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Atmospheric
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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).

[RC2.11] p. 2660: "Chloride constitutes a very small fraction of the total aerosol mass in both studies." Should be of the DETECTED aerosol mass, because the AMS can't see sea salt, e.g.

Author response: [Resp2.11] Indeed in this text we were referring to the chloride mass detected by the AMS, and have changed the sentences as a result to read:

"Non-refractory chloride constitutes a very small fraction of the total NR mass in both studies."

The objection that the reviewer raises is not a critical one, however. First, sea salt

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is most commonly in the course mode and, therefore, would not predominantly be within the size range of the AMS whether it was detectable or not. In addition, we are now characterizing a fraction of the "refractory" mass that has not been traditionally detected with the AMS by looking at the increases in the slowly evaporating species in the AMS background, as shown in Fig. 4 and discussed in Page 2663 L16 - Page 2664 L8 of the ACPD paper. Fig 4c shows that the "refractory" chloride is about a third of the NR chloride. It is possible that very non-volatile forms of chloride would not even appear on the AMS background. However, Johnson et al. (2008) show that in Mexico City the AMS detects 4x more chloride than is seen by PIXE techniques. If a major fraction of the chloride aerosol was not detectable in the AMS background, then the PIXE analysis would show considerably more than can be seen by the AMS. The fact that this is not the case strongly suggests that the combination of the NR plus background chloride measurements in the AMS capture all of the submicron chloride in Mexico City. This is consistent with the fact that Querol et al. (2008) report total chloride as 0.7 ug m-3 in PM2.5 at T0, while we reported 0.4 ug m-3 as NR-PM1 chloride at the same site (Aiken et al., 2009).

A sentence has been added to the revised manuscript discussing this point (at P2664 L8):

"Johnson et al. (2008) show that in Mexico City the AMS detects four times more chloride than is seen by PIXE (particle-induced X-ray emission) techniques. If a major fraction of the chloride was too refractory to be detected in the AMS background, then the PIXE analysis would show considerably more than can be seen by the AMS. The fact that this is not the case strongly suggests that the combination of the NR plus background chloride measurements in the AMS capture all of the submicron chloride in Mexico City."

[RC2.12] p. 2660: "The average of the MILAGRO species calculated in the same way is shown in black for each panel and shows similar behavior from the SOAR-1 averages with minor differences": why are differences referred to as minor here, but the 20%

excursion in overall sulfate contribution called significant?

Author response: [Resp2.12] The anomalous peak in the sulfate curve at 150oC does show the largest difference between the two studies. The differences between the MILAGRO and SOAR-1 studies are much smaller for a given species than between species for within a single study. This is further evidence that the technique is observing trends in species volatility separate from that of other species. To clarify this text we have replaced the quoted sentence with:

"The average of the MILAGRO species calculated in the same way is shown in black for each panel and shows similar behavior from the SOAR-1 averages with smaller differences between the two studies for the same species than are observed for different species in the same study ":

[RC2.13] p. 2660: "The fraction of these ions arising from organic species, however, is estimated to be small": what is the basis of this estimate? have lab experiments been done that show this?

Author response: [Resp2.13] The basis of this statement is the fact that the ammonium balance (the comparison of the detected ammonium with that which would be required to neutralize the inorganic anions) does not leave room for a large concentration of organic sulfates or nitrates. Lab studies are on-going in our group and will be presented in future publications.

The following text has been added here in response to a similar reviewer comment on Aiken et al. (2009), and is reproduced here as it describes the issue in more detail:

"In terms of the organic nitrates (ONs), at present we are only able to state that their contribution to total nitrate and total OA is minor based on the ammonium balance. If the AMS nitrate signal was dominated by ONs there would be a large "ammonium deficit" and large scatter when the ammonium balance analysis is performed assuming that all of the AMS nitrate signal is ammonium nitrate. Neither effect is observed

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in Fig. S-5, which indicates that ammonium nitrate is the dominant form of nitrate in Mexico City, consistent with aircraft measurements (DeCarlo et al., 2008) and previous studies (Salcedo et al., 2006). This is also consistent with Gilardoni et al. (2009) who report the contribution of ONs and organosulfates to be small based on FTIR measurements on MILAGRO samples at several sites. In Mexico City ONs should make a similar fractional contribution to submicron OA (when the mass of all OA molecules that have a nitrate group is summed) than to submicron nitrate. For example if 5% of the nitrate signal was due to ONs and we assume a MW of 250 amu for these species, the contribution of ONs to OA mass would be 4%."

