**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "

Condensational uptake of semivolatile organic compounds in gasoline engine exhaust onto pre-existing inorganic particles" *by* S.-M. Li et al.

S.-M. Li et al.

shao-meng.li@ec.gc.ca

Received and published: 6 June 2011

Response to the comments by Anonymous Referee #1

We will directly address the major points. The original comments are given in brackets.

[1] A core assumption underlying the experiments is that lab-generated inorganic seed particles represent 'ambient' particles that these gases might condense partition into better than the particles already in the exhaust stream, which are filtered out in the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

experiment.]

We never said "better", just that it occurred. Starting out with pure seed particles, and ending up with organic-enriched particles after exposure to the gas phase exhaust, shows that this process occurred, even under different dilution scenarios.

[In reality, vehicle emissions experiencing dilution ratios (80 – 2000) on time scales (2-7 minutes) considered here will mostly be exposed to particles in that vehicle's and others' exhaust. For example, overall dilution ratios of 1000 occur within a second and a few meters of the tailpipe and roadway concentrations are typically significantly elevated above background and dominated by carbonaceous particles [K. Zhang andWexler, 2004]. While it is clear that under experimental conditions used here VOCs or SVOCs are soluble in the seed particle material, it should be expected that they will be much more soluble in the primary OA (as they are presumably both largely comprised of hydrocarbons) that is in the tailpipe.]

We disagree. First of all unless one knows what is condensing one cannot be sure that it is more soluble in the primary aerosol. One can imagine that the non-polar compounds may be more soluble in the POA than the inorganic particles, and that polar compounds may be more soluble in the inorganic compounds. Our data do not allow us to make such an assessment; but the fact is that there are VOC or SVOC species that were soluble in these seed particles in the current experiments. This suggests that the compounds may be polar compounds. Indeed, the AMS organic mass spectrum (in the new Figure 6) shows a large m/z44/total organic mass ratio of 0.097 (and a few other mass fragment ratios), suggesting large content of oxygenated chemical species in the COM, not hydrocarbons as suggested. This is especially true since the COM is larger than the POA in the first place.

Secondly, in real world situations, exhaust gases will be in contact with POA from the same vehicle and other vehicles, and therefore re-partitioning may occur but not one of dissolution into the POA. The POA from one vehicle should have been in equilibrium

with the gases from the same vehicle at the exhaust point and should further evaporate upon dilution, not the other way around as suggested. Even within a few meters of the exhaust, dilution will have reduced the gas phase partial pressures by 1000's, and part of the POA will evaporate (an example is given by Robinson et al., 2007; Science for diesel particles).

This situation should apply to mixture of plumes from other vehicles since their exhaust gas-to-POA partitioning is statistically treated the same by models and even in policy frameworks.

[As mentioned in the Short Comment by R. Saleh, this may be in effect 'double-counting' these SVOCs, which are actually in equilibrium with an organic particle phase in the CVS, but partition into this new particle phase (the seed aerosol) when the equilibrium is disturbed by the HEPA filter.]

These comments are thought provoking and made us to explore the details of the organic mass spectra, originally planned for a follow-up paper. Although this comment is in contradiction with the previous comment that VOC will dissolve into the POA upon emission, we agree that in theory, re-partitioning of the POA with gas phase should have caused mass loss from the POA to the gas phase, potentially making materials from POA available for further dissolution in the seed particles (assuming that the evaporative and condensing species are the same) and may thus lead to "double" counting.

However, the results suggest that this effect is insignificant. Please see the reasoning as outlined in the response to Saleh's comments. Without knowledge of the evaporating/condensing species, if we treat the gas phase VOCs as one single species, then given the relative partitioning of the VOCs between gas and particles, most of the evaporated POA should stay in the gas phase. The ratio COM/PTHC is about 0.11 for M_s = 15 ug m-3 (equation 9, originally equation 7) in the present study, changing with the level of M_s. Hence, if there was a condensation of evaporated POA, assuming that COM(POA-evap)/P(POA-evap)= 0.11, only 10% of P(POA-evap) would condense on

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

the COM. The condensed P(POA-evap) would be less than 7% of the COM.

There is also the issue of whether the evaporated mass from POA is the same as COM. We do not have info on the chemical composition of the POA, but data published by Mohr et al. (2009) indicate mostly hydrocarbon-like materials for gasoline engine POA. In comparison, since COM is oxygenated (new Figure 6), evaporated POA was not the same mass as the COM. In such a case, we are NOT double counting; we are actually adding more mass that in the absence of the seed would be 100% in the gas-phase.

