

Interactive comment on “Chemically-resolved aerosol volatility measurements from two megacity field studies” by J. A. Huffman et al.

J. A. Huffman et al.

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Our response has been divided into two parts to fit within the allowed page length for Author Comments prescribed by ACPD (15 pages).

[RC1.5] Pg. 2660: They state "Chloride constitutes a very small fraction of the total aerosol mass in both studies." The authors should make it clear this is NR-submicron chloride (not KCl or NaCl). This statement, as written, implies the overall amount of Cl overall is low.

Author response: [Resp1.5]: This issue has been addressed in detail in response to comment R2.11 from reviewer #2. Indeed submicron chloride is also low. We note that the AMS can detect KCl (see e.g. Fig. 5 of Lewis et al., 2009).

[RC1.6] p. 2661-[1.6a] Could the delayed nitrate be due to the fact that there are other

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organonitrates or other types of nitrate species besides just ammonium nitrate that are volatilizing? [1.6b] Similarly, is there any way differences between SOAR and Milagro for sulfate could be due to the presence of sulfate fragments produced by organosulfate compounds?

Author response: [Resp1.6]: Organonitrates and organosulfates can indeed produce fragments which are nominally classified as inorganic in AMS analyses. However, the balance of ammonium to the inorganic anions implies that at most a small fraction of the nitrate and sulfate ions in the AMS can arise from those species. This is consistent with other studies, as to our knowledge the inorganic forms of nitrate and sulfate have always been found to dominate the organic forms in previous studies. For example Tolocka and Turpin (2009) report: "We estimate that organosulfur compounds could comprise as much as 5-10% of the organic mass at these [12 US] sites. [..] It should be noted that these compounds are a more substantial contributor to particulate organic matter than they are to particulate sulfur."

Since these species are responsible for a minor fraction of the nitrate signal, they cannot explain the shift to higher temperatures of the entire nitrate thermogram when compared to the thermogram of ammonium nitrate in the laboratory. Thus our conclusion that "This may indicate that the more complex matrix of ambient particles is tying the nitrate more strongly to the particle phase or delaying its evaporation, compared to pure laboratory particles" continues to appear to us as the most likely explanation for the observed shift.

[RC1.7] p. 2666-The authors state "Figure 7b shows two sulfur-containing ions: the inorganic sulfate-dominated SO^+ (m/z 48) and the organosulfur ion $\text{CH}_3\text{SO}^+_{25}$ (m/z 96) which is thought to arise from methanesulfonic acid (MSA)." Organosulfate compounds will also fragment to give SO^+ at m/z 48 due to extensive EI fragmentation in the AMS. [1.7a] The authors make it sound like this does not occur and state these two different m/z values separate inorganic from organic S compounds. This needs to be fixed. [1.7b] Throughout the paper, the authors really need to make it clear that they

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are only measuring the NR-PM1 and not the total aerosol mass. Some of their captions, for example, are very misleading. For example Figure 3 states "Fraction of the total aerosol mass contained..."-but this is really showing fraction of the non-refractory PM1 aerosol mass...

Author response: [Resp1.7]: Indeed the organosulfur ions have to arise from organosulfur species, while the "sulfate" ions such as SO_4^{2-} are dominated by the fragmentation of inorganic sulfate, as described in response to comment RC1.6 above. Thus the text in the manuscript is correct. We note that here we are referring to organosulfur species such as MSA and not organosulfates. The latter will produce some "sulfate" ions in the AMS, but again we can constrain their contribution to be much smaller than that of inorganic sulfate as described in response to RC1.6.

The fact that the AMS measures NR-PM1 is described in detail in the experimental section, and this is very well-known in the aerosol community. To avoid confusion, we have changed the text to refer to NR-PM1, such as in the caption of Figure 3 mentioned by the reviewer.

[RC1.8] p. 2666-Can the authors speculate why the MFR for the N-compounds remains significant even at the highest temps?

Author response: [Resp1.8]: Clearly a fraction of these CN-containing ions does not evaporate quickly at the hottest setting of $\sim 225^\circ\text{C}$ in the TD. Our best guess is that these signals may be due to amines which are strongly bound in the particles. However, several types of nitrogen-containing organic species can produce those ions so other explanations are also possible.

