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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterization of organic nitrogen in aerosols at a forest site in the southern Appalachian Mountains" *by* Xi Chen et al.

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Point-to-point reply to reviewer 1's comments:

Review of Chen et al I am reviewing this paper as someone with quite a lot of experience of measuring bulk organic nitrogen but with much less expertise in organic matter characterisation. Overall I think this is a useful paper that demonstrates the potential importance of the organic nitrogen in this region and also provides some useful characterization of the some of the organic matter in the aerosol. The provision of data on organic carbon and nitrogen together is for me particularly useful. The wide range of data does allow some inter-component relationships to be used to suggest something

about organic C and N cycling, although all the correlations may not prove a causal link. The sampling and analysis is state-of-the-art for the compounds analysed and provides a high quality and useful data set. I am happy to see it published but I would suggest a few changes before publication.

Specific comments

Comment: I do wonder if the title is really appropriate given how little of the organic nitrogen is characterised.

Response: One very important purpose of our study is to provide more information on N- containing species in aerosols in forest environments. Although the identified and quantified speciated N-containing organic compounds only contributed a small fraction of the total WSON, which is consistent with other studies, we feel our resultsadd to the current scientific understanding of the issue and emphasizes the need to further characterize aerosol organic N composition in the atmosphere. We think the current title is appropriate considering our aim and purpose.

Comment: Line 69 There is now a global model of atmospheric organic nitrogen cycling that should perhaps be referenced – Kanakidou et al 2012 Global Biogeochemical Cycles doi 10.1029/2011GB004277.

Response: The reference by Kanakidou et al 2012 is now included in the text.

Comment: Line 72 To my mind the work of Altieri cited here and their more recent paper (Altieri et al 2012 ACP 12 355703571) represent the best effort to characterise the atmospheric organic nitrogen and yet neither here or later in the paper is this work discussed. It is relevant because it identifies reduced nitrogen as a dominant component of the atmospheric organic nitrogen, yet the authors here are characterising oxidised nitrogen based organic matter. The rationale for their choice of compounds is not really explained in the section line 112-125 where I might expect it to be.

Response: The reference by Altieri et al 2012 is now included in the Introduction sec-

tion. The rationale for characterizing oxidized organic nitrogen is based on the possible sources of organic aerosols in a remote forest site. Emissions of the most abundant biogenic precursors, including isoprene, monoterpenes and sesquiterpnenes, from the forest are expected to favor the formation of oxidized low volatility compounds to nucleate or condense on to the particle phase. Also, the possibility of wildfires, which are believed to be a significant contributor to atmospheric OM loadings, is considered a potential source to our remote forest site.

Comment: Line 140 The site map needs to be in the main text not the supplementary material.

Response: The site map is showing the relative location of the sampling site as well as the whole research forest lab to the nearby roads and towns. Although it is providing useful information to understand the sources of the pollutants, we do not think the standalone site map will provide as much important information as other results figures and tables in the main text. We prefer to keep it in the supplemental section.

Comment: Line 145-148 Given their importance from the results at this site, the authors might want to comment on ammonia sources.

Response: A brief description of local emission sources is provided at Line 141 “Typical rural development is present to the east of the site, consisting of houses and small scale farming for hay and crop production including some scattered cow and horse pastures, which are small local ammonia emission sources.” And also at Line 338 “Nitrogen component contributions to WSTN are presented in Figure 1a, which shows NH4+ as the most abundant component, contributing 85$\pm$11% w/w to total WSTN mass. Typical NH4+ concentrations at the site were below 1.0 μg/m3(with an average of 0.32 μg/m3), which is expected for such a remote site with no major local and regional ammonia sources.”

Comment: Line 151 – how many samples in total? I guess about 60 but it does help to know when looking at the statistical work.

Response: The total number of samples collected is 58. This information is provided on line 156 in the main text.

Comment: Line 151-3 Gonzalez-Benitez discussed the issue of semi-volatile organic nitrogen and it may be useful to at least note this, although it is very hard for most of us to sample for this.

Response: The following sentence is added to the text regarding difficulty in sampling for semi-volatile organic nitrogen: “Under some conditions, the 24hr integrated filter sampling technique may not fully retain all semi-volatile organic nitrogen compounds (Gonzalez Benitez et al., 2009).”

Comment: Line 221 I think “less than” should be “better than” if I understand the point

Response: “less than” is changed to “better than”.

Comment: Section 2.4 Please explain what the PMF is being used to investigate. The section here is a detailed description of the mathematical manipulations but it does not explain anything about the process to the non specialist.

Response: The purpose and basic details of the PMF analysis are stated in the text as “Positive Matrix Factorization (PMF) was used to identify potential sources of compounds measured at Coweeta. Briefly, PMF resolves factor profiles and contributions from a series of PM compositional data with an uncertainty-weighted least-squares fitting approach. ”

Comment: Line 317-8 How does how ozone consumption lead to a seasonal maximum?

