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Atmospheric
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Discussions

Interactive comment on "Secondary organic aerosol formation from gasoline vehicle emissions in a new mobile environmental reaction chamber" *by* S. M. Platt et al.

S. M. Platt et al.

stephen.platt@psi.ch

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Response to Anonymous Referee #1:

Interactive comment on "Secondary organic aerosol formation from gasoline vehicle emissions in a new mobile environmental reaction chamber" by S. M. Platt et al.

Answer to general comments of the Referee:

Dear referee,

We thank you for taking the time to carefully review our article and for your valuable comments.

The scope of this paper is to present i) a new facility, the Paul Scherrer Institute mobile smog chamber and ii) demonstrate the utility of this smog chamber by presenting results which are of value to the scientific community. We believe that while a smog chamber is not novel, a mobile smog chamber is. We are aware of only two fully equipped mobile smog chambers in the world (at Paul Scherrer Institute and Carnegie Mellon). These facilities offer the capacity to investigate emissions and other aerosol sources relevant to the atmosphere which previous smog chambers cannot. Furthermore the use of a chassis dynamometer for smog chamber experiments can also be considered novel.

Even a limited communication on SOA formation from gasoline vehicle emissions is especially prescient. A recent ambient study concluded that secondary organic aerosol (SOA) from gasoline vehicle emissions can dominate background urban organic aerosol (Bahreini et al., 2012). Conversely, another recent study has suggested, using raw diesel fuel as a surrogate for real-world diesel vehicle emissions, that diesel vehicles produce more SOA than gasoline vehicles (Gentner et al., 2012). Therefore experiments on gasoline emissions are of great interest to the community. We suggest that in the context of such contradictory results, any additional analysis, albeit of limited scope, which may serve as an indicator as whether one vehicle type may be expected to produce more SOA is of value. This is especially true given the current dearth of literature data on SOA formation from gasoline vehicle emissions.

Major and minor points are addressed point-by-point as follows:

(1) "P28354, L2: The fact that the lower edge of the transmission window for this lens is somewhat concerning given that vehicle-emitted aerosols are often right in this range or below. SMPS or AMS particle time of flight data should be used to indicate that mass measurements are not biased. More information on the particle size distributions and how they evolve with coating would in general be a good thing to include/discuss."

The high pressure lens has a transmission window of 100->2500nm (Williams et al., Submitted to AMTD). Figure 1 (to be included in the supplementary) shows the evolution of SMPS volume distributions during photochemical aging for the second gasoline aging experiment. A single particle mode is observed to grow as it becomes coated with SOA. As shown, most particles are in the range 500-700 nm after SOA formation, with a considerable fraction above this diameter. Since the transmission window of the standard AMS lens is ~60-600nm, the high pressure lens provided more accurate measurements during the gasoline aging experiments. Volume distributions, e.g. Fig. 2, show that for the primary aerosol a negligible fraction of the mass is expected below 100nm. The volume distribution after aging is completely within the transmission window of this lens, and partly above the transmission of the standard AMS lens.

(2) "P28354, L3-9: No results based on this methodology are presented later on in the paper, though there are a large number of potential issues. This should be included in discussions of the results. For example, does the correspondence between mobility diameter and equivalent diameter change as the particles are coated? The initial OA/BC ratio is ~ 1:1, but this changes by more than a factor of 10 as the SOA formation occurs. How do the AMS collection efficiencies compare with what has been observed in other studies? "

It is to be expected that particles become increasingly spherical with coating. Thus one may expect more error in the primary (less coating) vs. the aged (heavily coated) aerosol. It is likely that the SMPS somewhat over predicts the size and hence mass of the primary particles with a large BC component. This point will be mentioned in the text in section 2.4 and discussed in the results. SOA is assumed to be very close to spherical. Primary emission factors derived from AMS measurements corrected using the SMPS may of course be expected to be an overestimation. Therefore we will now also include in Table 3 an alternative measurement from the gravimetric analysis of PM taken directly from the CVS tunnel. Primary PM emission factors at the CVS are close to the combined OA+BC taken from the chamber, with variation likely resulting from a number of factors including, but not limited to, i) adsorption artifacts on the filters ii) effects due to lower-than-smog-chamber dilution in the CVS iii) error in the Aethalometer estimation of BC iv) inaccurate correction of particle losses in the chamber during filling v) error in the SMPS measurement due to differences in effective and mobility diameters. These points are also highlighted in the updated results section.

