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Atmospheric
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Discussions

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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Reviewer #2 Evaluation:

[RC2.0] 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 improvements to the revised manuscript.

Author response: [Resp2.0] We thank the reviewer for his/her effort in reviewing this paper and many comments which allowed us to improve the manuscript. We are grateful for the overall evaluation that "this work merits publication in ACP."

[RC2.1] 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.

Author response: [Resp2.1] We understand that the manuscript is long and the reviewer's desire to make it shorter is understandable. However, this is the first publication of the application of this very complex hyphenated technique to ambient data, with implications for two major field campaigns. This technique is now being applied by multiple groups in the field and the lab. Many issues regarding the technique and results needed to be addressed specifically and documented in this first paper. We do not see how we could shorten the paper significantly without degrading its information content and the scientific quality of the discussion. We have shortened some text where possible, and address specific comments in responses of the following sections.

[RC2.2] 2. [2.2a] 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). [2.2b] 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

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these 20% uncertainties, are frequently noted as "significant" (I point out a few of these below). [2.2c] 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. [2.2d] Finally, while the PMF results are interesting, the Ulbrich paper is not finalized and clearly there are uncertainties associated with such analyses. [2.2e] 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.

Author response: [Resp2.2a] We think the reviewer may be confusing the concepts of corrections for systematic effects, accuracy, precision, and variability here (and similarly in following sections). These are all expressed as percentages in the paper, but they have distinct meanings. We clarified what we mean in each instance in the paper (when needed), and respond to the specific instances brought up by the reviewer below.

The loss corrections that s/he mentions here were published previously, and cited as such in the ACPD manuscript (Huffman et al., 2008, Fig. 4). The losses due to diffusion and thermophoresis are systematic and consistent as a function of temperature, as the measurement of particle losses within the TD were reproducible with low variability ($<$ +-10% std. dev.). As a result of this consistency the loss of particle mass to the walls of the TD is correctable. At the most, therefore, the uncertainty of this loss correction at 230oC would be $<$ +-10% of a 20% particle mass, meaning a maximum uncertainty in particle mass caused by the loss correction of $<$ +-2%. At 50oC, however, the uncertainty in particle mass concentration would be only $<$ +-10% of a 5% particle mass loss correction, corresponding to $<$ +-0.5% uncertainty in particle mass. Thus some of the "large uncertainties" that the reviewer is discussing are not so.

[Resp2.2b] The issues of uncertainty and variability may be getting confused here. As stated in the Figure caption, Figure 1 shows error bars of variability (as +- 1 standard deviation of the campaign median MFR values). This variability comes as a result of changing volatility due to different aerosol types over the course of the weeks of data averaged together and similar effects. The variability can be rigorously calculated and is shown in Figure 1 as an example for the following plots. The error bars in Figure 2 (as discussed in the figure caption) represent the accuracy of the measurement estimated at 20% of the MFR value. This accuracy is estimated, as discussed in the text, from a variety of instrumental reasons. It is also important to note, however, that any systematic errors in the AMS or SMPS measurements (such as e.g. an error in the IE calibration of the AMS or the sizing of the SMPS) will push the recorded data in some direction from the "true" value for both the ambient and TD data. The ratio of the TD-processed signal to the ambient signal, however, will cancel such effects. If the signal is erroneously high, for example, it will be so during both ambient and TD states, reducing the relative error of the MFR. The 20% was given as an upper limit to this accuracy.

The 20% was given as an upper estimate for the accuracy of the MFRs determined by each of the AMS and SMPS techniques, which is thought to arise mostly due to systematic effects, as discussed in the paper. The precision of the measurement is often higher, and allows us to see smaller differences on some quantities.

Specific issues addressed in following section are given response there as well.

[Resp2.2c]: The suggestion to clarify the use of the word "significant" is appreciated. It was used 22 times in the original ACPD manuscript. In English and in scientific publications, the meaning of "significant" is not only "statistically significant" but also "having or likely to have influence or effect; of a noticeably or measurably large amount" (see http://www.merriam-webster.com). We often used this word in the second sense. This is common in the scientific literature, e.g. a search for "significant" in the last 5 papers published in ACP revealed that "significant" was used in this sense in all 5, and e.g. Froyd et al. (ACP 9, 4363-4385, 2009) uses this word in this sense 12 times. Thus this use appears to be accepted by the community. Since perhaps an excessive use

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of the word can be confusing, we have reviewed its usage in the manuscript with the objective of improving clarity. As a result we have changed the word to another clearer term twelve times, defined the value of significance five times, left the word unchanged another five times, and deleted it once.