[RC1.9] One of the main conclusions of this paper is that BBOA and HOA have similar (high) volatilities. The authors make general claims about the overall volatility of BBOA, however one must not lose track of the fact that the AMS is very sensitive to a specific type of BBOA (i.e. with levoglucosan markers). Typically, BB formed with high amounts of OA are usually formed during smoldering conditions. This type should be quite

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volatile. But, the AMS will be less sensitive to more refractory OC in BBOA formed at higher temperature burn conditions (and/or with different fuels). The authors should be more open about their ability to detect a specific type of BBOA based on these few ion markers-making general claims about the volatility of all BBOA is dangerous without clearly stating they are seeing one type of BBOA with the AMS and could be missing other (less volatile) types (i.e. without levoglucosan).

Author response: [Resp1.9]: The reviewer makes claims about the relative sensitivity of the AMS to different types of BBOA which are not supported by any citation, and which we do not think are correct.

In our recent paper in ES&T (Huffman et al., 2009) we present volatility analysis for POA from 18 different biomasses burned at the US Forest Service Lab in Montana as part of the FLAME-1 experiment. We reproduce the relevant text from that paper here:

"Conversely, BBOA produced by burning sage and rabbitbrush (T50 248 °C) shows the highest MFR of any OA measured to date with the TD-AMS. A large variability in BBOA volatility has also been observed in ambient air, with MILAGRO BBOA being close to the high volatility end (Figure 1a and ref 7). Grieshop et al. (2009) also recently reported the relatively high volatility of woodstove BBOA emissions, which had T50 values of ~42 °C in a TD setup similar to ours. [...] Aircraft measurements during ICARTT reported a BBOA with much lower volatility (MFR=25% at 400 °C (Clarke et al., 2007)), though the much shorter RT (~1s) used for that study would lead to higher MFR and complicates direct comparison."

Thus, clearly the TD-AMS setup can detect BBOAs of widely varying volatility, as in fact we have published already that the least volatile OA that we have encountered to date in multiple field and source studies was a BBOA. The wide variability in BBOA volatility observed in our study is consistent with that observed in the field. The forest fires near Mexico City that dominate the BBOA detected there (Aiken et al., 2009a) burned pines, which produced the most volatile BBOA observed with the TD-AMS during FLAME-1,

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and consistent with the similar volatility of the ambient BBOA in Mexico City with that of the pine POA from FLAME-1 (as shown in Fig. 1a of Huffman et al., 2009).

[RC1.10] [1.10a] At the bottom of p. 2676, the authors speculate as to why their results differ from previous reports on the volatility of organic aerosols. All of their suggestions point to potential problems with the other techniques. Is it possible that the AMS could be missing something as well? Could the more refractory OC be "invisible" to the AMS? Could they be breaking down the oligomeric (less volatile) components in their vaporizer at 600 degrees C? It is possible the AMS is more sensitive and thus biased towards the more volatile forms of BBOA. It would be appropriate to include a more balanced discussion for the reasons these techniques do not agree with one another. [1.10b] The authors also neglect to discuss another more recent paper that shows the opposite result by Clarke in JGR (2007). In their paper analyzing the volatility of the ambient aerosol up to 400 degrees, they see the polluted air masses are far more volatile than biomass burning aerosols. The fact that the AMS sees the opposite of several other approaches should lead the authors to openly discuss how the AMS might be biased against less volatile species. At the very least, they should explain the reasons they get the opposite results as several other techniques and be more open to the fact it could be due to AMS biases.

Author response: [Resp1.10]: Again, the existence of some OA that is invisible to the AMS has not been reported to our knowledge and appears very unlikely since we have quantified the presence of organic species with up to 4 orders of magnitude lower volatility than typical non-refractory OA as only ~5% of the NR OA, as has been discussed in detail in response to comment RC1.1.

We are aware of the work by Clarke et al. (2007) and in fact we have cited that paper and compared it to our results in the text quoted above in response to comment RC1.9. We have already reported much less volatile BBOAs in a previously published paper and thus there is no indication of an AMS bias against those BBOAs.

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We have added the following text to the paper to clarify this point (at P2675 L2): "The BBOA detected in Mexico City has high volatility, consistent with its dominant source from pine forest burning (Aiken et al., 2009b) and the high volatility of the smoke from pine burning in laboratory experiments (Huffman et al., 2009). We note that BBOAs of much lower volatility are possible, and in fact the least-volatile OA detected to data with the TD-AMS setup is a BBOA from sage & rabbitbrush burning (Huffman et al., 2009)."

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