Never the less a comparison between the gravimetric and online methods is presented in Fig. 3 and will be included in the supplementary. Differences between the methodologies are negligible and can safely be assumed to be well within uncertainties of both techniques.We therefore consider a detailed analysis on how coating of black carbon changes effective diameter as beyond the scope of this paper, as even a large error in the estimation of the primary emission would not alter the conclusion that most of the particle mass from this gasoline vehicle eventually comes from SOA.

AMS collection efficiency was between 0.5 and 1.0 throughout both experiments consistent with both ambient and laboratory studies (Middlebrook et al., 2012) and (Matthew et al., 2008). This will be added to the revised manuscript.

(3) "Why are SMPS data not shown, described or used? More information on spectral characteristics of the POA and SOA are also appropriate given the focus of the paper."

SMPS data were used to correct for collection efficiency and additional supplementary figures using SMPS data are now included (please see answer to the question #1). Spectra from the primary particles, Fig 4, will be included in the revised manuscript.

(4) P28362, L11-13: If it is the case that you can identify much of the VOC reacting in the chamber, why are none of these data shown? This would seem to be a very important piece of the puzzle, yet no portion of it is included. Again, given the fact that there are 2 experiments worth of data, I would expect more time would be spent actually delving into this data.

We do agree with the reviewer that an exposition of gas phase data would greatly increase the value of this study to the scientific community. However, we present evidence of SOA formation from this particular car involving non traditional precursors (please see Fig. 5, to be included in revised manuscript), possibly from smaller hydrocarbons which may require fewer oxygenation steps to produce highly oxidized SOA, see e.g. Kroll et al., (2011), as observed for this car. The reader is cautioned that these results apply only to this vehicle and that this should be studied further, especially as the factors influencing such SOA formation are unknown. However such results do serve as a suggestion that assumptions made based on raw fuels or only consideration of traditional precursors alone is inadequate.

(5) P28363, L28-29: You suggest here that the addition of propene should not affect SOA measurements to a large extent, though it is well recognized that NOx levels can have a controlling effect on SOA yields (e.g. (Ng et al. 2007; Presto et al. 2005; Presto etal. 2010)). I take the statement to mean that the propene doesn't form SOA, which I expect is probably true, but the VOC-NOx ratio may have a substantial effect on yield and chemical composition of SOA.

The addition of propene as a method of enhancing OH was used as without it, the observed SOA formation would likely have occurred over a much longer timescale, too long to allow experiments to be conducted, since OH concentrations would be extremely low. Figure 6 shows the clear effect of the propene addition on the OH concentration inside the chamber. Conditions remained high NOX throughout experiments even after the addition of propene, as there were around 600 ppb of NOX in the chamber throughout each experiment. However, we accept the major criticism from the reviewer that additional explanation/ justification is required in the revised manuscript with regard to adjustments of the gas phase composition.

(6) P28345, L22-25: Awkward sentence and not fully justified point. Authors should specify from the beginning that this is referring to Europe and then justify using some fuel use data.

This sentence will now read:

"Without considering SOA, diesel vehicles have traditionally been considered the most significant contributor to urban vehicular PM in Europe. This is because primary PM emission factors (EF) of older diesel vehicles are orders of magnitude higher than those of gasoline vehicles and because diesel vehicles constitute a large proportion (an estimated 57% by 2010, IIASA, (2005)) of the European fleet."

(7) P28347, L12: Missing punctuation? Should be a new sentence. This will be corrected for the revised manuscript.

