

Interactive comment on “Organic nitrogen in PM_{2.5} aerosol at a forest site in the Southeast US” by M. Lin et al.

Anonymous Referee #1

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The study presents a novel technique to measure total organic nitrogen in fine particles. The technique was deployed for one month in winter and one month in summer at a forested site in the U.S. Nitrogen-containing organics represent a sub-class of the organic aerosol that is not well characterized. For this reason, the study is of interest to many in the aerosol and atmospheric science communities. The manuscript is generally well written and well organized. However, there are a few fundamental issues, as well as specific comments, that need resolution before the manuscript can be published.

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

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Interactive Discussion

Discussion Paper



blank, giving an LOD value of 0.14 $\mu\text{g}/\text{m}^3$. 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 – 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.

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. In my opinion, 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, NO_x , Temp., NO_3^- , NH_4^+ , 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.

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.
- Pg.17160, In. 13-14: “exhibits photochemical activity” is awkward as written.
- Pg.17160, In. 17: “. . .atmosphere at sizes ranging from nanometers to millimeters.” Citation is needed here.
- Pg.17160, In. 27-29: a bit clumsy, it reads, “. . .and temporal variability of ON were investigated. . .to elucidate its temporal variability. . .”
- Experimental section (pg. 17161, In. 17) lists the summer study period as “31 May –

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30 June” however later in the manuscript, (e.g., page 17169) the authors give results for July. This should be clarified and presented consistently.

- Pg.17162, In.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 ‘water-soluble ON’.

- Pg.17162, In. 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.

- Pg. 17164, In.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%?

- Pg. 17164, In. 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.

- Pg. 17164, In. 24: LOD for ON measurement is given as 0.14 ug/m³, however, for

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Discussion Paper



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Comment

the entire study, the average ON concentration was 0.18 $\mu\text{g}/\text{m}^3$. 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, $\frac{1}{2}$ 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).

- Pg.17165, In. 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?

- Pg.17165, In. 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.

- Pg. 17166, In. 10: remove “robust”

- Pg. 17166, In. 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.

- 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.

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- Pg. 17167, In. 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?

- 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.

- 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.

- Pg.17167 In.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 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?

- Pg. 17168, In. 1-2: “their ratios change dramatically, which may be an indication

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Interactive
Comment

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.

- Pg. 17168, In. 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.

- Pg. 17168, In. 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).

- Pg. 17168, In. 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.

- Pg. 17168, In. 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 anti-correlation 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 NO_x. This seems to indicate a dilution effect from an expanding BL, not necessarily volatility (though dilution and volatility can be related).

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

- Pg. 17168, In. 23-26: What is the average increase in the ON concentration from

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the afternoon to the night, to make the assumption that nighttime chemistry is playing a role in ON formation?

- Pg. 17169, In. 5-6: “Both NO_x 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 (NO_x-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.

- Pg. 17169, In. 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?

- Pg. 17169, In. 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.

- 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.

- Figure 6: it is very difficult to view these diurnal profiles – specifically, qualitative

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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.

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Discussion Paper

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