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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 #1

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This paper describes the relative volatility of the ambient NR-PM1 aerosol sampled in Riverside and Mexico City. Differences in the volatility of different organic species are presented. The paper is well written overall, however there are a number of questions that need to be addressed suitably before publication is merited as delineated below:

1) In the abstract, the authors state "Our results strongly imply that all OA types should be considered semivolatile in models." Since the AMS cannot detect some of the non-volatile OA that doesn’t vaporize, this statement could be misleading and possibly incorrect. What does this statement mean exactly? Isn’t this result biased towards the more volatile particles the AMS detects with the highest efficiency? Also, a recent AMS paper published on ACPD by Cross et al. (cited below) mentions how the AMS only produces a prompt ionization signal for 23% of the ambient particles in Mexico

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City. The particles that were being detected were biased towards the very smallest (i.e. freshest) sizes. If there is a bias to the particles the AMS does detect, how much can the authors justify such broad general conclusions about the volatility of all organic particles based on a minor subset of ambient particles? This should be addressed in the revised manuscript.

Single particle characterization using a light scattering module coupled to a time-of-flight aerosol mass spectrometer E. S. Cross, T. B. Onasch, M. Canagaratna, J. T. Jayne, J. Kimmel, X.-Y. Yu, M. L. Alexander, D. R. Worsnop, and P. Davidovits Atmos. Chem. Phys. Discuss., 8, 21313-21381, 2008

2) On p. 2650, the authors state: "show that the oxygenated species which these techniques can detect in ambient aerosols (which should be dominated by SOA)." Also, on p. 2655, they state again "OOA (oxygenated organic aerosol), however, is dominated by secondary OA (SOA) (Alfarra et al., 2004; Zhang et al., 2005b, 2007a)." It has been shown that oxygenated species are also produced by other sources such as biomass burning so is it correct to state that all oxygenated species are SOA? This will be highly dependent on the location where you are sampling–in Riverside in the summer, it is probably relatively accurate. But it is far less accurate in Mexico City which has been shown to have a significant fraction of ambient aerosols produced by biomass burning.

3) p. 2651: "The AMS measures non-refractory (NR) species, operationally defined as those that evaporate at 600_C on the AMS vaporizer, which in practice includes organic material and most inorganic salts, but excludes crustal material, black carbon, and sea salt.:" This statement is incorrect. Many inorganic salts, in addition to NaCl, such as KCl, K2SO4, etc. do not evaporate until well above 600 degrees. KCl and K2SO4 have been shown to represent as much as 30% of the mass of biomass burning particles in some regions of the world. The AMS detects only a very small percentage of K-salts (<1%) due to surface ionization processes occurring at 600 degrees; it does not volatilize 100% of these salts. This needs to be discussed more accurately.

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4) On p. 2658, they state: "The concentration of crustal materials was determined by multiplying the measured mass of each of the elements common in soil (in the nominal size range 0.07–1.15 μm) by a scalar value to estimate, the total mass of the metal oxides present (Malm et al., 1994)." This correction factor Malm used was derived based on dust/soil mineralogy typical of the western United States. How similar is the dust in Mexico City? How much error is there in this estimate method? It seems like a different mineralogy could make the values be significantly different.

The authors also state on this page that "Non-crustal metals such as Zn were added to the refractory mass following the same procedure." How is this done? More details are needed.

The authors state: "To obtain an alternative estimate, we used the report from Querol et al. (2008) that 15–28% of the PM2.5 mass at urban sites in Mexico City during MILAGRO was crustal material with additional trace metals approximately 1%. We added soil plus metal estimates of 15 and 20% of the mass, respectively, to the measured AMS and black carbon measurements, taking into account that the fraction of these species should be lower in PM1 than PM2.5."

This is lacking important detail. How much lower did the authors make it for PM1 and how was this value verified? Also, they state they are using an SMPS to estimate and compare mass for PM1, but most SMPS systems only effectively measure particles up to about 600-700 nm–how do the authors account for the missing mass in the significant 600-1000 nm size range? What density do they assume for their conversion of SMPS number to mass? Is it size dependent (as one would expect it to be)? This entire section used for Figure 2 is vague and needs to be re-written so the reader can understand the assumptions that were made, the resulting error in each of their assumptions, etc.

On p. 2658, they state: "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)."

This is an important point. Give the size cuts for each instrument. The AMS has reported vertical cuts above 0.7 microns for the aerodynamic lens system. Is this a different lens system–if so the authors should discuss and show the transmissions efficiency curve in the supp. info. section.

Also, they state "Second, particles may become irregular as more volatile material on their surface evaporates and reveals, for example, part of the soot cores on which other species had condensed. This effect will lead to an overestimation of the volume in the SMPS since irregular particles are sized larger than their actual size by mobility-based techniques, and even a modest change in the dynamic shape factor from 1 to 1.1 will result in an overestimate by _25% of the apparent SMPS volume (DeCarlo et al., 2004), while soot particles can have shape factors as large as 3.5 (Slowik et al., 2004).

What is "their actual size"–in aerodynamic, vacuum, or geometric diameter? Provide an estimate of how much this could affect their values–they mention 25% but that is for a very small change in shape factor.

On p. 2657, they state: "Previous results show a potential change in Eb of the order of 10–20% for ammonium sulfate particles in the temperature range 90– 175_C during laboratory tests (Huffman et al., 2008), while similar effects are observed 5 for ambient sulfate as described below. Potentially the AMS shape-related collection efficiency (Es) (Huffman et al., 2005), which is typically close to one for ambient particles (Salcedo et al., 2007), could lead to similar effects if the particles become highly irregular after heating (Huffman et al., 2008)."

This part contradicts (and ignores) the recent paper on ACPD by Cross et al. showing that only 23% of the particles produce a prompt ion signal in the AMS for ambient particles detected in Mexico City. Other papers have used a CE of 1. Yet, other papers have stated the CE for dry ammonium sulfate particles based on lab studies is 0.25 (also mentioned in Cross, ACPD, 2008). This portion of the paper needs serious clarification–at a minimum, the authors should be consistent and accurately quote values from previous publications, especially more recent ones that have provided greater insight into AMS detection biases.

After listing many possible sources of error, they then state "Despite the effects that complicate the comparison between the two techniques, the agreement between the reconstructed AMS and SMPS mass for SOAR-1 is good, and the observed differences for MILAGRO are within the nominal accuracies of both techniques. Given the impact of each of the possible biases described above, we estimate the nominal accuracy of each technique at approximately ś20% for the ratios of concentration at ambient and elevated temperatures."

What significance does a "good" comparison have? How can they possibly state their accuracy is 20% when their collection efficiencies for different particle types could vary by as much as a factor of 4-5? How was this error calculated?

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.

p. 2661–Could the delayed nitrate be due to the fact that there are other organonitrates or other types of nitrate species besides just ammonium nitrate that are volatilizing? 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?

p. 2666–The authors state "Figure 7b shows two sulfur-containing ions: the inorganic sulfate-dominated SO+ (m/z 48) and the organosulfur ion CH3SO+2 25 (m/z 96) which is thought to arise from methanesulfonic acid (MSA)." Organosulfate compounds will

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also fragment to give SO+ at m/z 48 due to extensive EI fragmentation in the AMS. 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.

Throughout the paper, the authors really need to make it clear that they 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…

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

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 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).

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. 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.

Overall, the paper has some nice findings, but there are a number of places where the discussion could be strengthened as detailed in this review.

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

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