(8) P28347, L13: 'chamber' misspelled This will be corrected for the revised manuscript.

(9) P28352, L26-28: Very awkward sentence. This will be corrected for the revised manuscript.

(10) P28360, L13: missing a 'h'

This will be corrected for the revised manuscript.

(11) P28360, L22-23: I think this should indicate that lower yields are observed at lower OH exposure intensities this sentence makes it sound as if SOA evaporates when the OH intensity is reduced.

Our understanding of the work under discussion is that the relative importance of SOA decay (due to photolysis pathways) compared to SOA production via OH oxidation is increased when OH concentration is lowered. The text will be altered to make this clearer.

References

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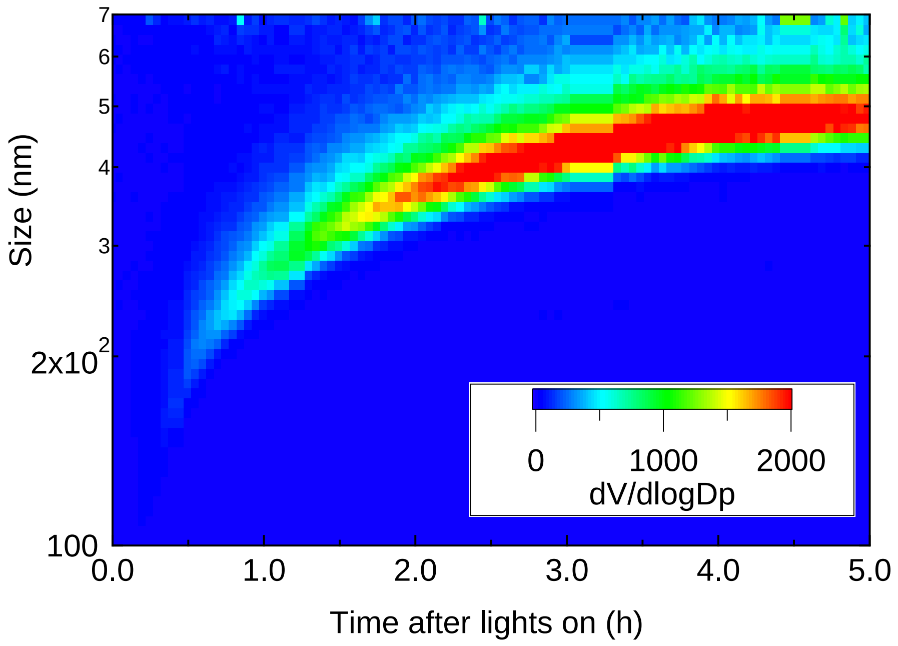

Fig. 1. Size and time resolved scanning mobility particle sizer volume distributions measured during the aging of gasoline vehicle emissions inside the smog chamber from experiment 2.