The sentence has been modified as follows to be clearer:

"The fraction of these ions arising from organic species, however, is estimated to be small, based on the molar neutralization balance of ammonium vs. sulfate, nitrate, and chloride anions. This is consistent with the recent evaluation of Tolocka and Turpin who estimate that organosulfates may account for 5-10% of the organic mass and a smaller fraction of the sulfur mass at 12 US locations (Tolocka and Turpin, 2009)."

[RC2.14] p. 2661: "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": This reminds me of a general question. What particle sizes were laboratory experiments conducted for? Could the observations referred to here, for example, be due not only to chemical differences in the nitrate, but potentially to the nitrate being found in larger-sized particles that do not evaporate as quickly as smaller pure particles in the laboratory?

Author response: [Resp2.14] The laboratory experiments referred to here were with AMS mass size distributions that peaked at ˜100 nm (dva) and had a envelope of mass went from ˜30 - 300 nm. In addition, the effect of particle number loss was quantified in the laboratory for 50, 100 and 250 nm particles (Huffman et al., 2008, Fig. 5). Differences in size distributions are unlikely to dominate the differences being

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discussed here. For example Faulhaber et al. (2009) show that a shift from a 200 to 300 nm particle will shift the T50 by ˜5oC, but with consistent shape, so this effect will certainly not be a dominant one in the overall appearance of the thermograms.

[RC2.15] In Figure 3, is the lower volatility of the sulfate in MILAGRO not potentially due to size effects? Prior observations (using impactors to get mass distributions of species) have often noted sulfate in larger particles. If this is the case for MILAGRO, then the apparent lower volatility is due to mass gain from larger particles shifting into detectable range. Indeed, the sulfate and chloride closed signal enhancements (Figure 4) may both be due to particle size effects as those species could be expected to occur in larger particles.

Author response: [Resp2.15] We are not clear on which prior observations the reviewer is referring to, or whether these are for Mexico City or elsewhere, since no reference is provided. In addition, as shown in Figure 4b the volatility of the sulfate in MILAGRO and SOAR-1 is similar, so the reviewer is perhaps misinterpreting Fig. 3 (see also response to R2.16 below).

[RC2.16] p. 2661: "except that the MILAGRO sulfate lies somewhat below the SOAR-1 sulfate for most temperatures": This is different from what might be inferred from Figure 3. The data in Figure 4b look strange. The SOAR sulfate increases 20% above ambient concentrations with heating, which is attributed as most likely being due to changes in collection efficiency, with the final comment "It is also possible that other unknown effects are responsible for some of the observed variation (Huffman et al., 2008)." While I understand that the data are complicated and not every aspect can be explained satisfactorily at this point, it brings me again to the comment that in this case, probably there are too many conclusions being drawn from data with high uncertainties and that the discussion should be shortened to those points that can be reasonably explained and clearly justified given the available data.

Author response: [Resp2.16] First, the sentence the reviewer is referencing here discusses Figure 4b. The "bump" in the sulfate thermogram from 100 - 150oC is significantly more pronounced in the SOAR-1 data. The reviewer also suggests that Figure 3 relays different conclusions than does Figure 4. Figure 3 is the same data as Figure 4, simply re-plotted as a fraction of total aerosol mass and therefore can not be fundamentally different. The reviewer is likely misinterpreting Figure 3 in some way.

Second, the reviewer uses the current uncertainty in the causes of some of the observed variations in the sulfate thermogram as a reason to suggest shortening the paper. We disagree, however, and believe that highlighting aspects that are still unknown or uncertain is an important aspect of providing honest scientific results. This is especially important as we are documenting the first ambient application of a new technique, which has not yet been exhaustively studied to determine the source of all effects. Many groups are now using this TD-AMS technique because of the exciting information that can be gained about some aspects of aerosol volatility, which are not accessible with any other technique at present. The additional details of both certainty and uncertainty are helpful for the community to allow building our scientific understanding.

[RC2.17] Figure 5: given 20% uncertainty, can differences in ammonium for various time periods really be discerned?

Author response: [Resp2.17] As discussed above, even if the accuracy is 20%, the precision can be much better than that and allow the evaluation of small changes in the same quantity when systematic effects should cancel out. The fact that e.g. there is a continuous trend in the thermograms in Fig. 5a vs. time suggests that this trend is likely real. Given that this is the first time these measurements have been performed, we feel it is still important to report these data, also to serve as a comparison point with future measurements. This was already qualified in the following text of the ACPD paper (P. 2665, L1-4):

"The diurnal pattern of the ammonium balance is also shown on the same graph, show-

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ing small variations in both cases. Slightly higher nominal acidities are observed early in the morning while lower values are observed in the afternoon, which are consistent with the daily variations of the AMS Eb, as discussed below."

