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Comment

Interactive comment on “Fine aerosol bulk composition measured on WP-3D research aircraft in vicinity of the Northeastern United States – results from NEAQS” by R. E. Peltier et al.

Anonymous Referee #1

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Peltier et al., “Fine aerosol bulk composition measured on WP-3D research aircraft in vicinity of the Northeastern United States - results from NEAQS”.

This paper presents an important new data set on the regional and vertical distribution of water soluble organic carbon in aerosol (WSOC) measured from the NOAA WP-3D. It complements an earlier paper by the same group (Sullivan et al., 2006) which provides more detail on the operation and characterization of the new PILS-OC system used to make high time resolution measurements of WSOC from an airborne platform for the first time. The present paper combines WSOC measurements with ionic composition measurements (by PILS- IC) and particle size distributions to establish the

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relative contributions of organics and ions to fine particle mass throughout the study region above northeastern North America. Most of the findings were expected, based on long-term, extensive ground based measurements and limited prior airborne measurements, but the prospect of making high resolution measurements of both ionic and organic components of the fine aerosol in less well studied regions has been firmly established by the Weber group during NEAQS.

In general the key points are made and explained clearly and well. However, I offer a series of comments that I feel would improve what is already a pretty nice manuscript.

Comments are given in order of encounter in the manuscript, not ranked by importance. A few minor editorial points are noted at the end.

In the abstract it is stated that “organic mass to sulfate was similar within the BL, but was significantly higher” above. Similar to what? As written this is not completely clear, but it appears the reference is to the study wide median, e.g., median in BL is similar to overall median of 40%. If this is the correct interpretation, it raises a small logical issue that probably should be clarified or reworded, especially in the abstract. If this ratio is enhanced above 2.5 km compared to lower altitudes, and is even more elevated in distinct biomass burning plumes, it would seem that the boundary layer mean would have to be depleted in comparison. Perhaps there are many more samples below 2.5 km than elsewhere, so that the boundary layer dominates the overall data set, but it seems that somewhere in the troposphere the OM/mass ratio has to be generally less than 40% if half the 1 minute samples were below this value.

Section 2.1 on the PILS-IC. I have been impressed by the evolution and increasing use of this technique, and the steady improvement over time. Neuman et al. (2003) pointed out dramatic improvement in detection limits (due to changes in the IC components), specifically for nitrate, in the airborne system flown on the same platform for ITCT2K2, compared to earlier prototypes used in ground campaigns. As a result, I have to wonder what happened during NEAQS to cause the reversal of this trend? For nitrate the

stated detection limits are 20-fold higher than for ITCT2K2. Similarly, the current detection limit for ammonium is 13 times higher than was stated in the original submission from Neuman et al. (published version acknowledges a poorly understood blank contribution to ammonium that could not be constrained, so precise detection limits were not stated). Preliminary analysis of data reported for the PILS-IC system flown on the NCAR C-130 during MIRAGE and IMPEX (in 2006) indicates high detection limits again, more like NEAQS than ITCT2K2.

In the present manuscript, I would urge the authors to consider a short statement about what they feel has caused this decrease in sensitivity, and whether it can readily be solved. More importantly, they should strive to regain the performance they achieved in ITCT2K2 for future missions. Considering that blanks were not detectable for most ions, and nearly insignificant for the single exception of sulfate, it would seem that the likely problem is in the chromatography, perhaps suggesting more extensive and frequent calibration would be helpful.

Section 2.2 on the PILS-TOC. Given my concern that the IC was only calibrated 3 times through NEAQS, I was curious how often the TOC instrument was challenged with oxalic acid. Were any tests done to confirm that the sensitivity was not impacted by changing conditions (pressure and temperature) in the aircraft cabin? Recognizing that Sullivan et al. (2006) is nominally the “technique” paper of this pair, I had hope this information would be found there, but it is not presented. So, I would urge the authors to clarify these points here.

Section 2.3 on other instruments. I note in passing that this section is quite similar to section 2.8 in Sullivan et al. (2006), which is probably fine. One minor point, shared by both papers, is the fact that a gap in the particle size distribution measurements from 55 - 150 nanometers is clearly spelled out, but how this is dealt with in data analysis is not mentioned. Granted, these small particles will not contribute much volume or mass, so the gap would seem likely to have limited impact on the subsequent analysis in the present paper. However, it would seem easy enough to add a few words describing

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the approach taken. Presumably, Brock et al. (2007) will provide these details, but that manuscript is listed as still “in prep”.