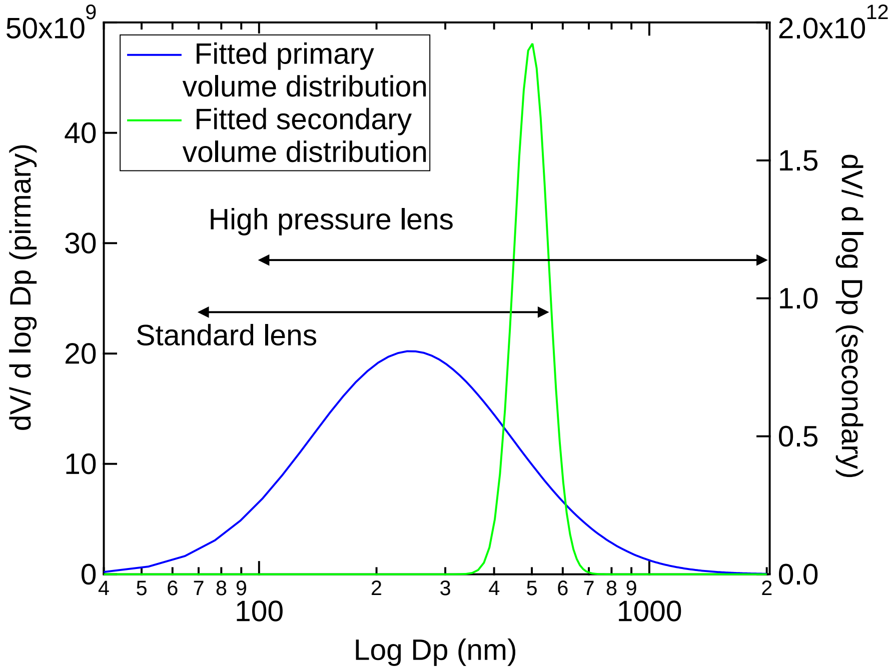

Fig. 2. Lognormal fitted scanning mobility particle sizer (SMPS) volume distributions of primary (blue) and aged aerosol (green) from a gasoline light duty vehicle measured from the mobile smog chamber.

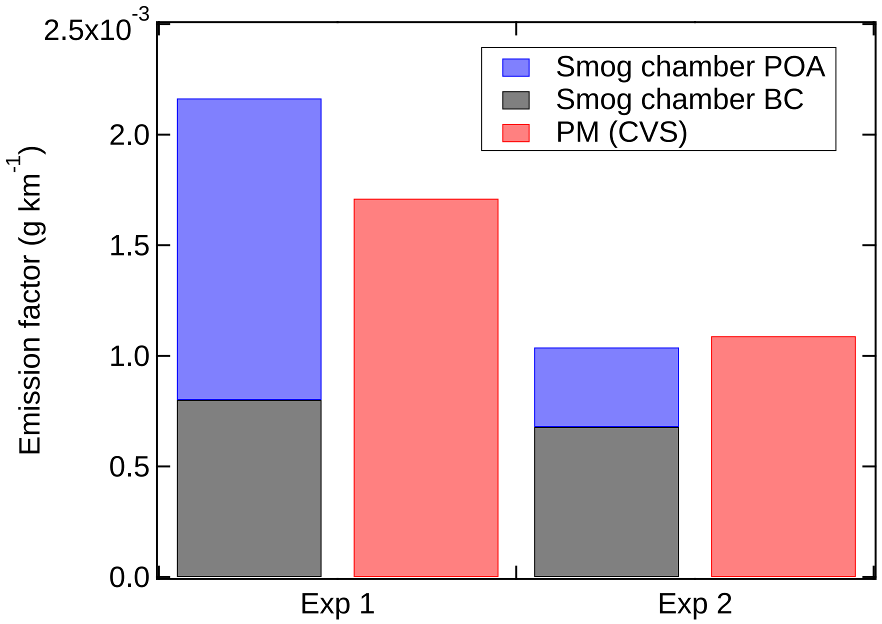

Fig. 3. Primary aerosol emission factors for a Euro 5 gasoline light duty vehicle measured from the CVS and at the mobile smog chamber (sum of black carbon and primary organic aerosol).

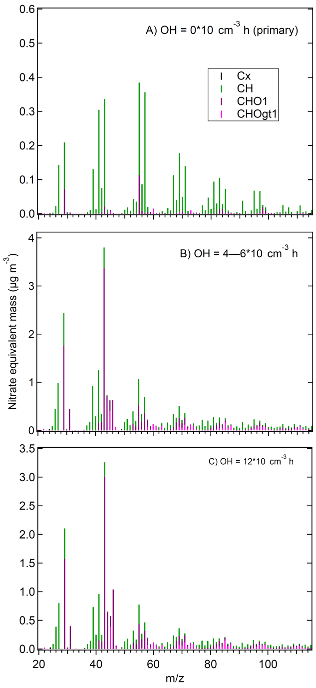

Fig. 4. High resolution AMS spectra measured at the mobile smog chamber of A) Primary B) Aged C)Highly aged gasoline car emissions.

