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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.

Anonymous Referee #2

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This interesting paper reports the results of ambient measurements using a thermodenuder (TD) coupled to a high-resolution Aerosol Mass Spectrometer (AMS), from two field campaigns, one in Riverside, CA and the other in Mexico City (MILAGRO). The temperature dependencies of the following were studied: (1) major AMS "species" (e.g., sulfate, nitrate, organic carbon); (2) individual m/z and marker ion concentrations; (3) species defined from PMF analysis of the study data set (e.g., HOA and several types of OOA). While some results, such as the volatility of sulfate species relative to other species, confirmed expectations, a rather surprising finding was that the volatility of species with low O:C ratios, associated with the HOA fraction, was higher than the volatilities of more oxidized organic carbon species.

This work merits publication in ACP. I have the following suggestions for the authors for

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improvements to the revised manuscript.

1. The paper is very long, and would benefit from editing to streamline some sections and perhaps remove some figures. As a minor example, the Introduction describes the TD technique and states that the residence time can very from 1-10 s, then on the next page the specific residence time used in this study is mentioned.

2. There seem to be quite large uncertainties associated with the method. For example, loss corrections of 5-20% in number concentration, varying with temperature, are applied (how these propagate into mass uncertainties is not indicated). While it's great that the comparison with the SMPS was done to try to understand quantification better, there is a lot of discussion in this section about the many reasons why agreement isn't better, summarized by: "Given the impact of each of the possible biases described above, we estimate the nominal accuracy of each technique at approximately +/-20% for the ratios of concentration at ambient and elevated temperatures." However, it seems that small differences, that seem well within these 20% uncertainties, are frequently noted as "significant" (I point out a few of these below). Indeed, the term "significant" is used throughout, but if it is used in its statistical sense, this is not explained; if it is not meant to indicate statistical significance, then different wording should be applied. Finally, while the PMF results are interesting, the Ulbrich paper is not finalized and clearly there are uncertainties associated with such analyses. In summary, it seems that some of the detailed comparisons and discussions that serve to increase the length of this paper are not completely justified in light of these large uncertainties, although certainly there are major points that can be made.

3. One of the toughest things about interpreting TD data is understanding how much mass, that is outside of the upper size range of the detector at ambient conditions, shrinks into the size range at higher temperatures. In this regard the distributions shown in the Supplement do not convince me that this is not a significant problem in these data sets as well. The smooth mass distribution curves shown for the AMS at least in part look the way they do because the sampling efficiency decreases sharply

above ˜700 nm. The SPMS data have a lot of unresolved mass above their upper cut points, although it is impossible to say what the mass distributions might look like near 1 micron diameter; it doesn't take very many particles to create another peak near this size range. In any case, the estimates of mass losses due to evaporation are confounded by the possibility that some mass is "gained" by larger particles shrinking into the AMS size range. This possibility isn't discussed here (other factors, such as particle bounce and shape factor changes, are mentioned). Is the aerosol dried before being sent to the SPMS or AMS when measuring ambient particles? If not, the particle sizes could be significantly shifted because of the presence of water, even if the RH in the sample stream were only ˜50-60%.

Specific comments:

Abstract: "Reduced hydrocarbon-like OA (HOA, a surrogate for primary OA, POA), oxygenated OA (OOA, a surrogate for secondary OA, SOA), and biomass-burning OA (BBOA) separated with PMF were all determined to be semi-volatile": I understand what the authors mean here, but, since volatile material is not in the aerosol phase, and the AMS cannot see nonvolatile species, this sentence as written does not really convey the point that the authors are trying to make.

Abstract: "The similar or higher volatility of HOA/POA compared to OOA/SOA contradicts the current representations of OA volatility in most atmospheric models and has important implications for aerosol growth and lifetime:" I agree that this is an interesting result. However, this sentence as written assumes the equality of HOA=POA and OOA=SOA, whereas the sentence before it indicates the HOA and OOA are "surrogates" for POA and SOA, and furthermore, if a species were truly nonvolatile the AMS would not detect it. While a case is made in the text for revisiting current modeling assumptions, it seems like more careful wording is in order here.

Introduction: " if a large fraction of the aerosol evaporates upon mild heating it implies that much of the aerosol mass is semi-volatile and therefore that a significant amount of SVOCs is present in the vapor phase to maintain equilibrium with the particle phase. Conversely, if little evaporation occurs upon mild heating it suggests that the aerosol species have low volatility and that the amount of gas-phase species in equilibrium with them is also small." Is it possible that the results are influenced by the mass concentrations of aerosol that are processed through the denuder? We would expect that the chemical nature of the species that are in the aerosol phase would vary depending upon not only the environment (CA vs. Mexico) but also depending on the total mass concentrations. From the volume distributions shown in the Supplement one can deduce that the mass concentrations were substantially higher in MILAGRO than in SOARS. (Is it ever mentioned what the total average mass concentrations were in the two studies?)

"the boundary layer is relatively low" $- >$ shallow might be better term?

OOA (oxygenated organic aerosol), however, is dominated by secondary OA (SOA) (Alfarra et al., 2004; Zhang et al., 2005b, 2007a): this really has not been shown to be true in all places, has it?

p. 2658: "The MILAGRO comparison shows slightly larger differences than that for SOAR-1": unclear, as the differences look large, 20%?

p. 2659, end: "Sulfate increases in relative concentration to a maximum at _140_C due to its slow evaporation and the smaller effect of increased CE as discussed above": here is an example where it seems to me that all of the observed variation is within the uncertainty.

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.

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?

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?

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?

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.

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.

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

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?

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?

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? Futher, Fig. 9 doesn’t really seem to support this argument : the aerosol appears to be about 50/50 composition in these components during the entire morning, yet the volatility changes.

Fig 10: HOA and OOA-2 look similar in volatility in both experiments?

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.

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

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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.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 2645, 2009.

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