**Atmospheric
Chemistry
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Discussions**

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.

R. E. Peltier et al.

Received and published: 16 May 2007

We thank the reviewers for their helpful commentary. We will address each main point for this manuscript below. The reviewer's comments have been copied to this response. Our response follows each comment.

REVIEWER 1 COMMENTS

REFEREE: 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.

AUTHORS: We agree that the wording in the abstract is unclear. The point of this sentence is to show that the ratio of organic matter to sulfate is generally constant (e.g. uniform) at altitudes below 2.5km - typically 30-35%. Above this altitude, the OM/sulfate ratio increases by a factor of two, suggesting that, relative to sulfate, significantly more OM is present at altitudes higher than 2.5km - ranging from 30-50%. The manuscript will be changed to reflect this by: The relative fraction of organic mass to sulfate was similar within the boundary layer (altitude less than 2.5 km), but was significantly higher in the free troposphere (above 2.5 km). The relative fraction of organic mass to sulfate was similar throughout all altitudes within the boundary layer (altitude less than 2.5km), but was significantly higher at altitude layers in the free troposphere (above 2.5km).

REFEREE: 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 detectible 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.

AUTHORS: The stated limit of detection is a function of chromatography column choice, eluent concentration, and sample flow rates (air and liquid sample). Prior to this field campaign, extensive method development was conducted in the lab to shorten the sample integration times by using higher eluent concentrations. As a consequence of using higher concentrations of eluents, chromatographic baselines tend to increase in noisiness, thus decreasing our ability to accurately measure very low concentrations of ions. During this campaign, sample collection was shortened to 90 seconds (and analyzed over 2.45 minutes), resulting in nearly twice as many measurements during a given flight as compared to ICTC2k2. Given the generally polluted region sampled, and relatively high speed of research aircraft (and therefore relatively short duration of point source plumes), we believe a faster measurement provides more useful information, especially when expected aerosol concentrations were more likely to be significantly higher than during ICTC2k4. As new chromatographic columns and instruments become available, the PILS technique will continue to be refined to provide better limits of detection, and/or faster integration times, depending on the specific research objectives of the mission.

The reviewer is surprised by the increase in sensitivity between the first generation PILS systems and the second generation system (e.g. system referenced by Neuman, et al, 2003) used during ICTC2k2. The improvements in sensitivity are largely due

to chromatography column selection. During this work, the same column was used as in ICTC2k2, but with substantially higher eluent concentrations to improve the time resolution of the data which resulting in a faster, but less sensitive measurement.

REFEREE: 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.

AUTHORS: While the TOC analyzer calibration was verified before and after the field campaign, it was not challenged with oxalic acid (or other organic standard concentration) during the field campaign. According to the manufacturer (GE Water Systems, Boulder, CO), the operational altitude range of the TOC analyzer ranges from 0-2000m (e.g. 1013-800 mbar). The temperature specifications range from 10-40 degrees C. The WP-3D research aircraft is capable of maintaining cabin pressure, typically above 950mbar, as well as keeping cabin temperature within the operational range of the analyzer. In addition, we found that the WSOC measurements didn't track the altitude profile for a specific flight. This included background measurements as mentioned in Sullivan et al. (2006). Thus, we feel confident that during flights, the TOC analyzer adequately operates without environmental interference. We have, however, found that the TOC analyzer is sensitive to rapid changes in temperature (e.g. if a fan or an air conditioning unit were to sudden blow cool/hot air on the analyzer). We have also found that the analyzer does not function properly when the temperature range has been exceeded. Efforts have been made to properly ventilate the TOC analyzer, as well as shield it from large changes in temperature (e.g. due to excessive HVAC).

REFEREE: 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

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

AUTHORS: The particle volume data is derived from a combination of 5 CPCs, a Lasair particle sizer, and a white-light optical particle counter. By themselves, the particle volume instruments are not continuous across the entire size spectrum, but consist of several dozen size bins of data. The data are processed by an inversion technique which determines a smooth size distribution that is consistent with the experimental response of the instruments, as well as with the instrument uncertainty. For further explanation, we would refer the reviewer to Brock et al, 2002, JGR for specific discussion on these instruments.

Since we extensively rely on particle volume data throughout this analysis, we will add the following to our paper (Page 3080, Line 1): "The data are processed by an inversion technique which determines a smooth and continuous size distribution that is consistent with the data and experimental response of the instruments, as well as with the instrument uncertainty". We will also add a reference to Brock et al, 2002, JGR.