To clarify, we have included a figure (the new Figure 6) to show the aerosol organic mass spectrum from the study. The spectrum has the highest organic fragment at 44. This is an indication that a large fraction of the COM is oxygenated. Based on the current North American gasoline vehicle emission inventory VOC profiles (US EPA, http://cfpub.epa.gov/si/speciate/ehpa_speciate_browse_source.cfm?ptype=G), aldehydes and ketones account for 30% of the 65% of what one can measure in the gas phase. If only 1% of that 30% ends up in the seed particles, it will lead to the observed oxygenated COM during the experiment.

Please note that most of the discussions above are now incorporated into the text.

[While I think I understand the motivation for this experimental design (to have a single particle distribution to monitor), the capabilities of an HR-TOF-AMS are such that the same experiment could be conducted with both the full diluted vehicle exhaust and an introduced inorganic seed in the flow tube to provide a more realistic assessment of the proclivity of the SVOC to partition/dissolve into the seed particles (while also controlling for the influence of particle coagulation). This would give a more realistic picture of what might happen in the atmosphere immediately outside of a vehicle tailpipe.]

The primary particles in the CVS are of the size of 10-15 nm (geometric mean diameter) based on the SMPS and likely smaller after dilution (due to OC evaporation). These particles were thought to be outside the AMS detection size range and no measurements were made on these particles using the AMS. Given the argument above,

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

there should be little difference for the COM with or without the presence of the primary particles.

[2)Related to the above, SVOCs evaporate off particles collected on Teflon filters in ambient monitoring and elsewhere, leading to 'negative artifacts' in mass measurements [Subramanian et al., 2004]. Likewise, trapped SVOCs may sorb/desorb from the HEPA filter used to remove particle from the CVS stream and then condense on seed particles, leading to 'double counting'. Was this considered during experiments or data analysis?]

See the replies above on the relative magnitude of primary particle mass compared with the gas phase VOC. The HEPA filters may sorb and/or desorb VOCs, but each experiment was run over an extended period of time that the filters should have been equilibrated with SVOCs.

[2) AMS data should be included in the MS or supplemental material.]

Agreed. A new figure showing the AMS mass spectrum is now added to the manuscript (new Figure 6). This figure provides many answers to the reviewer's questions below.

[For example, particle size distributions should show an internal mixture of organics and sulfate.

Mass spectra presumably appear like a combination of the seed particle spectra and that of Hydrocarbon-like Organic Aerosol (HOA) observed in primary vehicle emissions. These data should be shown to enable this work to be placed in its broader context and compared to the large body of ambient and laboratory studies conducted with the AMS.]

As shown in the new Figure 6, the spectrum does not look like POA (published results by Mohr et al., 2009) or HOA (Ng et al., 2011). The key point in this figure is that the COM has the largest organic fragment at m/z 44, suggesting that it contains oxygenated species, unlike the POA or HOA which is hydrocarbon like. In fact, the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

spectrum looks somewhat like a mixture of OOA and HOA as reported in the AMS community.

[Further, were issues such as potential changes in particle collection efficiency with changing RH/organic uptake considered?]

RH was kept constant for each experiment and the mass was dominated by sulfate, and so, the collection efficiency should have remained constant and thus not an issue. In any case, COM is normalized to sulfate and CE does not change the relative amount of COM to sulfate.

[AMS data analysis should be discussed as there may be choices and assumptions made during the process that affect the interpretation of data.]

The AMS data extraction and analysis was made using the fragmentation table as outlined by Aiken et al. (2008).

[Also, do the PTR-MS data provide any insight into changes in gas-phase concentrations/composition with varying seed concentrations and dilution levels?]

The short answer here is NO. Small changes in a big number make it impossible to do so.

[4] If AMS data do indicate that COM looks like HOA, how can one reconcile the claim that the proposed mechanism is an important source of atmospheric OA with the fact that HOA has been observed to correlate poorly with atmospheric sulfate and nitrate in ambient AMS studies (e.g. [Q. Zhang et al., 2005]). Studies have instead found that aged, oxygenated organic aerosol (OOA), and in fact the more oxygenated, lower volatility fraction of OOA (LV-OOA) levels correlate well with sulfate [Ng et al., 2010; Ulbrich et al., 2009]. Further, models have typically under-predicted secondary OA (SOA) and not been able to explain the high level of oxygenation in ambient observations [M.K. Shrivastava et al., 2008], not under-predicted primary PM, so a mechanism that adds more HOA-like aerosol into the atmospheric OA budget needs to be espe-

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

cially convincingly backed up. These observations provide major challenges to the conclusions of this work if the COM spectra do not appear like OOA. It would support the conclusions if the observed OA were highly oxygenated (though I would be very surprised by this). Including AMS spectra enables such comparisons]

Although PMF has been used extensively in AMS data analysis and has yielded numerous factors with plausible physical factors that can explain the variance in the AMS data, one must remember that the factors resolved from PMF are merely a (non-orthogonal) rotation of the correlation/covariance matrix of the AMS spectral data. HOA resolved this way possibly (or even probably) represents some primary particles from combustion sources, and has in fact been interpreted this way.

