Atmos. Chem. Phys. Discuss., 9, C7368–C7374, 2009
www.atmos-chem-phys-discuss.net/9/C7368/2009/

Atmospheric Chemistry and Physics Discussions

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

M. Lin et al.

andrey@duke.edu

Received and published: 21 November 2009

We thank the reviewer for constructive and useful comments that helped us improve the manuscript.

I agree with Referee 1 that the quantification of LODs should be improved and that the results should be analysed and interpreted more fully, with less speculation.

We have extended the discussion of LOD calculations and of the data interpretation, see answer to Reviewer 1.

The authors seem to suggest that HULIS dominates the C/N ratio of the organic aerosol at this site. This is both highly speculative and very unlikely, especially for PM2.5. AMS factor analysis, for example, indicates that the aerosol is dominated by oxygenated organic aerosol, usually attribute to SOA production (see Zhang et al. 2007 reference above). Indeed, the authors use the C/N to argue that it is consistent with HULIS and later argue that it is consistent with organo-nitrates. Elsewhere they point out that the C/N ratio is dependent on wind direction.

We agree that the similarity of the C/N ratio with HULIS is quite speculative and have added a statement to the text that this is most probably coincidental. The C/N ratio was used to judge whether some of the proposed compounds, such as organo-nitrates, may have contributed to ON. Volatility of organo-nitrates is higher at lower C/N ratios. Thus, the average C/N maybe a very rough check of whether these compounds contribute significantly to ON. However, we agree, that this test will not necessarily preclude these compounds to be present in the aerosol even if the average C/N ratio is relatively low. We have added this discussion to the text.

How does the C/N ratio compare with recent measurements by AMS (e.g. Aiken et al., 2007; Anal. Chem. 79, 8350-8358)?

In general it is lower than that measured by the AMS. We have added this discussion to the text.

In addition, I have another major concern that should be addressed: in general, the authors should discuss there results more fully in the context with other previous aerosol measurements at this site, e.g. by Aerosol Mass Spectrometry (Stroud et al., 2007; J. Atmos. Sci., 64, 441-459; Zhang et al. 2007, GRL, 34, L13801, including auxiliary material). In particular, I am concerned that these previous measurements identified significant amounts of nitrate during warm periods in July 2003 (0.38 ug *m-3) and September 2004 (0.1 ug m-3), while no nitrate was identified in the present work. This makes me wonder whether the nitrate detection was working properly. Maybe NH4NO3 volatilised within the cyclone or NO3- was de-nitrified to NH4+ during sampling? Because ON is derived as the difference between total N and inorganic N, this would obviously feed through to the quantification of ON. In the light of these earlier measurements, temperature can clearly not be used as a reason why no nitrate was seen.*

None of these processes would affect ON measurements. We have taken precautions to avoid temperature changes of the air in the sampling lines, which were insulated. Even if volatilization occurred, it would not bias ON measurements: gaseous components are removed by the denuder. Even if they were not, the products of ammonium nitrate decomposition would still be measured as inorganic species. If volatilization occurred, the only bias would be in the aerosol inorganic nitrogen content. Suppose, there was x ug/m3 of IN and y ug/m3 of ON. The TN then is (x+y) ug/m3. If z ug/m3 of IN is evaporated, then TN = (x+y-z) ug/m3 will be collected. Then, ON = TN - IN = (x+y-z) - (x-z) = y, i.e. ON is not affected by losses of IN before the SJAC.

We believe that the possibility of denitrification is also small, because the lines were changed regularly and the residence time in the liquid lines is quite short. Futher, denitrification is favored in anoxic conditions, while the water collected in the SJAC is exposed to a constant air stream during sampling. Even if denitrification occurred, it would not affect ON measurements, because IN content would be preserved (only its chemical form would change from the anion form to the cation, ammonium). If there are losses of IN in the transfer lines, they should be the same in both IN and TN lines (the tubing and flow rates are similar). Therefore, they would bias IN measurements low, but will not affect ON.

