

***Interactive comment on “Characterization of the sources and processes of organic and inorganic aerosols in New York City with a high-resolution time-of-flight aerosol mass spectrometer” by Y.-L. Sun et al.***

**Anonymous Referee #1**

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“Characterization of the sources and processes of organic and inorganic aerosols in New York City with a high-resolution time-of-flight aerosol mass spectrometer” by Y.-L. Sun, Q. Zhang, J. J. Schwab, K. L. Demerjian, W.-N. Chen, M.-S. Bae, H.-M. Hung, O. Hogrefe, B. Frank, O. V. Rattigan, and Y.-C. Lin

This paper discusses observations of the atmospheric aerosol at a location in the city of New York, NY during the summer of 2009. There are a number of components to this paper, but a significant focus is the analysis of the high resolution aerosol mass spectra using PMF and other techniques. The strengths of the paper are in the analysis

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of the high resolution mass spectra and discussion of diurnal variations of the analyzed components of the organic aerosol. There are also some weaknesses in my view as discussed in the major comments that follow.

Major comments

1) On page 22677, section 2.3.1 you indicate that you use a CE of 0.5 across the entire dataset. This is a critical assumption that is not justified in the discussion.

In one sentence (lines 8-11), the authors suggest that transmission and oven bounce issues are corrected by the simple application of a constant factor of 2. The atmospheric aerosol is composed of a variety of compounds (as you demonstrate) and size distributions. There have been many lab measurements that indicate the CE of pure dry ammonium sulphate is in the area of 0.25, whereas sulphuric acid is close to unity. AMS calibrations are done with pure ammonium nitrate in part because its CE is close to 1.0. Some studies have looked at the CE for pure organics, but organic components are many and varied. As well, evidence is mounting for the presence of organics in crystalline forms in the atmosphere and in general particle phases vary with ambient relative humidity and temperature (e.g. Matthew et al., AS&T, 2008). Particularly in urban areas, significant particle mass can reside in particles near the transmission limits of the AMS (as the authors demonstrate). Compositions vary with particle size also. So why should the CE for AMS' be a constant at 0.5?

You state that the 0.5 value is validated by comparisons with other collocated instruments. In Figure 1 your mean comparisons with sulphate and nitrate indicate that the AMS measured 70-75% of the mass concentrations measured with the PILS. Your comparisons of OM with OC indicate the AMS OM is 2.6 times the OC. You state the average OM/OC is 1.62 based on the high-res analysis, which means that your AMS OC is 1.6 times higher than the Sunset OC. You claim that this is due to volatilization during the carbon analysis, but if your mean CE was 0.8 rather than 0.5 then the AMS and Sunset would agree. A mean CE of 0.8 would result in the sulphate and nitrate

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being about 50% of the PILS values. Certainly a difference in the CE between the inorganic and organic components is reasonable since you indicate that some of your OM is externally mixed and at smaller sizes than sulphate and nitrate. It is also reasonable that in these high emissions areas substantial amounts of the sulphate and nitrate can accumulate in particles larger than the AMS can adequately sample, which leads to another point - the AMS is not a NR-PM1 instrument. The 50% cut size on the upper end is about 700 nm VAD (e.g. Liu et al., AS&T, 2009), which is also suggested from ambient measurements in your region of influence (Fig. 15; Rupakheti et al., AS&T, 2005). A 50% cut at 700 nm VAD means that the AMS measurement is closer to PM0.5 than PM1. The comparison with the TEOM, which can have significant volatilization problems, indicates that the AMS (based on 0.5 CE) is 68% of the total PM2.5 on average. This also indicates that there is significant mass above the upper transmission limit of the AMS and 2.5  $\mu\text{m}$ . The fact that your apparent nitrate CE is so low is another indicator that there was significant nitrate mass above the AMS upper transmission limit.

The justification for the use of a constant CE of 0.5 to describe bounce and transmission losses as well as for calling these mass concentrations NR-PM1 needs significant improvement before the paper can be fully considered.

2) On pages 22683-22684 you discuss nitrate and its diurnal cycle. Your nitrate peaks occur predominantly during late evening and early morning hours. AMS observations of such nighttime nitrate are common (e.g. Rupakheti et al., 2005) and most likely results from the formation of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ , the nighttime analogue of  $\text{HNO}_3$ , which is initiated by the reaction of  $\text{NO}_2$  with ozone. The process is aided by the increased RH's overnight, presumably because water in the particles enhances the absorption of the  $\text{N}_2\text{O}_5$  and  $\text{NH}_3$ . The apparent correlation of your diurnal cycle of nitrate with your diurnal patterns in HOA+NOA (Fig. 13) is further evidence of this process. You present your diurnal nitrate pattern as being a result of the daytime volatilization of ammonium nitrate. This may be a factor, but you need to discuss the source of the increased

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nitrate overnight.