However, the COM as determined during this study need not look like POA or HOA, primarily because the condensing chemicals are expected to be different from those residing on the primary particles. Indeed, the COM organic mass spectrum (new Figure 6) does not look like POA or HOA, in that fragments m/z 43 and 57 are small and m/z 44 is the largest of all organic fragments. With a m/z 44/ total organics = 0.097 and m/z 43/44 ratio of 0.59, this spectrum in fact appears to be similar to the mixture of a local SOA factor (LOA) that was resolved by Ulbrich et al., (2009) and Slowik et al. (2010). This apparently oxygen-containing primary organic mass would in fact help solve the issue (at least partially) pointed out by the reviewer, i.e., that models typically under-predicted SOA and unable to explain the high level of oxygenation in ambient aerosols – if the ambient aerosol oxygen is in fact partially attributable to primary materials condensing from primary gas phase VOCs.

We are not surprised that COM contains significant levels of oxygenates, given that we anticipate large oxygenated fraction in the total VOC emission inventory (US EPA, http://cfpub.epa.gov/si/speciate/ehpa_speciate_browse_source.cfm?ptype=G). Our past lab studies have shown large and fast uptake of oxygenated VOCs on particles (Liggio et al., 2005, 2007).

We have now included some of this discussion in the text, bearing in mind that the results are not directly intended for comparison with these statistically resolved aerosol factors.

[While the paper shows convincing evidence that the observed organic condensation is a mass-mediated rather than a surface area-driven (adsorptive) process, it immediately then assumes that solubility is the proper framework in which to present the results, rather than discuss the different theoretical frameworks which might be used to explain the observed condensation. For example, R. Saleh's Short Comment shows that the observations can be viewed in terms of a single particle phase's equilibrium partitioning with vapors (although organic components in equilibrium with an inorganic condensed phase would seem unlikely to have an activity coefficient anywhere near 1). If dissolution is the assumed to be the mechanism for the organic condensation observed here, there should be some theoretical basis for this assumption (e.g. modeling the activity and solubility of potential solvent/solute combinations). Otherwise, if dissolution/solubility are terms used in a more descriptive sense, then consistent terminology should be used to indicate this ('effective solubility' ' pseudo-solubility') and the issue of the uncertainty in the actual mechanism should be discussed in the paper. In short, this result is a surprising one considering how we think about aerosol mixtures and, especially given model results discussed later in the paper and this review, there needs to be thorough investigation of its feasibility.]

See the replies above and replies to R. Saleh. We thank the reviewer for the suggestion of using 'effective solubility', which is essentially what we observed. This is now used throughout the text. The truth is that it is difficult to come up with a more detailed dissolution mechanism given that COM is really a composite of different organic compounds and there was no detailed speciated VOCs data to indicate the potential condensing VOC species, and hence it is nearly impossible to model the activity coefficients in the seed particles for these compounds. We feel that more research needs to be conducted, at least on quantifying the condensing compounds in the gas phase,

before such attempts can be made.

[6] The statement, "What has not been considered in the automotive primary PM emission studies to date is the condensational uptake/evaporation of gaseous pollutants to and from pre- existing ambient particles upon the initial mixing of engine exhaust with ambient air." (line 25, page 3463) is not accurate. CMU's SVOC/IVOC partitioning work has explicitly considered this [Robinson et al., 2007; Shrivastava et al., 2006]. For example, Shrivastava et al. consider the impact of different background OA levels on the partitioning of primary OA emissions under different levels of dilution.]

The text in this section has been re-worded to specifically refer to condensational uptake onto pre-existing ambient particles. Shrivastava et al (2006) is now referred to in the section above.

[7] In calculating Fpp (Eq. 4), all PM measured by the SMPS is assumed to be organic, but a study of similar vintage catalytic gasoline engines found that OC/PM2.5 was 32% or 44% (depending on whether a denuded sampler was used) [Schauer et al., 2002].Were this engine's emissions really so organic-dominated?]