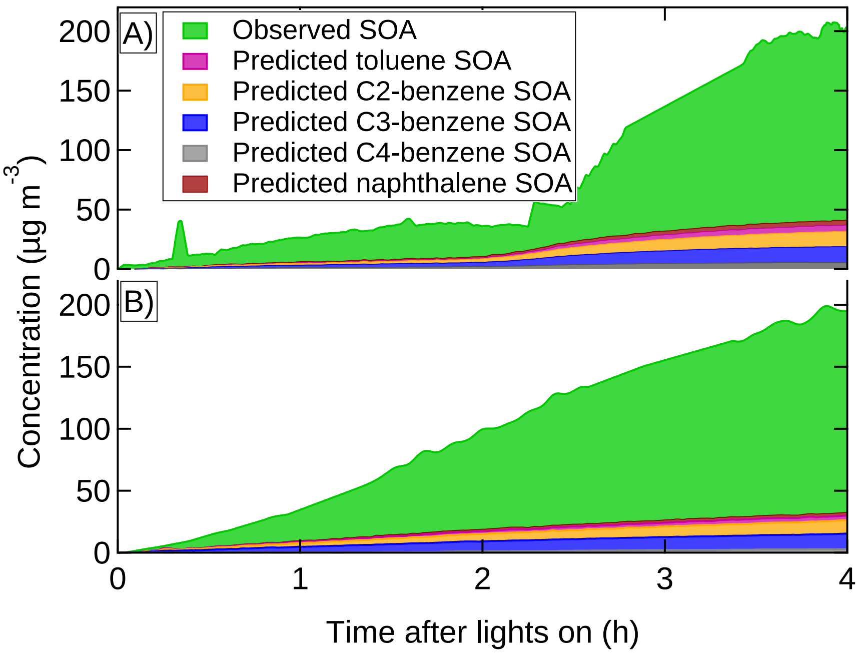

Fig. 5. Observed SOA formation during A) Exp. 1 and B) Exp. 2 vs. predicted SOA formation from aromatic oxidation.

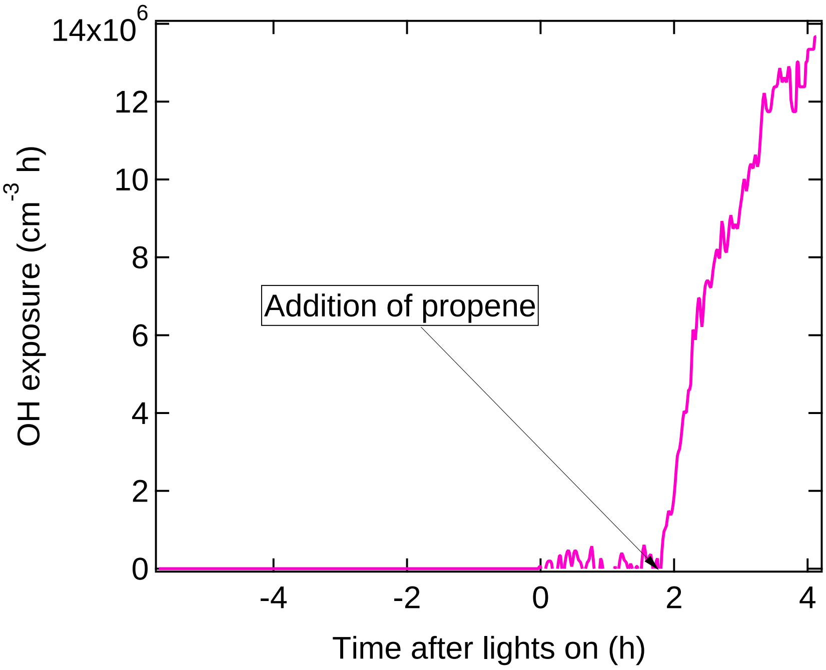

Fig. 6. OH exposure (cm-3 h) in the smog chamber during Exp. 1. The addition of propene two hours after lights on was observed to significantly enhance photochemistry in the chamber.