Atmos. Chem. Phys. Discuss., 9, S2777–S2790, 2009
www.atmos-chem-phys-discuss.net/9/S2777/2009/

Atmospheric
Chemistry
and Physics
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.

Received and published: 19 July 2009

Reviewer #1 Evaluation:

[RC1.0] 0) 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:

Author response: [Resp1.0]: We thank the reviewer for the effort s/he put in this review which will help us improve the quality of the paper. We note the overall positive evaluation. As a clarification, our paper also describes the volatility of inorganic species and not just organic components. Responses to individual comments are addressed below.

[RC1.1] 1) In the abstract, the authors state "Our results strongly imply that all OA types should be considered semivolatile in models." [1.1a] Since the AMS cannot detect some of the nonvolatile 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? [1.1b] 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 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-offlight 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

Author response: [Resp1.1]: 1) Regarding possibility of volatility dependent OA bias:

We already described in the original version of our ACPD paper (P2663 L16-25) that there is a clear means of detecting species that evaporate slowly in the AMS. The relevant text is pasted below:

"Also shown in Fig. 4 is the relative amount of material that remains in the AMS signal during the closed phase of the chopper cycle. During MS-mode data acquisition the particle beam is blocked at regular intervals in order to quantitatively subtract the residual gas background from the particle signal (Jimenez et al., 2003). It is observed that this background may increase during periods of elevated particle concentration, which can be due to species that evaporate more slowly than the open/close cycle of the AMS chopper (typically 3-5 s), or due to slow evaporation of particles that bounce from the AMS vaporizer and land on colder surfaces, e.g. 250C in the ionizer region instead of 600C. Thus it is of interest to evaluate the magnitude of this signal, as a qualitative indicator of the presence of less volatile species."

This method allows the detection of species which evaporate in the AMS background with timescales of several hours, which allows the detection of species with vapor pressures four orders of magnitude lower than with the 3 seconds used in typical AMS mass spectrum-mode analysis. This method allows us to quantitatively evaluate the presence of OA species of much lower vapor pressure in ambient aerosols. We included this information for the inorganic species measured by the AMS in Fig. 4, but we had mistakenly left it out for the organic species. We have added this information to Figures 8(c) and (d), which shows that the slowly evaporating fraction of OA is ˜5%. We have added the following text to the paper (at P2671 L3, ACPD-version) to explain this point:

"Figures 8c-d also show the excess OA signal in the AMS background as a fraction of the mass spectrum mode signal under ambient conditions, with very similar results for MILAGRO and SOAR-1. The signal appearing in the background when the aerosol has been heated at 230oC is ˜5-6% of the ambient signal, and this is our best estimate of the signal due to OA of vapor pressure low enough not to evaporate in the few second timescale of the MS mode. The excess signal under ambient (non-TD) analysis is ˜17-18% of the standard signal of ambient OA and corresponds to both the ˜5% low volatility OA, plus ˜12% signal from particles which may have bounced in the colder surfaces in the vaporizer, and which are accounted for in an average sense with the CE and RIE corrections."

And also at P2677 L29: "A new technique using the AMS background signal was demonstrated to quantify the fraction of species up to four orders-of-magnitude less volatile than those detectable in the MS mode, which for OA represent ˜5% of the NR OA signal."

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

We are also not aware of any reports of "nonvolatile OA" which is not detected with the AMS. Many OA standards, including some considered non-volatile such as humic and fulvic acids have been analyzed with the AMS, and they are readily detected (see e.g. Alfarra, 2004; Alfarra et al., 2004; Zhang et al., 2005a). The reviewer does not provide any reference to support that statement.

There is also no reported evidence that the AMS detects in the field some types of OA much more efficiently than others. Some difference in sensitivity would not be totally unexpected, and e.g. Aiken et al. (2009b), who report the main results of the Mexico City T0 study, state that: "it is possible that the different PMF-AMS OA components could have slightly different relative ionization efficiencies (RIEs), and/or bounce-related collection efficiencies (Eb) to the extent that they are present in externally mixed particles. Both of these effects would lead to a positive bias of the chemically-reduced and more volatile components (HOA, BBOA, LOA) and a negative bias against OOA (Jimenez et al., 2003; Huffman et al., 2005, 2009; Zhang et al., 2005b)." However, as described later by Aiken et al. (2009b) and also Docherty et al. (2009), this effect is not apparent on detailed intercomparisons with other instrumentation, and it appears that all types of OA are detected with approximately the same efficiency.