[Resp2.2d] The Ulbrich paper (2009) has now been finalized and published in final form on ACP. It is true that there are uncertainties with a PMF analysis, but so are there uncertainties with e.g. linear regression (which conceptually is a 1D version of PMF) and that should not stop a scientist from trying to use the technique in the best possible way while being careful about the uncertainties. In fact the work of our group in the Ulbrich et al. (2009) paper is distinct from previous PMF literature in the large effort invested in characterizing when PMF gives real vs. spurious results and the uncertainties of the method, compared to many previous reports where large numbers of "sources" were reported without much regard to whether these could just be "splitting" artifacts of the technique. In the context of the TD-AMS data, PMF is extremely useful because it provides a way to summarize a large amount of data (thermograms of hundreds of individual ions changing in time, with each ion potentially arising from multiple sources) into a short, physically-and-chemically meaningful description that would not be possible otherwise. The fact that the conclusions drawn from the PMF analysis are consistent with the other techniques mentioned serves as additional support for this technique.

[RC2.3] 3. [2.3a] 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). [2.3b] 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%.

Author response: [Resp2.3a] The reviewer seems to have missed that this effect had already been addressed in our ACPD manuscript (P2658, L18-22) with the following text:

"First, as particles are heated, they shift to lower size bins in both instruments. Mass present above the upper size cut of the SMPS or beyond the limit of the lens transmission for the AMS can then become available for detection after the particles diameters have been reduced. This effect may be larger for the SMPS which has a "vertical" size cut vs. the more gradual cut in the AMS (Jayne et al., 2000)."

Indeed, this is one of the reasons why the +-20% uncertainty was deemed appropriate. However, we do not believe this is a large effect, due to the characterizations of the size distributions available for each field study. Both of the studies had a clear peak in the submicron mode and did not have a peak at 1 micron (a peak at 1 micron is very unusual in urban areas in our experience, although not unheard of). For example in Mexico City Salcedo et al. (2006) in their Fig 3 compare the AMS size distributions to those from a LASAIR OPC and shows that the amount of mass around 1 micron is small. Querol et al. (2008) and Aiken et al. (2009) report similar results for MILAGRO, while Docherty et al. (2009) report that the NR species concentrations were similar in PM1 vs. PM2.5 during SOAR-1. We have added the following text (at P2659 L8, ACPD-version) to the revised paper to clarify this point:

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"The fact that only a minor fraction of the non-refractory submicron particle mass is present above the AMS size cut during MILAGRO and SOAR-1 is confirmed by the results of Salcedo et al. (2006), Querol et al. (2008), Aiken et al. (2009), and Docherty et al. (2009). It would obviously be advantageous to perform size-resolved TD-AMS analysis (with pre-classification using a DMA) to avoid the influence of some of these problems, but when using the average signal ("MS") mode of the high-resolution AMS the signal-to-noise is too low to be useful. Also, when characterizing only one particle size there is a loss of information on the rest of the size distribution, which one has to weigh against the uncertainty created by some mass entering the analysis window through the upper end."

[Resp2.3b] The aerosol was dried with a nafion drier (MILAGRO) or diffusion drier (SOAR-1) before entering the AMS or SMPS instruments. The following sentence was modified (P2652 L8-9 of ACPD manuscript) to make this clear:

"During sampling the ambient flow is dried ($< \tilde{}$20% RH) and then split into a portion that goes directly to the AMS and other instruments (e.g. SMPS) without heating and another that passes through the TD before entering the AMS."

Specific comments:

[RC2.4] 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.

Author response: [Resp2.4] We disagree with the reviewer's comment and nomenclature here. First, the AMS cannot detect refractory species, such as mineral dust, black carbon and most NaCl from sea salt. The AMS detects, therefore, what is operationally defined as non-refractory aerosol components if signal appears from flash vaporization

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at 600oC. It is incorrect to say that the AMS cannot detect nonvolatile species. Ammonium sulfate, for example, has virtually no vapor pressure (and is therefore considered nonvolatile) but is detected by the AMS.

Further, the use of the term "semi-volatile" to refer to species which are partly present in the particle and gas phases is standard in the organic aerosol literature. For these reasons we believe that the sentence as written is clear and appropriate.

[RC2.5] 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.