Thanks for spotting this discrepancy. There are no data from the current experiments to show the fraction of OC in the overall primary particle mass. The only data we had was for a few filters collected on Teflon filters from the CVS, which were weighed, and the concurrent SMPS measurements of particles sizes. The resulting mass agreed reasonably well. As the reviewer points out, we have now used the Schauer et al. (2002) result of OC/PM =43.7% to give the OC content of the primary particles to recalculate the Fpp, which is now 0.11 ± 0.06. This does not change the conclusion that Fcom becomes more than Fpp at only modest amount of Ms. The text has been revised accordingly, particularly when Fcom and Fpp are compared.

[8] P 3474, Lines 9-12. These points are taken under varying engine operating conditions and with a very small change in dilution ratio. Given the uncertainty in your measurements, what change in partitioning would you expect to see given the obser-

vations of Lipsky and Robinson [2006] or the volatility basis set fit of Grieshop et al. [2009]? Would it be sufficient for this statement to have any meaning?]

The uncertainty in the power fit parameter a is small; a = 0.012 ± 0.0001, resulting from the fitting (now shown in Figure 4). This function is over a factor of 27 change in the THC concentrations (from THC = 0.66 to 18.1 ug m-3, Figure 6). This THC concentration range corresponds to a dilution ratio range of 81.5 to 2230 (as shown in Figure 3), representing moderately to highly diluted conditions to near ambient conditions. The varying engine operating conditions during the experiments mainly served to provide different levels of THC.

[9) Why are error bounds not given for the intercept in Eq. 6? If they overlap with zero, the statement on the asymptotic value of S at high dilutions is not meaningful. If there were non-volatile compounds in the flow tube, how would they have gotten through the HEPA filter?]

See above. We agree that the significance of this intercept in EQ. 6 is not clear. It could also be artificial result from the choice of function fitting to the data in Figure 4. We have revised the text accordingly.

[10) The comparisons of modeling results and data in the SI are hard to interpret and seem to be critical in evaluating the potential for the experimental results to be applied in the model. Figures S1 and S2 are poorly described or not described at all in the SI or the manuscript.]

We have added a description of Figure S1 and S2.

[It appears that Figure S1 is for the 'base' model, without the COM parameterization (Eq. 6) included?]

We have updated Figure S1 to include traces for the traditional SOA, the POA and the gasoline vapour uptake to sulfate (COM).

[Are the SOA and POA concentrations cumulative (stacked) or should they be added to

compare to the AMS data? I assume that modeling results in Fig. S1 do not include the COM parameterization because Figure S2 has the COM calculation (right axis, lower panel) and the peaks shown are larger than either of the POA or SOA peaks in Figure S1. If the SOA/POA traces in Fig. S1 are supposed to be added, then it looks as if the 'base' model is doing a decent job of recreating the magnitude and some of the temporal trends in the AMS organic data, without the COM added. If the COM trace from figure S2 is added to the SOA and POA traces from Fig. S1, the resulting modeled OA contribution would be well above that measured by the AMS.]

In the original version the SOA and POA were not stacked and therefore the concerns raised in the review are valid. Models are now rerun incorporating POA evaporation based on the volatility base set reported by Robinson et al. (2007). This is now included in the Supplementary Information. This modification to POA evaporation makes a substantial difference to the modelled POA.

Based on the new model runs, the highest COM shown in S2 is 20 ug m-3 on June 27; unfortunately there was no AMS data on that day. The next highet COM shown in S2 is 15 ug m-3 on June 25. On June 25, the AMS OC mass is approximate 25 ug m-3, the modeled POA+SOA+COM is about 23 ug m-3 (Figure S1) and actually very close to the AMS data.

Therefore, the ambient monitoring data appear to provide no support for the applicability of the COM mechanism in modeling regional air quality. If this is true, and given the concerns discussed above, why bother showing modeling results (Figs. 5 and 6) at all? And why make claims about the importance of these finding to regulatory testing and controls? The only 'model validation' that is included in the paper (actually the SI) appears to provide no support for the model, this seems to me a relatively important point to discuss.

On the one day with available AMS data and high modeled COM (June 25), the model and measurement agreement is reasonable (see the reply above). If one looks at

other periods of AMS ambient measurements, the agreement between the modeled POA+COM+SOA with the AMS data is generally improved with the COM being included; in some cases the COM can be a major component of the total OA. Furthermore, the COM is usually higher than that of POA. Further measurements in locations with coincident regional high sulfate and mobile VOC emissions are recommended. As a complement to the AMS, future measurements of tracer species would be helpful for a chemical mass balance analysis to separate primary and secondary organic aerosol, as well as C14 measurements to separate biogenic SOA from primary SOA.