Section 3.1 and reference to Table 1. First comment is that the format of the table is very hard to read in the pdf (font is way too small). Changing it so that the 3 bins were vertically stacked would allow larger font (e.g., overall stats above low altitude, above high altitude). Second point, it does not seem possible that the median for sodium over the entire mission could be 6 times higher than it is in either of the bins. It seems likely that the 0.6 is a typo, and that the median should be 0.1 (half the LOD). Likewise, it is not clear how the overall median for ammonium could be 0.1, when it is 10 x that below 2 km and 5 x higher above 2 km. Transposing the overall medians for sodium and ammonium would make more sense. Third point, for the 8 ions across 3 bins there are a total of 48 means/median reported; 31 of these (probably 32) are equal to the inserted value of 0.5 x the LOD. In my opinion, this is a lot of marginally useful data (e.g., a lot of page space with little information). It might be better to simply list the fraction of samples that had detectable chloride, nitrate, sodium, calcium, potassium, magnesium. At a minimum, an extra column with this fraction could be added, especially if the table is reformatted as suggested above.

Regarding the discussion of potassium being rarely above detection limit, I would like to point out that filter measurements of bulk aerosol, including particles up to 4-5 micron diameter (made from the NASA DC-8) during NEAQS found mixing ratios greater than 250 ng potassium/m³ in approximately 50 5-10 minute long samples (mainly in similar biomass burning plumes as were encountered by the WP-3D). In 20 of these samples the mixing ratios exceeded 500 ng/m³ (nominal LOD for the PILS-IC on the WP-3D). Interestingly, potassium was also never quantified above detection limit by a PILS-IC system that was operated on the DC-8 (by the Weber group). Does this suggest that potassium enhancements in long-traveled biomass burning plumes are dominantly carried by supermicron aerosol? Or, is the PILS-IC detection limit for potassium even higher than stated?

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Section 3.3 regarding Fig 4 a and c. In both of these plots the regression lines for biomass burning have small negative slopes. The correlation is weak, but I am wondering why the slope in c is reported as 0. For these 2 lines it might be adequate to simply report the very low R2 values and leave out the slopes and intercepts.

Section 3.4 on converting measured WSOC to OM mass. I find this section to be overly long, and more convoluted than it needs to be. The approach of combining the two conversion factors, WSOC/OC and OM/OC into the lumped term CWSOC = OM/WSOC appears to be a good one since the single factor can be constrained by the measurements. However, this does not really allow any conclusions to be drawn about the likely values of WSOC/OC and OM/OC and how they may have varied with time, location and altitude. I also have two minor quibbles with equation 1 and how it is presented. First point is conceptual, but it seems to me that the density of OM is probably not constant, and variations are likely to be related to changes in WSOC/OC and OM/OC. So, does using the single value of 1.2 for OM density make the analysis a little circular? Second minor point is that the “unmeasured” term on RHS is not mentioned when the equation is presented and discussed, but the reader is asked to recall that it was assumed to be 8% near the bottom of page 3087. Perhaps more importantly, is it truly useful to include this small, likely variable, but poorly constrained term as an arbitrary constant, given all the other uncertainties in the approach.

I am more puzzled by the decision to use the single value of 3.1 in subsequent analysis, since it appears that equation 1 was applied to all possible sampling intervals, and CWSOC was found to vary significantly (the reported 1 sigma range extends from 1.5 to 4.7, and we are told that the low end of the entire distribution extends to < 0). Would the findings in subsequent sections of the paper be modified if the estimated CWSOC for each sample was used instead of 3.1? It would be interesting to at least know if CWSOC varied systematically throughout the geographic and vertical extent of the NEAQS study region, even if it is not possible to use the estimates from equation 1 to make conversions from WSOC to OM at 1 minute resolution.

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It should be noted that using the Jaffrezo and Turpin estimates of WSOC/OC and OM/OC, respectively, suggests that OM/WSOC will generally lie between 2.1 and 6.4. Thus the range and central value found using equation 1 for the NEAQS data set is on the low end, suggesting that simply adopting a single value from the literature (perhaps the midpoint of the range at 4.3) would probably have indicated a larger contribution of OM to fine particle mass in the region. Maybe the main point is that the values of OM presented in Table 1, and their contributions to total mass in different regions and air masses, must be highly uncertain if any constant value of OM/WSOC is used to estimate OM.

Section 3.4 last paragraph. This should probably be deleted, since there is no evidence that WSOC/OC is necessarily anywhere close to 0.61, either at the ground stations or in the airmasses sampled by the plane.

Section 3.5 regarding Fig. 6. The profiles of OM/PM_{1.0} and OM/sulfate are not all that similar if one notices that the scale is linear for the first and log for the second.

Editorial points: referenced by page #/line #

3074/14 there is extra “.” 3081/8 “than that” should be “than those” 3092/10 “measure” should be “measured” 3095/27 “attitude” should be “altitude”

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 3073, 2007.

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