Author response: [Resp2.5] We disagree with the reviewer regarding this point. The close correspondence of HOA with POA and OOA with SOA has been shown in many studies, including MILAGRO and SOAR-1. E.g. Docherty et al. (2008) compare four other methods of estimating SOA and find them to be consistent with the assumption that the AMS OOA is dominated by SOA. Similarly Aiken et al. (2009) show that the assumption that OOA is SOA is consistent with the results from the Chemical Mass Balance of Organic Molecular Markers in Mexico City. The reviewer does not provide any reference that would suggest otherwise. In the sentence quoted by the reviewer we state both as "HOA/POA" to remind the reader of this use of HOA as a surrogate for POA. It is not practical to keep reminding the reader that HOA is a POA surrogate in every sentence within the manuscript.

Further, while it is true that the AMS cannot detect refractory aerosol components, to our knowledge no organic material (as opposed to black carbon, for example) has been

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shown to be refractory in the AMS. See response to comment R1.1 from reviewer #1 for further details. As a result, we therefore assume that the AMS is able to detect all OA components.

[RC2.6] 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?)

Author response: [Resp2.6] It is possible that the results of the TD-AMS analysis are somewhat influenced by the mass concentration arriving at the thermodenuder. However, the measurements of aerosol volatility are reported here at ambient concentrations already, not at arbitrarily high or low levels with respect to ambient. The partitioning between gas and particles phases, therefore, is most appropriately studied at precisely these concentrations.

Changes in ambient mass concentrations may contribute to the variability in the thermograms during different periods of time, and to differences between studies performed at different concentrations. However, we do not believe this is a major effect for the data presented here. For example, the results from Mexico City and Riverside are very consistent, despite a factor of two difference in ambient aerosol concentration. In addition, several other previously published works address this issue and also suggest

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that it is not a dominant issue. Faulhaber et al. (Fig 4, 2009) show that for a 200 nm oleic acid particle the temperature at which 50% of the mass has evaporated (T50) increases by ˜4oC after increasing mass concentration from ˜0 to 200 ug/m3. Huffman et al. (2009) also show that the affect of aerosol composition dominates the effect of aerosol concentration for several POA sources. Finally, Huffman et al. (2008) show that recondensation onto particles exiting the heated section appears to be a minor effect.

To make the readers aware of this issue, we have updated the text with the following sentence added to the introduction at P2653 L6 (italics show new text):

"Faulhaber et al. (2009) further characterize the kinetics of particle evaporation in the TD and show that a diameter shift from 200 nm to 300 nm increases the evaporation temperature by ˜5oC. The mass concentration of ambient aerosol may also influence the evaporation of mass within the TD to some degree, but this effect has been shown to be small for a wide range of concentrations (Faulhaber et al. 2008, Huffman et al. 2009)."

[RC2.7] "the boundary layer is relatively low" - > shallow might be better term?

Author response: [Resp2.7] The sentence has been modified as suggested.

[RC2.8] 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?

Author response: [Resp2.8] True, the relationship between OOA and SOA has not been shown in all locations. This is obviously impossible, however, and the statement is true for all locations that have been analyzed in detail (as e.g. in the papers referenced) and certainly for Mexico City and Riverside. Also see response to [RC2.5].

[RC2.9] p. 2658: "The MILAGRO comparison shows slightly larger differences than that for SOAR-1": unclear, as the differences look large, 20%?

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Author response: [Resp2.9]: It is true that the comparison of SMPS and reconstructed AMS + refractory species is closer for SOAR-1 (Fig. 2a) than for MILAGRO (Fig. 2b). Some of this uncertainty does not stem from the TD-AMS, however. For example, the MFR of the reconstructed AMS + refractory varies by ˜25% at 230oC, depending on which estimate is chosen for the refractory components. This has nothing to do with uncertainty of the TD-AMS points themselves.

To be clearer we have changed the sentence to be as follows (with "slightly" removed from text): "The MILAGRO comparison shows larger differences than that for SOAR-1 and more dependence on the chosen estimate for crustal and metal material."

[RC2.10] 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.

Author response: [Resp2.10] Again, the absolute accuracy on MFR was given as ś20% of the value at each temperature, which is consistent with the comparisons with the SMPS discussed in section 3.1.2. The low variability, however, indicates that the process governing this distinct shape in the sulfate curve is systematic. For example, it is similar for different sulfate ions (Fig. 4b) and it has a clear diurnal cycle (Figure 7).

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

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