REFEREE: 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

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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 detectible 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 PILSIC 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?

AUTHORS: We thank the reviewer for identifying this problem and suggesting a useful solution. We will re-format this table as suggested, and include a new column to state the fraction of measurements that were above the limit of detection. The reviewer is correct in noting that the median concentrations (for 'all altitudes') are incorrect for sodium and ammonium. They are, in fact, reversed with median ammonium = 0.6, and median sodium = 0.1. We will make this correction in the revised manuscript.

We were somewhat surprised that submicron potassium was not detected during this mission, especially since there were a number of relative pure biomass burning interceptions. However, we are confident with our calibration of potassium ion, and feel that our limit of detection of 500ng/m3 is accurate. Wollny et al (manuscript in prep, 2007)

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discuss these forest fire observations and conclude that there may have been significant precipitation scavenging, which would deplete potassium ion. (Ma et al (2004) showed that the PILS system is capable of detecting submicron potassium, but these observations were conducted much closer to the source of biomass burning (whereas these measurements involved transport times of 3-10 days). It is possible that, after significant transport time, potassium ion from biomass burning could be associated mainly with the supermicron size range; however, there were no measurements of supermicron aerosol composition aboard this research aircraft and therefore, we can not decisively comment on this.

REFEREE: 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.

AUTHORS: We agree. Since the data is clearly not correlated, we will remove the regression lines, but will just report the r2 value for biomass burning in Fig 4a,c.

REFEREE: 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

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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.

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.

AUTHORS: In this section, we have made an attempt to estimate the organic mass fraction of aerosol from an operationally-define quantity (e.g. WSOC). As referenced, WSOC/OC and OM/OC ratios can be quite variable, and depend on a number of physicochemical factors, such as air mass age, oxidizing strength of the atmosphere, precursor VOC gases, or pre-existing available aerosol. While it would be desirable to discuss WSOC/OC or OM/OC ratios, we believe too much uncertainty remains to present a meaningful discussion. Carbonaceous aerosol is still not well understood, and this work attempts to simplify some of the complexity associated with organic

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matter by taking advantage of the somewhat self-correcting features of the ratios of WSOC-to-OC and OM-to-OC, as discussed in the paper.

The reviewer is correct in stating that particle density for carbonaceous material is likely somewhat variable from our assumption of 1.2 g/cm3. This number has been estimated from the work of Turpin and Lim (2001), and represents their best estimate of particle density. While organic particle density may vary as WSOC/OC and OM/OC varies, we have no way direct way of determining these individual fractions. Thus, we believe a particle density of 1.2g/cm3 is the best possible estimate for use in this analysis.

During this work, there were no discernable patterns for the WSOC-to-OM ratio across sampled longitude, latitude, or altitudes. This statement will be added to the manuscript.

In contrast to the work of Jaffrezo et al (2005) and Turpin et al (2001), this work measures in-situ airborne particulate matter. Extrapolating their work, the reviewer points out that the OM/WSOC ratio would range from 2.1 to 6.4, while our estimate is on the lower end of the range at 3.1. As shown in Jeffrezo et al, the lowest WSOC/OC fraction was reported by Ruellan and Cachier, (Atmos. Environment, 2001), which was reported to be 12.5%. This work was conducted in the immediate vicinity of a large highway near Paris, France and represents observations that are likely mainly influenced by very fresh, mobile source emissions (in fact, Ruellan and Cachier report that their location is so close to a highway, when comparing night and daytime data they can detect no photochemical modification of the aerosol) . Our work, on the other hand, are observations of regional pollution, which are likely more aged aerosols. Thus, we do not believe the work of Ruellan and Cachier can be extrapolated and compared with our results. By further examining the results presented by Jaffrezo et al, WSOC/OC tends to range from 30%-75% for results that are not in the immediate vicinity of highways (though several are described as 'urban'). Using OM/OC from Turpin and Lim, the OM/WSOC range is more likely to be 2.8-4.3. Given the uncertainty of our results (50%), an estimated OM/WSOC ratio of 3.1 appears reasonable, and is espe-

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cially useful since using a constant value fits most of the data, even for widely varying sources.

REFEREE: 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.

AUTHORS: We agree, and will delete this paragraph.

REFEREE: 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”

AUTHORS: We thank the reviewer for the editorial comments - these changes will be made in the manuscript.

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

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