Response: The sentence is revised as “In addition, a spring maximum [O3] may be due to higher chemical consumption of O3 by reactive monoterpenes and sesquiterpene emitted in the forest during summer.”

Comment: Line 337-340 For a wider audience I would suggest it is worth noting this

%organic N is consistent with other data from the world beyond the USA.

Response: The following sentence is added “Moreover, the observed WSON contribution to WSTN in particles at Coweetais consistent with a global estimated range of 10-39% (Cape et al., 2011).”

Comment: Line 342-344 The claimed seasonal cycle looks very small to me from the graphs.

Response: The differences of OC during spring and summer compared to fall are discernible, but do not reflect a dramatic seasonal cycle..

Comment: Line 349-352. The correlations are presented for each season, and that is OK although with only about 20 samples and so many variables I wonder about the statistical validity of the approach. I would therefore suggest that the equivalent correlation for the whole data set should also be presented. The observation of the correlation of WSON and WSOC is interesting and there is rather limited such data valuable. I also note a much stronger correlation of WSON and NH4 than NO3. This is consistent with other data (see Cape et al 2011 cited) and points along with the Altieri work above, to a key role for reduced nitrogen in WSON formation.

Response: The correlations for the entire dataset are now included in Table 2. We appreciate the comment regarding “a much stronger correlation of WSON and NH4 than NO3”. The following statement is now included at line 368 “It is also noted that a stronger correlation of WSON with NH4+ thanwith NO3- was observed, which might suggest a key role of reduced nitrogen in WSON formation (Cape et al., 2011; Jickells et al., 2013)”.

Comment: Line 359 “source contributions” of what? presumably WSON and C

Response: Yes. The sentence is revised as “However, the weak WSON-WSOC correlation suggests a variety of source contributions to WSON and WSOC over the different seasons.”

Comment: Line 374-7 We have all had problems such as described here, but is it really useful to include the samples collected when local burning impacted the sampler? This is particularly relevant because throughout much of the paper the authors show they can only characterise a few percent of the WSON. Then suddenly on line 508 they say they can characterize 28% which would be very impressive but I think this is for these local burning episodes and so by including this high percentage the authors may mislead readers into thinking as a community we are beginning to be able to characterise quite a lot of the WSON. This is also relevant to line 587 and the abstract. As the authors note in line 552 they and the rest of us have yet to be able to characterise very much of this material

Response: Yes, the particular sample characterized as 28% of WSON was impacted by local biomass burning. We agree that this was a special event and not typical of the other samples. However, we think it is relevant to be included as an example of the impact of local burning (i.e., “fresh” smoke). In order to avoid misleading the readers, we have revised the statement regarding this 28% characterized WSON: “On average, identified nitro-aromatic and nitrooxy-organosulfate compounds accounted for a small fraction of WSON, ranging from ïĄ¿ 1% in spring to ïĄ¿ 4% in fall, though were observed to contribute as much as 28% w/w of WSON in individual samples which were impacted by local biomass burning.”

Comment: Line434-5 Given how small a percentage of WSON appears to be made up of N containing organosulphate compounds, I’m not sure its correct to make the statement “which reflected: : : to WSON” here.

Response: The emphasis of this statement is the importance of nitrogen containing organosulfate in summer to WSON relative to the other seasons based on the significant correlations observed. The statement is now revised to “Organosulfates exhibited statistically significant correlations with WSON only in the summer ($r=0.64$, $p<0.01$), which reflected the importance of N containing organosulfates or their formation chemistry to WSON during summer compared to the other seasons.”

Comment: Line 440 group of ORGANIC compounds Line 447 is 6-9% (which is what I think your report) really “a substantial proportion”?

Response: Composition of atmospheric particulate OM is expected to be complex and could comprise hundreds and thousands of individual compounds. A single class of compounds with a particular functional group which contributes up to ∼10% of overall OM loading is substantial considering the complexity and numbers of potential component groups.

Comment: Line 446-453Here and elsewhere I think the authors need to be careful about interpreting correlations as showing causal links.

Response: We agree and appreciate the comment.

Comment: Line 562-565 I think the authors conclusions are valid for the material they have characterised, but that does not necessarily mean that all of the organic aerosol has been similarly aged.

Response: Thanks for the comment. We agree. The biogenic SOA tracers are most likely to reflect aging of the SOA portion of the organic aerosols, which was the intent of our statement in the text: “Warm periods in spring and summer exhibited highest production of terpenoic acids, when SOA correspondingly showed a higher degree of aging.”

Comment: Line 581-3 I do not understand what the sentence starting “PMF analysis” means. I am not really sure that figure 5 and 6 add much to manuscript

Response: One important piece of information the PMF analysis adds to the study is the contribution of resolved WSON containing OM contributed 20% to WSOC, demonstrating a significant portion of OC is nitrogenated in PM2.5 at our study site. While our speciated analysis only identified a small fraction of the nitrogenated OC, there is definitely a need to conduct more in depth research to unveil a complete picture of organic N composition. We feel the results of the PMF analysis shown in Figures 5 and

6 provide useful information to readers.

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