2) Regarding possibility of detection bias for different particles:

With respect to the Cross et al. paper, the reviewer is confusing apples with oranges. That paper is the first demonstration of a new type of single particle mass spectrometer based on the combination of the AMS with an internal light scattering unit. It also used a different AMS than was used here for a period of 3 days, and pending additional experiments, it is not clear that those results apply to every AMS. The light-scattering single-particle (LSSP) operating mode in the Cross et al. (2008) study and the MS operating mode used here have significant differences in sampled particle size range, measurement timescales, and the use of particle number vs. nonrefractory particle mass. For example, the LSSP prompt particle measurement quoted by the reviewer is a particle number based measurement for 1 of 2 types of particle vaporization

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

events that led to measurable mass spectrometric signal in a small diameter size range (dva>250nm). In contrast, the mass spectrum (MS) average mode used in our study measured total mass spectrometric signal for all NR-PM1 material in/on all particles sampled into the AMS.

Detection of MS signal in the LSSP mode requires that (a) the particles must contain non-refractory (NR) material to produce a signal pulse above the instrument background and (b) the vaporization of the NR material needs to occur in a few tens of microseconds. Some particles will not produce a signal pulse large enough for detection because they contain mostly refractory material. The mass fraction of refractory materials in PM2.5 in at the T1 site where Cross et al. operated their instrument is 41% (Querol et al., 2008). While that fraction will be somewhat lower for submicron particles, dust, metals and especially black carbon are important in the submicron mode (e.g. Johnson et al., 2006). Thus there is clearly a sizeable percentage of ambient particle number that will not be detectable with an AMS-based single-particle instrument. Other particles may evaporate more slowly (e.g. in hundreds of microseconds or milliseconds, or even in a second). In fact, as measured by Cross et al., while 23% percent of all the particle number were classified as having "prompt"; vaporization, another 26% display "delayed" vaporization on the LSSP timescale. Non-refractory material in particles that are not detected in the LSSP mode due to both of these effects, will still be quantified by the MS mode used here, in which the total signal is averaged for a few seconds. Due to the difference in timescales, the MS mode can reliably detect species with vapor pressure four-to-five orders-of-magnitude lower than those detectable with the LSSP mode.

The only reliable way to verify the quantification of the AMS when using the average mass spectrum mode is to intercompare it to other quantitative instruments. As discussed by Cross et al. in their responses and revised manuscript, evidence that the NR particulate measurements of the AMS represent the NR ambient aerosol chemistry and mass loadings come from detailed studies comparing the AMS measurements with

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

independent instruments. For ambient AMS measurements the CEs derived from intercomparisons to a large number of total PM and speciated instruments range between 0.45 and 1 (e.g. Canagaratna et al., 2007, and references therein). Previous publications have shown that for any given study, a single AMS CE factor not only reproduces the total mass but also the speciated mass to within +/- 20% (e.g. Drewnick et al., 2003; Hogrefe et al., 2004; Takegawa et al., 2005; Zhang et al., 2005a; Quinn et al., 2006) and also the fractions of different types of organic species (Takegawa et al., 2005; Zhang et al., 2005b; Kondo et al., 2007; Docherty et al., 2008; Aiken et al., 2009b). This suggests that the different vaporization modes do not result in a significant bias in the average non-refractory mass concentrations and compositions obtained using the MS mode.

[RC1.2] 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.

Author response: [Resp1.2]: The reviewer is misunderstanding the text at this point. We do not state that all oxygenated species are SOA. POA from sources such as motor vehicles, meat cooking, and biomass burning do contain some oxygen, as e.g. we have quantified in several recent papers (Aiken et al., 2008; Huffman et al., 2009; Mohr et al., 2009). The text in page 2655 is introducing the background on the OA components identified with PMF analysis of AMS data, one of which is denoted as OOA because of the high oxygen content it its spectra. As shown in those papers and also by Aiken et al. (2009b) for the Mexico City dataset analyzed here, all OA components have some oxygen, but ˜2/3 of the total organic oxygen is accounted for by the OOA component (Fig. 6 of Aiken et al., 2009b).