[11] It is generally unclear in the text and especially in the figures which experiments' data are being considered. Since various potentially important variables changed between experiments (engine operating conditions, seed composition, etc.), it seems important that this is clarified either using different symbols, colors, detailed figure captions, etc: : : It is not at all clear that data from all of the experiments listed in Tables 1 and 2 are even included.]

Figures 3 and 4 are revised for separate NH4NO3 and (NH4)2SO4 seed particles and for (NH4)2SO4 seed particles in different engine modes as suggested. A few more data points for engine mode 1 have been added after more experimental data were analyzed. T and RH varied over small ranges and hence their impacts cannot be resolved. Text has been revised accordingly.

[12] The paper concludes with a section on the implications of the findings on the regulatory testing and control of emissions. Considering the questions raised here, it seems prudent that such a section (if an of these points can still be made) should also include substantial discussion of the potential limitations of this study, alternative explanations for the observations and suggestions for future investigations.]

The section has been revised to discuss some of the uncertainties as raised here.

[Minor points]

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

[13] "although it was found that the effect of initial linear velocities of either the particles or the exhaust gases was minimal" (Line 16-17, p3467) – What does this mean? Please qualify.]

This effect refers to the effect on organic condensation. Text revised accordingly.

[14] First sentence in Section 3.2 essentially the same as last sentence on P. 3470]

Thanks for spotting this repetition. Repetition is now eliminated from Section 3.3.

[15] P3474, L14-16: This statement is not clear.]

The statement is revised.

[16] P3475, Line 4-6: It might make sense to show the data backing this statement.]

This sentence has been revised. There was an error in the original statement ('But there are no corresponding changes in the fraction Fcom with the dilution ratio'). The correct statement is 'But there are no corresponding changes in the aggregate partitioning coefficient Kp with the dilution ratio'. Fcom does change, depending on the seed particle loading.

[17] What do error bars in figures indicate – repeated experiments? Estimated uncertainty? This should be included in figure captions.]

These are from the uncertainties in the slope of linear fits to the COM versus seed particle mass. Clarifications are given in the figure captions now.

[18] Use the symbol for 'mu' in text and figures. 'ug' isn't appropriate.]

Revised Figure 2.

[19] Figure 2a and 2b should be two panels of one figure or should be changed to be separate Figure numbers (i.e., Fig. 2 and 3).]

Revised figure numbers as suggested.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper
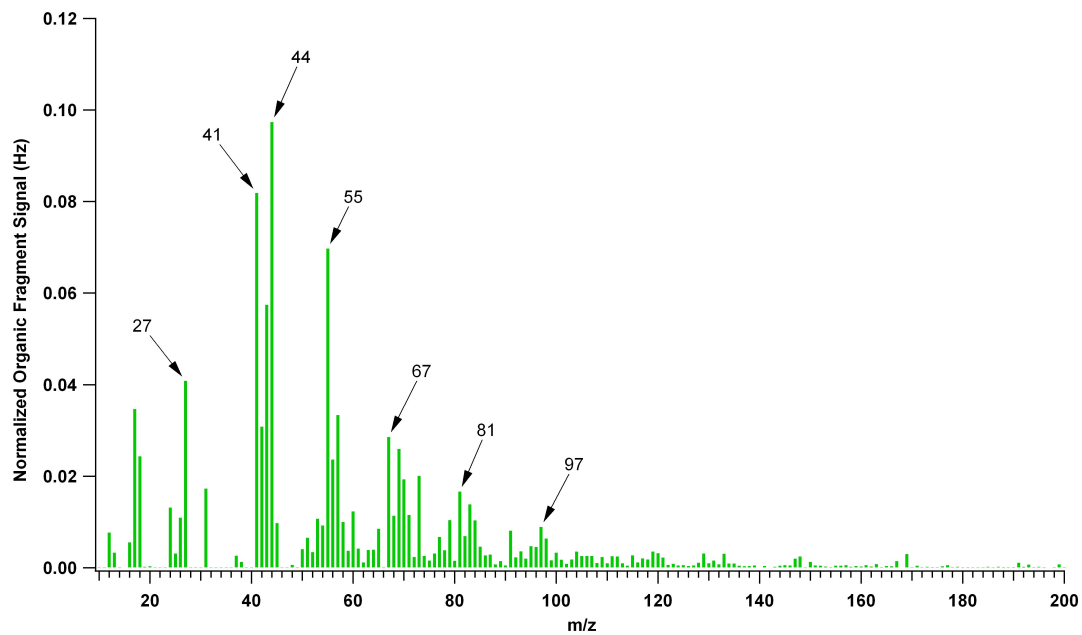
Interactive comment on Atmos. Chem. Phys. Discuss., 11, 3461, 2011.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Fig. 1. new Figure 6