3) In the abstract and the conclusions, you discuss a chemical evolution of SV to LV. But I can not find where this is explicitly discussed in the text, and it is not clear to me that this evolution proceeds as suggested. Also, there is some evidence that a significant fraction of your SV-OOA may have had biogenic origins; see several of the more detailed comments below. This possibility needs to be discussed.

Other comments

P 22673, line 20 – Rather than AMS study, perhaps atmospheric aerosol studies using an AMS.

P 22674, lines 10-14 – A bit more detail is needed here about why the advantages of using the HR.

P 22675, lines 13-14 – are the SP-AMS data used here? What is the point of this sentence?

P 22676, line 22 and P 22677, lines 21-22; P 22678, line 3 – you need to specify what you mean by elemental compositions/analysis. Are ion fragments elemental compositions, or what are elemental compositions of ion fragments?

P 22678, line 9 – performed ON the HRMS...?

P 22678, lines 14-18 – Does excluding what are effectively zeroes from the PMF analysis bias the differentiation of the OA components?

P 22678, line 22 – grammar.

P 22679, line 4-5 - perhaps say "The 6-factor solution splits the SV-OOA into two components. However, since we can not offer a physical interpretation of such a split, we choose the 5-factor solution."

P 22680, lines 8-10 – Please consider also Buset et al., Atmospheric Environment 40,

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2006, S482–S499.

P 22681, lines 6-9 – Your choice of CE could also be the reason. Also, blank correction may be an issue at low concentrations, but I don't see how that can be responsible for your slope?

P 22686, lines 1-2 – C<sub>3</sub>H<sub>5</sub>O:C<sub>4</sub>H<sub>9</sub> was estimated by Liggio et al. (JGR, 2010) at  $\leq 0.1$  for vehicle emissions, which appears consistent with that shown here for particles less than 100nm (Fig. 7). Liggio et al. also show that C<sub>3</sub>H<sub>5</sub>O<sup>+</sup> dominates the m/z 57 in the biogenic aerosol. From your SV-OOA spectrum (Fig. 8), it appears that m/z 57 is mostly C<sub>3</sub>H<sub>5</sub>O<sup>+</sup>. Could some (or most) of the SV-OOA have come from biogenic sources? There also seems to be pretty good correspondence of your SV-OOA spectrum with that of Shilling et al. (ACP, 2009) for ozonolysis of alpha-pinene.

P 22686, lines 19-22 – Please consider also Broekhuizen et al., 2005. Atmos. Chem. Physics, 5, 6263-6293, 2005.

P 22686, lines 23-25 - Fractionally speaking EC may only be a small component of the accumulation mode particles, but its influence on the particle number concentration may still be significant.

P 22688, lines 16-19 – this may depend more on the proximity and types of sulphur and VOC sources influencing the urban site. E.g. such a correlation was not evident in the urban AMS measurements described by Buset et al.

P 22688, lines 20-28 - If SVOA does not correlate well with NH<sub>4</sub>NO<sub>3</sub>, does this not contradict your argument that both nitrate and SVOA are controlled by volatilization? It may be another argument in favour of a significant contribution from BVOCs to your SV-OOA.

P 22689, line 2 – define Ox.

P 22689, lines 10-14 – The diurnal pattern of the SV-OOA is different from all others, with the exception of the midday increase that appears to correlate with the COA pat-

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tern. The absence of a clear connection with the HOA suggests a non-local source - again, perhaps SOA from BOVCs? Is the daytime reduction of SV-OOA related to boundary layer dilution?

P 22691, lines 24-28 - In contrast, Liggio et al. (2010) found an increase of O/C associated with lower particle loadings. Results such as this can be very strongly location dependent.

P 22693, lines 5-8 – It is unclear to me how these results suggest this. Can you be a little more explicit?

Figure 15a - your northwesterly trajectory passes over Toronto and Egbert, Ontario that have been sites of a number of (already mentioned) studies using AMS' during late spring and summer. The high organic composition of mostly SV-OOA may indicate a significant biogenic component to that aerosol as shown by Slowik et al., ACP, 2010 at the Egbert site.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 22669, 2010.

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