

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

Anonymous Referee #3

Received and published: 21 December 2012

This paper describes a new portable smog chamber designed to study SOA formation from combustion sources. The paper provides results that characterize the performance of the new chamber (e.g. jNO_2) and then presents some initial data for gasoline vehicle emissions. The paper is a blend of an experimental methods (e.g. AMTD) and a research (e.g. ACPD) paper. As discussed below, there are a number of issues that are important from an experiment methods perspective that were not addressed in the manuscript (particle losses, blanks from CVS, repeatability, precision, etc.). The SOA data are interesting and seem qualitatively consistent with what the Carnegie Mellon group has been presenting at meetings. The conclusions about vehicle contributions to ambient PM seem too strong given the very limited number of vehicles (one) and

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experiments (two).

I recommend that the paper be published in ACP after the authors have addressed the following comments:

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_x, 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_x) and therefore should not simply used as emission factors. Calling it an emission factor will create all sort of confusion.

Methodology Issues:

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

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inlet system (transfer line and dekatris, 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 might be substantial.

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.

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).

Page 28349 "preventing losses of emissions" heating transfer lines will not prevent wall losses of emissions. At best it will reduce them. Were the walls of the transfer lines passivated?

Collection efficiency correction – More details are needed here. How big was this correction? A large part of mass size distribution from vehicle emissions can be below

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100 nm. Was there any nucleation in chamber?

"A background OH concentration of $3.6 \times 10^6 \text{ cm}^{-3}$ was calculated, with possible 5 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 4×10^6 of OH?

Vehicle SOA issues:

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_x levels are an order of magnitude (or more) higher than typical ambient conditions. For example, Figure 4 indicates initial NO_x mixing ratios of ~ 500 ppbv. The paper needs 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.

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.

"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 O₃. 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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The conclusions are overly strong given that they are based on two experiments with one vehicle.

Typo

Page 28362 “ Chirico et al. (2010)”

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

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