We also note that biomass burning can produce SOA (e.g. Yokelson et al., 2009) which will be much more oxygenated than the original POA and will likely be part of the OOA. Current AMS factor analysis techniques generally separate OOA components of different photochemical age, oxygen content, and volatility, but cannot generally separate SOA formed from different types of precursors, and additional information from co-located measurements are needed for that estimation. Aiken et al. (2009a) addresses that issue for the Mexico City dataset.

[RC1.3] 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 Ksalts ($<$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.

Author response: [Resp1.3] We did not state that the AMS can detect all inorganic salts. To clarify this point we have changed the text to "The AMS measures submicron non-refractory (NR) species [..] which in practice includes [..] the most abundant inorganic salts."

We note that the AMS can detect KCl (see e.g. Fig. 5 of Lewis et al., 2009).

We also note that some of the less volatile salts may be analyzed with the technique that uses the AMS background introduced in our ACPD paper (P2663 L16-25) and also described above in response to comment RC1.1, since that technique can de-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

tect species with vapor pressures four orders-of-magnitude below those of "AMS non-refractory&" species. The possibilities and quantified approach of this method are just starting to be analyzed in detail by our group and others. We have added a note to the manuscript suggesting this possible method (at P2671 L3).

[RC1.4a] 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.

Author response: [Resp1.4a]: This detail is explained more fully by Aiken et al. (2009b) and we have added a citation to that paper to direct the interested reader to further details. The relevant text of Aiken et al. is quoted here:

"Soil mass is estimated from the PIXE measurements by the method of Malm et al., 1994 (Malm et al., 1994; Salcedo et al., 2006). Metal concentrations in fine PM are estimated using averaged chemical compositions reported by Moffet et al. (2008b) for those with high concentrations (from highest to lowest cation concentration: Zn: ZnCl2, Zn(NO3)2 and ZnO; Pb: PbCl2 and Pb(NO3)2; Na: NaCl and NaNO3; PO4) and the average soil factor for the metals with very small concentrations (Cu, Cr, Hg, Mg, Mn, Ni, Sn, V, and W)."

There can be small differences in the estimated soil concentrations if different assumptions are used for the soil calculations, but most of the soil mass is accounted for by silicates, aluminosilicates, and carbonates (Querol et al., 2008) which are also present in the Western US.

[RC1.4b] 4b) 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-[1.4e] 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.

Author response: [Resp1.4b]: The fraction of the soil between PM1 and PM2.5 was calculated using the results in Fig. 2b of Aiken et al. (2009b), who report the size distributions of soil from the PIXE technique measurements of Laskin et al. (PNNL group). Most of the soil mass in the PM2.5 size range is below PM1. We have clarified this point in the manuscript.

Unfortunately we cannot account rigorously for the mass in the 600-1000 nm size range, due to differences in the transmission and sizing of the AMS and the SMPS in that size range. This is one of the reasons why the MFRs calculated from the SMPS and the AMS are not expected to agree perfectly, as we explain in this section.

As already stated in the ACPD paper (P2657 L13-15): "In order to compare with the TD-AMS, the SMPS total apparent volume was converted to total mass using Eq. (4) from DeCarlo et al. (2004) to estimate the total aerosol density." Since this seems to

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

still have been unclear, we will add another reference to Equation (2) of Salcedo et al. (2006), which is written more explicitly.

We have added additional detail on these topics (and also other topics discussed in other comments by reviewer 1) to section 3.1.2.

[RC1.4c] 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.

