

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

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Response to Anonymous Referee #3

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

Dear referee,

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

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

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(1) The paper uses the terms SOA emission factor. I have a strong negative reaction to that term because SOA is not emitted (I have no problem expressing SOA production on a per fuel basis). As the authors well know, the problem is that the amount of SOA will depend on many atmospheric parameters (COA, VOC/NO<sub>x</sub>, OH exposure, etc.). Therefore it will vary over the atmospheric lifetime of the emissions from zero at the tailpipe to some varying but non-zero value in the atmosphere (as shown in Figure 4). A better term might be SOA production factor. In addition, the authors need to add some discussion to the paper that the values reported here are for these particular experimental conditions (e.g. very high COA, very high NO<sub>x</sub>) and therefore should not simply used as emission factors. Calling it an emission factor will create all sort of confusion.

We completely agree with this point. As stated in answer 1 to Anonymous Referee #2, many factors may influence SOA formation and so we will alter terminology to reflect this. SOA emission factor becomes “potential SOA formation factor”.

(2) Transfer line losses are an important issue. The paper provides some information on this but more is needed. Page 28363 “Using this methodology an average THC loss of 20% was determined” this statement is not consistent with the data in Table 2 which indicates that the THC emissions factor measured in the chamber was more than 40% lower than that measured in the CVS tunnel. Loss of nonmethane hydrocarbons were even bigger – 50%. I would not characterize 50% as “minor” (page 28363 line 9). Since this is a method paper it would be useful to understand how these losses vary from compound to compound. My guess is that they might be weighted towards SOA precursors, which are higher MW and lower volatility. Was the PTR used to investigate these issues on a compound specific basis? Since the paper claims that the PTR identified something like 80% of emissions it seems like. Since the only PM data are based on chamber measurements particle losses in the inlet system (transfer line and dekas, etc) are important. What were the losses of particles in the inlet system? The paper discussed losses of NMOG but not particles. Given the losses of NMHC they

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might be substantial.

We agree that transfer line losses are in general a very important consideration. Therefore, for this study emissions were sampled directly at the tailpipe, not at the CVS (please see pg 28352 L20). The CVS may have significant losses since i) Transfer lines to the CVS are heated to 70 °C with no dilution ii) Dilution at the CVS is typically ranges between 2 and 100, e.g. an average 37 for the NEDC cycles of this study. iii) Temperature of the dilution air at the CVS was 27°C while the CVS was heated to only 40.2±0.6°C. For comparison the transfer lines to the smog chamber were heated to 150°C while final dilution at the chamber was a factor of around 150. Furthermore, transfer lines to the smog chamber are made of silica steel which minimizes losses of VOCs. Of course, no system is perfect, but we believe that our methodology keeps transfer line losses to an absolute minimum. Figure 3, Response to Anonymous Referee #1, would suggest that particle losses are not a serious issue. Figure 1 shows how the total hydrocarbon emission factor actually varies over an experiment. The only stable period for an emission factor of hydrocarbon is prior to lights on and this value was used in Table 2. This value is relevant to subsequent SOA formation as it is this hydrocarbon at this point in time from which SOA is formed. However it is clear to us that Table 2 is therefore misleading in its current form and the text and table caption must be altered to say that concentrations presented are those at lights on in the smog chamber and not those emitted from the tailpipe (this is the original reason for presenting both sets of data). We still consider a normalisation to the fuel (i.e. units of g kg<sup>-1</sup> fuel) as more appropriate than raw concentrations. Regarding estimation of losses (page 28363 line 9) these were made on average concentrations and not emitted masses, hence the apparent discrepancy.

The PTR was indeed able to quantify much of the emission, but fragmentation is an issue especially as much of the emitted hydrocarbon from vehicles is in the form of long chain alkanes. A species by species comparison at the tailpipe and at the smog chamber is therefore not possible.

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(3) What was the repeatability of the experiments? Table 3 suggests that there was some variability in the primary PM data (POA and BC) but excellent repeatability for SOA. Of course n=2. Is this the correct interpretation? Given the complexity of the system and the scatter in smog chamber data for simple systems (e.g. toluene), I suspect the results in Table 3 are not very representative of true precision of the experiments. The paper would benefit from a discussion of these issues. Ideally the authors would establish the precision of the technique by performing multiple repeat experiments as is normally done when evaluating a new method.

The THC emission from vehicles during driving cycles is very repeatable. Under similar aging conditions (OA concentrations, NOX, OH exposure, RH, etc) SOA production is very consistent. Such observation holds for different cars we have tested in other studies. SOA production results are always valid only for the conditions at which the experiment is conducted (see answer to Anonymous Referee #2 comment 1). The variability represented here, or indeed in any feasible study, cannot fully capture the wide variability in SOA production in the ambient atmosphere, under different conditions.

(4) Section 3.1.1 discusses a chamber "blank." However, it only mentions particle concentrations adding exhaust to the chamber. So this demonstrates that there are few particles in the clean air system. A more important consideration is the blank associated with filling the chamber with air from the CVS but no exhaust (i.e. an experiment without running a vehicle). In addition to particles (which likely are not significant in the CVS dilution air) it would be useful to report data for NMHC and individual VOCs. Finally, a true blank or control experiment would then oxidize the dilution air from the CVS in the chamber to see how much SOA was formed without adding exhaust. Given the contamination that exists in vehicle testing systems this would be a good test to make sure that the overall experimental blank is low (as opposed to simply stating that the air from the AADCO is clean).

A further blank was performed after the measurement campaign described in this paper. Ambient air was sampled into the chamber via the same sampling system. No

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particle formation could be detected with the AMS following irradiation with UV lights, please see Fig. 2. This figure indicates that emission of VOCs and particles from the transfer lines is negligible and will be included in the revised manuscript.

(5) Collection efficiency correction – More details are needed here. How big was this correction?

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. The maximum applied correction was therefore a factor of two.

(6) A large part of mass size distribution from vehicle emissions can be below 100 nm. Was there any nucleation in chamber?

Please see Fig. 3, response to Anonymous Referee #1, for size distributions and our response to Anonymous Referee #1. All of the mass increase was due to an increase in coating of the primary particles by SOA.

(7) A background OH concentration of  $3.6 \times 10^6 \text{ cm}^{-3}$  was calculated, with possible sources including HONO off-gassing from the chamber walls, previously suggested as a significant OH source in smog chambers” I did not understand this. You are saying in a dark bag you have  $4 \times 10^6$  of OH?

The background OH was observed after the lights were switched on, when only formaldehyde was injected into the chamber. Furthermore, after revisiting this section, we believe it rather too “involved” to demonstrate what is, ultimately, a very minor point and it will be removed from the revised manuscript.

(8) Based on analysis of the AMS data, the paper claims “the mobile smog chamber provides a good approximation of real atmospheric aging.” However, VOC and NO<sub>x</sub> levels are an order of magnitude (or more) higher than typical ambient conditions. For example, Figure 4 indicates initial NO<sub>x</sub> mixing ratios of  $\sim 500$  ppbv. The paper needs

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provide a table with initial conditions inside the chamber, compare them to typical ambient conditions, and then discuss how any deviations from ambient conditions might alter the result. This would help them better justify that the chamber provides a good representation of the atmosphere.

A table of initial conditions inside the chamber will be included in the supplementary material. In response to the high NO<sub>x</sub> issue we note that this is unfortunately unavoidable as this is what comes out of the vehicle tailpipe. This issue, then, is a fundamental problem for all studies on the aging of emissions from vehicles, or at least for those operating with higher engine temperatures and or engine load. However the point will now be noted in the revised manuscript.

(9) The wall loss corrected organic aerosol mass inside the chamber at the end of the experiment is very large ( $\sim 200 \text{ ug/m}^3$ , Figure 4). This will bias partitioning of the SOA causing the experiment to overestimate the SOA production compared to more dilute atmospheric conditions. Therefore the SOA “emission factor” given in the paper may substantially overestimate the SOA production.

It is certainly true that the final concentration was very high, though not impossibly so, as these concentrations may be attained in heavily polluted regions. It is also true that partitioning is yet another factor that will influence the SOA formation (please see answer to Anonymous Referee #2 comment 1).

(10) “Emission inventories as well as vehicle legislation do not account for SOA production,” This is not totally true. Emission inventories often contain data for SOA precursors. Since SOA is not emitted the precursors should be in the inventory not SOA itself. (same comment applies to statement on line 9 page 28366). Although legislation has not specifically targeted SOA there are very stringent controls on NMHC emissions at least originally motivated for O<sub>3</sub>. Those have regulations (and the TWC) have had dramatic effects on emissions of SOA precursors. So to say that it is unregulated may be true from a very narrow perspective it seems misleading.

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We agree that this statement is misleading in its current form and it will be removed for the revised manuscript. The new version would read "Emission inventories as well as vehicle legislation do not directly account for SOA production nor the effects of variable composition thereon"

Page 28344, line 9: The units for J(NO<sub>2</sub>) are incorrect and should simply be s<sup>-1</sup>

This will be corrected for the revised manuscript.

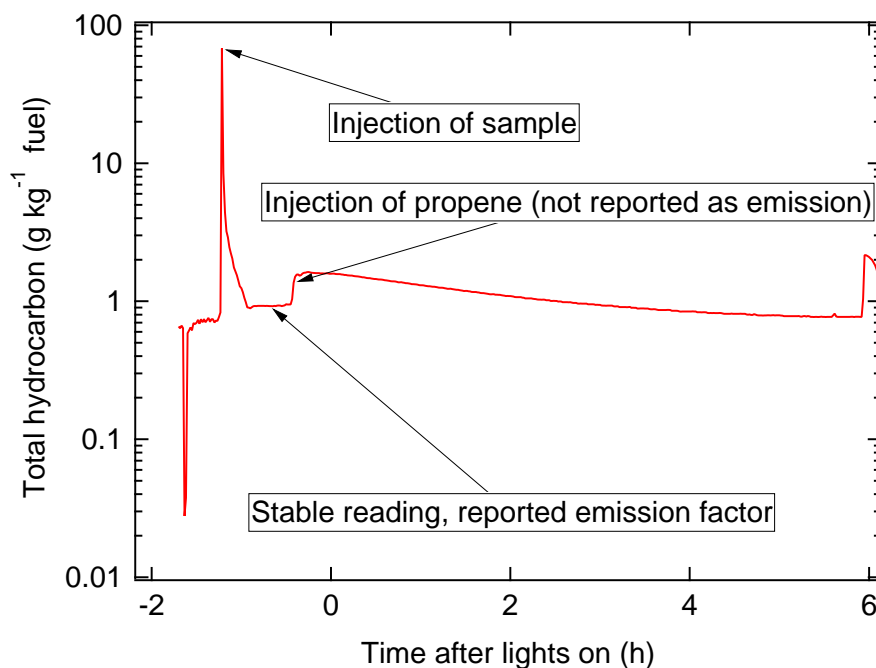
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Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of composition-dependent collection efficiencies for the Aerodyne aerosol mass spectrometer using field data, *Aerosol Science and Technology*, 46, 258-271, 2012.

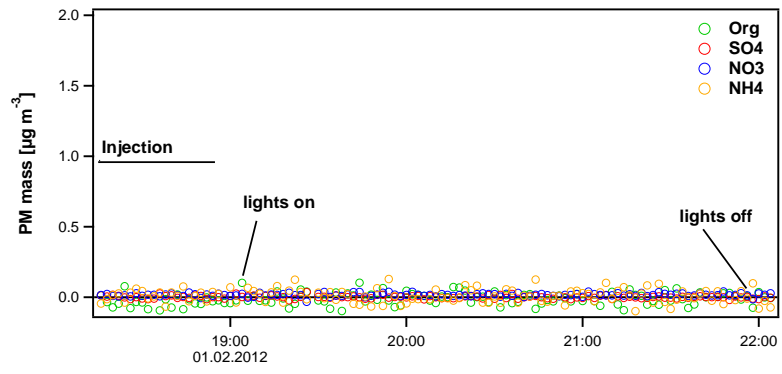
Interactive comment on *Atmos. Chem. Phys. Discuss.*, 12, 28343, 2012.

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**Fig. 1.** : Total hydrocarbon (g kg<sup>-1</sup> fuel) as a function of time after lights on in the smog chamber during experiment two.

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**Fig. 2.** : Particle phase concentrations measured inside the smog chamber after sampling (and irradiating) ambient air through the heated inlet system.

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