and volatility can be related).

What we meant here is that the diurnal profile of ON in January is opposite to that of ambient temperature, which may indicate volatilization of ON at higher afternoon temperatures. We have re-phrased the sentence to clarify this.

- Pg. 17168, ln. 17-19: Sentence is awkward as written.

We have re-phrased the sentence.

- Pg. 17168, ln. 23-26: What is the average increase in the ON concentration from the afternoon to the night, to make the assumption that nighttime chemistry is playing a role in ON formation?

In January it was about 66%. This is a statistically significant difference. We have added this information to the text.

- Pg. 17169, ln. 5-6: "Both NOx and EC are combustion related pollutants and thus suggests the linkage of ON with combustion. The similarity of ON and EC diurnal profiles in January suggests that biomass burning may have a contribution to ON." What is the basis for these statements? First, what are the correlation coefficients (NOx-ON and EC-ON) to make the conclusion that ON is combustion related? Also,

how do the authors distinguish biomass burning combustion from motor vehicle combustion based on the measurements made during this study? From Figure 6, it is difficult to assess the similarities in diurnal profiles between ON and other species.

We have reconsidered our evaluation of the possible contribution of combustion sources to ON. Indeed, based on our measurements we can not distinguish between biomass and other combustion sources. Still, our observations indicate that at least some of ON could be due combustion sources. We have expanded the discussion of this in the revised manuscript, including quantitative comparisons of concentration changes over the course of the day, as well as the correlation between different components.

- Pg. 17169, ln. 13-14: "This indicates that the ON concentration in June was significantly influenced by photochemical activity." First, was the correlation between ON and OC significant during June, compared to January? Second (see above comments), the magnitude of the increase in the afternoon ON concentration is not apparent from Figure 6. Finally, the OC concentration was a factor of 2.6 higher in June than in January, likely due to biogenic emissions and SOA formation. But there's no difference in the ON concentration between January and June, so how much of an effect could photochemical activity have had on ON concentrations? Why was there no difference in January-June concentrations?

The correlation of ON with OC was weak, but significant in both months, being slightly higher in January (0.36 vs. 0.3). However, both ON and OC have a wide variety of sources, both primary and secondary. Even though the difference between ON concentrations in June and January is small, the concentration in June is still 13% higher. This increase is certainly smaller than that in OC concentrations (162%). However, this could be due to numerous reasons, such as the photochemical conversion may be more efficiently producing OC than ON; the emission that can be converted are stronger in C content, than N content; the volatility of formed ON compounds is higher than that of OC compounds, etc. The weekday/weekend comparison (see our reply to a comment below) indicates the effect of anthropogenic sources in combination with photochemical activity in summer. Therefore, there are indications of the effect of photochemistry on ON concentrations. However, we can not quantify their relative effect without information on the chemical composition of ON.

We have added quantitative night vs. day comparisons to the text to supplement the figure showing the diurnal profiles.

- Pg. 17169, ln. 15-18: This sentence is very confusing. In which month were weekday concentrations higher than weekend concentrations? If ON was a factor of two higher during the week than on weekends, doesn't that suggest a prominent local influence? Also, see above comment; July should be changed.

We have re-written this sentence and have added a table with values of the average weekday / weekend concentrations. The higher concentrations during the workdays do not necessarily indicate a local influence. For example, in June weekday ammonium and sulfate concentrations were also higher than its weekend concentrations. Since SO4 originates mostly from long range transport, the higher weekday concentration does not necessarily indicate a local source. Rather, we believe this difference is more indicative of anthropogenic influence. The typo "July" has been changed to "June".

- Table 1: Minimum ON concentration for January and June is listed as '0'. Since the LOD for ON is 0.14 ug/m3, the minimum should be "Below LOD", "< 0.14 ug/m3" or something similar.

The table now shows the actual minimum observations.

- Figure 6: it is very difficult to view these diurnal profiles – specifically, qualitative changes (up/down) in the diurnal profiles can be seen, but it's almost impossible to judge the quantitative nature of these changes. Figure should be much easier to read.

The figure needed to be made smaller in its vertical size to fit the landscape format of the Discussion paper. The figure should be easier to read in portrait orientation. We have also extended the vertical dimension of the figure to make it more readable.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 17157, 2009.

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