

## ***Interactive comment on “***

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

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### Comment 1. Solubility versus equilibrium

We agree with most of the comments here and we can see that there are some confusing statements in the original manuscript. With regard to solubility, we have revised the manuscript to distinguish between solubility and the equilibrium concentrations.

However, some of the scenarios described in the comments are not relevant to the real

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atmosphere, particularly where the quadratic equation on the COM/Ms versus Ms is concerned. See our reply below.

On the original manuscript statement on page 3471 line 22 “...for a dissolution process that reaches equilibrium with the gas phase, the ratio of COM/Ms is the solubility and remains a constant for different single particle size.”, please note that we did NOT say that “COM is dictated by solubility”; we stated that “...the ratio of COM/Ms is the solubility...”. On page 3471, line 5-6, we stated that “...COM is expected to be influenced by the vapor pressures of the SVOCs, and hence by the degree of dilution.”

Technically the ratio COM/Ms is equivalent to the equilibrium concentration of COM in the seed particles and should be affected by the partial pressure in the gas phase. It should not reach the saturation concentration (ie., the solubility) under our current study conditions, as Mr. Saleh pointed out. We have removed the reference to solubility in this section. This sentence is now changed to “the ratio COM/Ms remains a constant regardless of particle sizes.” In the revised manuscript, the solubility discussion is presented in the paragraph preceding this paragraph.

Second, whether COM/Ms stay a constant versus different particle sizes (as stated in the original text; please note that Ms was not mentioned) may cause the concern as given in the comment; the fact is that they do over the range of Ms studied (Figure 2b, now Figure 3); to fit a quadratic curve to the data in Figure 2 will be no different from fitting a linear line statistically. For the experiments with different particle sizes, the range of Ms did not allow a full examination of the potentially quadratic dependence of COM/Ms versus Ms; it did reveal that the COM/Ms remained approximately constant over this range. The results shown in Figure 2 are for experiments conducted under ONE dilution ratio of 395 (page 3470, line 20 and page 3471, line 7). Under this condition, the partial pressures of the condensing organics are kept to a constant of approximately 0.377 ppmC (the value is calculated using the results in Table 1; the total dilution ratio of 395 results from the primary dilution ratio of 22.3 in the CVS multiplied by the secondary dilution ratio of 17.7). The condensed COM is less than 1  $\mu\text{g m}^{-3}$

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3, or less than  $4 \times 10^{-5}$  ppmC (assuming H:C ratio of 1.2 in the organics) for particles of different sizes (and masses, Figure 2a), making no significant changes to the gas phase vapor pressure. Thus PTHC is for all practicality a constant. Again, invoking the Henry's law will lead to a constant C.

The comment is concerned about the effect of high  $M_s$ ; in that case a perceived significant amount of the gases may partition into the seed particles, leading to draw-downs in PTHC, and the relationship between COM/ $M_s$  and  $M_s$  becomes a quadratic one. We agree that under such scenarios, the quadratic function is more appropriate in describing the relationship between COM/ $M_s$  and  $M_s$ . However, the non-linearity only manifests at unrealistically high seed mass (about 3 orders of magnitudes higher than the  $M_s$  studied to have the nonlinear effect); we believe that such a high  $M_s$  scenario is not representative of ambient conditions. To reflect this discussion, we have revised the manuscript to discuss the possibility of quadratic response versus the reality of linear response.

In a sense, a second study will be desirable to test the response of COM/ $M_s$  to various seed mass loadings, although whether it is relevant to reality is a different matter.

Comment 2. Transfer of primary particle mass to the condensed mass

In theory, transfer of semivolatile organics from the original primary particles can happen, if they had been allowed to come into contact with the seed particles. In practice, there will be no difference whether the primary particles were allowed to come into contact with the seed particle. If anything, the POA should be even smaller than the emissions reported at the tailpipe due to the evaporation of semi-VOCs from these particles. The absolute amount of POA mass is small compared to the gas phase organics; using the SMPS data obtained for the CVS, we have calculated the original PM to be about 11% of THC, assuming a particle density of 1 g/cc, a chemical composition of 43.7% organics, and total evaporation of all organics from the primary particles (all unrealistic assumptions to set the upper limit). If we use a loss factor of 2-3 for the

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organics from primary particles over the dilution range (using the results from Robinson et al., 2007, Science) due to evaporation process, then the resulting increase in gas phase VOCs would amount to about 7% of total gas phase VOCs. Most of the organics will be in the gas phase, and its condensation onto the seed particles should not be significantly affected by small particle evaporation. Hence, at most, 7% of the condensed materials on the seed particles will be comprised of re-condensed materials that come from the POA evaporation. This condensed mass of evaporated POA would be less than 10% of the total evaporated POA.

Considering that the evaporative species from the POA (possibly non-polar components of VOCs) and the condensed species in the COM (more oxygen-containing species), the contributions from the evaporative POA will be even smaller. This is further discussed in light of the AMS organic mass spectrum in (new) Figure 6.

For the same reason, the evaporative loss from the original PM will be limited if they were allowed to mix with the seed particles.

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