Author response: [Resp1.4c]: This point has been addressed in detail in response to point R2.3a from reviewer 2. The size cuts of the SMPSs which were set up after the TD can be observed in Fig S1 of the ACPD paper and were 820 and 660 nm in SOAR-1 and MILAGRO respectively. A lower size cut was used during MILAGRO due to limitations with arcing of the DMA column at the highest voltages, due to the lower ambient pressure of Mexico City (2240 m above sea level). The lower size cut of the SMPS during MILAGRO may have enhanced the effect of particles entering the detection size range of the SMPS in this campaign, and may help explain the larger differences observed in Fig. 2b vs. Fig. 2a. The AMSs used in these two studies used "standard" lenses, which do not have a vertical cut above 0.7 microns but a more gradual cut with some transmission above 1 um dva. The size cut was similar to that of Bahreini et al. (2009) who report: "constant transmission (close to 100% in the size range of dva ˜100-700 nm [..] The transmission of larger particles decreases and approaches 50% for particles at dva ˜900 nm".

[RC1.4d] Also, they state "Second, particles may become irregular as more volatile

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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.

Author response: [Resp1.4d]: We have replaced "their actual size" with "their volume-equivalent diameter" to clarify the first point. This is the diameter that the particle would have if its components "melted" to form a sphere, keeping the same average density and preserving any internal void spaces (DeCarlo et al., 2004). When the total volume is calculated from a number size distribution vs. volume-equivalent diameter, the correct total volume is obtained. When mobility diameter is used (as for SMPS data), the total volume is overestimated when non-spherical particles are present, as described in the manuscript.

The overestimation of particle volume from SMPS data for other values of the dynamic shape factor can be evaluated with the results in Figure 6 of DeCarlo et al. (2004) (The overestimation of particle volume by the SMPS is the inverse of the effective density type I in that figure). For example for a dve of 200 nm and dynamic shape factors of 1.5, 2 0, and 2.5 the overestimation of particle volume by the SMPS would be x2.6, x5.6 and x10 respectively. The impact of this effect cannot be evaluated quantitatively for the data presented here because the distribution of dynamic shape factors in the ambient aerosol population (before and especially after heating) is not known. However, it is clear that there is a high potential for overestimation of particle volume by the SMPS (especially after heating) in areas where soot particles are important such as in the studies presented here, and this may explain part of the difference observed in Fig. 2b.

We have modified the text in the manuscript to better address this point (at P2659 L9):

"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. (2009b), and Docherty et al. (2008). 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 ratio 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 weight against the potential inaccuracy created by some mass entering the analysis window through the upper end."

[RC1.4e] 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 MILA-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

GRO 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 20% 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?

Author response: [Resp1.4e]: The reviewer is again misunderstanding and incorrectly interpreting the results of Cross et al. Again we note that their findings apply to the instrument they used and not to "the AMS" meaning every AMS, and that 41% of the particles at T1 where they operated the instrument may be composed of refractory material which is not detectable with the AMS. We also note that the prompt detection that is essential for the single particle mode is irrelevant for the average mass spectrum mode used in our paper. Here in addition the reviewer appears to be confusing the shape-related CE (Es) with the bounce-related CE (Eb). The differences between these terms are explained in Huffman et al. (2005), which is cited in the manuscript precisely for this reason. Es was indeed shown to be approximately one for multiple datasets including in Mexico City by Salcedo et al. (2007), as correctly stated in the manuscript. We are not aware of any ambient AMS study which has reported an Es lower than one, although Es has not been studied after thermal denuding, as we are explaining in the paper. The following text (at P2658 L29) has been modified for clarification:

"Finally, while shape-related collection efficiency (Es) has not, to our knowledge, been reported to be significantly below 1.0 for any ambient conditions, the bounce-related collection efficiency (Eb) ... . This has not been studied in detail, however."

Regarding the uncertainty estimated for MFR, we note that the MFR is the ratio of two concentrations, and that systematic effects which affect the concentration before and after the thermal denuder in the same way (such as uncertainties in nitrate ionization efficiency, relative ionization efficiencies of different species, and at least partially the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

uncertainties in particle collection efficiency) cancel out since they affect the numerator and the denominator in the same way. For this reason the uncertainty in the AMS MFRs is actually lower than those on the absolute concentrations of the different species. The overall uncertainties were estimated by uncertainty propagation of the estimated uncertainties of the most important effects.

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper