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Interactive comment on “

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

Anonymous Referee #1

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This paper presents the results of a very interesting set of experiments to determine the potential influence on atmospheric organic aerosol (OA) levels of the combination of gas-phase organic compounds emitted by spark ignition engines and background particles. Experiments involved removing primary particles from dilute vehicle emissions and mixing the remaining gases with size-selected inorganic seed particles with various properties (size, concentration, composition) in a flow tube. Particles in the flow tube (composition and presumably size) were measured using a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-TOF-AMS) and gas phase data were

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Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Interactive
Comment

collected using a Proton Transfer Reaction Mass Spectrometer (PTR-MS; data are not discussed in this manuscript). The authors observed substantial OA condensation (condensed organic matter; COM) to seed particles across the ranges of seed sizes, compositions and mixing times used. The observation that condensed mass increased with seed concentration and was not affected by particle size leads to the authors' conclusion that the uptake is due to dissolution, rather than sorption. They then generate a parameterization of the solubility of the organic vapors into inorganic particles as a function of the total hydrocarbon (THC) concentration. This parameterization is applied in a regional photochemical model, which predicts substantial condensation of organic matter, especially during periods with high background PM levels (up to over 20 times the mass of the primary OA emissions from gasoline-fueled engines in their model domain).

These results are fascinating and puzzling and the proposed mechanism for OA production may end up being an important one with implications for emission inventories and emission control policies, as suggested by the authors. However, the current manuscript does not at all convince me of this for a range of reasons: it lacks sufficient detail in describing basic experiments, data and data interpretation, it lacks a consistent and defensible theoretical framework upon which to extend or understand the observations, and no effort is made to compare the results (especially AMS chemical composition and the output of modeling efforts) to the extensive available laboratory and ambient monitoring data (even that which is included in the paper's supplemental materials!). In sum, while it certainly presents interesting data, the manuscript seriously over-reaches in its attempts to interpret this data and apply the interpretation to the atmospheric context (and eventually to regulatory relevance). This is especially true when one considers the potentially contradictory data that are included in the manuscript's supplemental information and never given a proper critical assessment. In order for this work to warrant publication in ACP, these issues would need to be thoroughly addressed, potentially via further experiments, but definitely via more convincing presentation of data and comparison of modeling results with ambient mon-

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itoring data. Here I list major limitations or questions that should be addressed before his paper should be considered for ACP.

Major points:

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 experiment. In reality, vehicle emissions experiencing dilution ratios ($\sim 80 - 2000$) 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 and Wexler, 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. 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. 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.

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

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Interactive Discussion

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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?

3) AMS data should be included in the MS or supplemental material. 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. Further, were issues such as potential changes in particle collection efficiency with changing RH/organic uptake considered? AMS data analysis should be discussed as there may be choices and assumptions made during the process that affect the interpretation of data. Also, do the PTR-MS data provide any insight into changes in gas-phase concentrations/composition with varying seed concentrations and dilution levels?

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 especially 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

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surprised by this). Including AMS spectra enables such comparisons.

5) 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 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.

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.

7) In calculating F_{pp} (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/PM_{2.5} was 32% or 44% (depending on whether a denuded sampler was used) [Schauer et al., 2002].

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Were this engine's emissions really so organic-dominated?

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 observations 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?

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?

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. It appears that Figure S1 is for the 'base' model, without the COM parameterization (Eq. 6) included? 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. 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 findings to regulatory testing and controls? The only 'model validation' that is included

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in the paper (actually the SI) appears to provide no support for the model, this seems to me a relatively important point to discuss. . .

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.

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.

Minor points

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.

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

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

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

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

18) Use the symbol for ‘mu’ in text and figures. ‘ug’ isn’t appropriate.

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).

20) Panels in model output figures should be labeled (a, b, c, and also a descriptive title) rather than their relative location described in the caption.

21) Table 1 includes unnecessary information about the primary particle size distribution, especially considering these particles filtered out in the experiments.

22) Table 2 should indicate the seed particle composition for different experiments

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