[RC2.18] example of unclear use of "significant": p. 2667: "have MFR significantly below the average CHO+ line" p. 2673: "This component has a significantly lower volatility relative to total OA": the difference is 20% - is it not within uncertainties?

Author response: [Resp2.18] See response to [2.2c].

In this example the sentence was modified as follows:

"...significantly ($>$ 0.1) below the average CHO+ ..."

[RC2.19] Figure 8d is not very convincing: the dominance of certain PMF-deduced fractions is used to make statements about the volatilities of those fractions. Could the discussion of Figs 6-8 be condensed?

Author response: [Resp2.19]: To be able to draw new conclusions from a complex and multidimensional data set from a new technique it is important to compare results from a variety of different angles. Further, it is may not always be practical or possible to do PMF on the full TD-AMS data set. The fact that simply analyzing the thermograms of periods dominated by different OA types already hints at the main conclusions of the manuscript is exciting and can be very useful for operation in the field and on-the-fly data analysis. We have also found that it can be more convincing for some researchers, who may view PMF as an obscure black box and trust its results less than those from the type of simple analysis shown in Fig 8d. Thus we feel very strongly that Fig. 8d should stay in the paper.

[RC2.20] p. 2671: "While the diurnal variability of OA composition and concentration is clear, (in SOAR) there is very little diurnal variability in average OA volatility." Does this not contradict the assertion in the prior section that HOA is more volatile than OOA? Further, Fig. 9 doesn't really seem to support this argument : the aerosol appears to

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be about 50/50 composition in these components during the entire morning, yet the volatility changes.

Author response: [Resp2.20] A main conclusion of the paper, as stated e.g. in the abstract, is that the volatility of HOA is similar or higher than that of OOA. The diurnal cycle of total OA volatility at SOAR-1 suggests that in this particular case the volatility of HOA and OOA is more similar, while in MILAGRO the average OOA is less volatile than HOA.

The following text has been modified for clarification of this point (at P2672 L3):

"... suggesting that HOA is more volatile than OOA in Mexico City, contrasting with their similar volatility in Riverside."

And we also disagree with the reviewer's assessment of Figure 9. The steady rise in HOA concentration as there is a steady drop in the MFR at each temperature appears clear to us. Then, in the afternoon the MFR peaks when the HOA fraction is the lowest. Further, this is consistent with other evidence (e.g. PMF of TD-AMS, Fig. 10) for MILAGRO. Again we are trying to support the same conclusion from multiple angles given the novelty of the technique and the data.

[RC2.21] Fig 10: HOA and OOA-2 look similar in volatility in both experiments?

Author response: [Resp2.21] It is true that HOA and OOA-2 have similar volatility profiles in both experiments, and this was already stated explicitly in the ACPD paper with the following text (P2673 L11):

"The thermograms of the HOA and OOA-2 components are similar, except at the highest temperatures when HOA shows a larger MFR. Again, this is consistent with trends from the individual ions that are important for each component."

[RC2.22] Conclusions: "Our results show, however, that HOA and BBOA are similarly or even more volatile than other OA components in urban air. Furthermore, SOA, which dominates the OOA, is of similar or lower volatility than any other OA component. These results strongly support the suggestion by Robinson et al. (2007) that atmospheric models should treat all OA components as semi-volatile." These statements seem to be supported by the text more than those in the Abstract.

Author response: [Resp2.22] We do not understand the criticism that the reviewer is trying to give here. This seems to be a re-statement of his/her problem with the statement in the abstract, which was dealt with in response to [RC2.4].

[RC2.23] Conclusions: "Sulfate showed low volatility, with a likely increase in AMS collection efficiency peaking at 142_C." It seemed to me that either differences were attributable to uncertainties or other effects and that the argument for CE changes was not convincing enough to attribute fluctuations solely to that effect. Further, it is likely that the sulfate was mixed with other constituents, so if CE changed for sulfate species it should have varied for others as well. It seems more defensible to note uncertainties in the results and to make sure these are also propagated to other species and that any conclusions bear these in mind.

Author response: [Resp2.23] See response to [RC2.16].

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