In addition to temperature, other parameters such as humidity and the amount of free ammonia and nitric acid would play a role in determining NH_4NO_3 concentration, see

our reply to Reviewer 1 comment. It should be also noted that the observed molar ratios of NH_4^+ to SO_4^{2-} 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.

It should be also noted that the AMS measurements were reported to have difficulty in attributing NO_2^+ peaks. For example, organonitrates can form ions nominally considered to be inorganic (Aiken et al., 2007; Aiken et al., 2008). This may lead to overestimation of inorganic nitrate and underestimation of ON.

Minor scientific comments
P17159, L13. The authors may want to add non-US evidence, e.g. from Europe (Cape et al. 2005, Water Air Soil Poll. Focus 4(6), 1573-2940.

We have added this reference.

P17163, L6. The authors should discuss potential artefacts. For example, cation IC for NH4+ may be cross sensitive to amines and amino acids (cf. Husted et al. 2001, Physiologia Plantarum, 109(2), 167-179).

We were not aware of this interference. In general, it is not certain that the interference observed in the above paper with a different IC system (Waters) and a different elluent would also happen in our system (Metrohm). This interference, it it occurs, would lead to an overestimation of ammonium measurements (and consequently under-estimation of ON content). The observed molar ratios of NH4 to SO4 were, on average, around 1.5, which does no indicate any obvious bias in NH4 measurements. Still, this is a good questions and needs to be investigated in the future.

This artifact would underestimate ON and overestimate IN (NH4) measurements. On the other hand, the observed molar ratios of NH4 to SO4 were, on average, around 1.5, which does not indicate any significant bias in NH4 measurements.

P17164, L7. Was the TN instrument also calibrated with organic N. This referee has found that organic N components can absorb to tubing, providing losses for ON which would not be seen for IN.

No, this was not done. The manufacturer recommends calibrating the instrument with KNO_3. Given the composition of ambient aerosol, we have used ammonium sulfate for calibration. We have used only Teflon tubing for the transfer lines, which should minimize losses. If there were still ON losses in the transfer lines, then our ON values are probably underestimated. Unfortunately, without information on ON chemical composition it would be difficult to determine these losses.

P17164, L22. It is counter-intuitive that the error on a difference measurements (ON) is smaller than the error on the component from which it is derived (TN, IN).

We have revised the calculations of LOD and uncertainties, see the reply to Reviewer 1.

P17164, L24. What is the definition of a blank here? Is this a blank of the entire sampling system, e.g. operation without air pump and steamer?

The blank includes the whole system blank plus any artifacts from gas interference. It was determined with a HEPA filter installed at the inlet of the whole system. The system was operated as it does during normal sampling, i.e. with air being drawn, the steam injected, etc. This is stated in paragraph 2, Section 2.4

P17165, L1. Presumably the charge balance should be tested including nitrate. Is it only because no nitrate was detected, that nitrate was ignored?

There were a few days when nitrate was observed, with the maximum concentration being 0.26 ug/m3. However, its mean and median for the study were indistinguishable from 0. Still, nitrate was not ignored. If nitrate was observed, it was included in inorganic nitrogen concentration to calculate ON.

P17168, L11. The anticorrelation between ON and temperature could also be due to effects of boundary layer height dynamics which would also correlate with temperature. Similary, the fact that in January NO, OC and EC show similar patterns could just be caused by boundary layer dynamics.

Yes, this is certainly true. This is discussed in the third paragraph of section 3.3.

Technical comments
P17163, L13. 'in detail by Geron (2009)'

Fixed.

Table 1. Add units to caption. State averaging time. Why is the minimum concentration of ON not negative? The diurnal cycles indicate that negative values were derived (which is to be expected since it is a difference measurement).

As we have explained in the reply to the Reviewer 1, the negative values were inadvertently excluded from the analysis. This is fixed now and all values are used in calculations. We have added the units in the Table.

P17167, L12. 'While elevated concentrations of ON ...'

Fixed.

P17169, L25. 'demonstrated that at this site'

Fixed.

Reference list: this needs careful formatting with sub- and superscripts where appropriate.

Fixed.

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