

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 #2

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.

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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. We will therefore present evidence of SOA formation from this particular car involving non traditional precursors (please see response to Anonymous Reviewer #1, Fig. 5) and we will also present a summary of emitted VOCs at the tailpipe for this vehicle as very little such data exists in the literature for very modern vehicles. Furthermore the supplementary section will be expanded to include more information on driving cycle parameters, e.g. exhaust temperature, oil temperature etc. Such data form regulatory driving cycles are not generally available in peer reviewed literature and may make the article more relevant to a wider readership. Furthermore such parameters are attained during the legislated New European Driving Cycles. We believe that any future smog chamber studies should include values for these parameters to ensure repeatability and comparability of tests and for better comparison to real world driving.

We address the major concerns as follows:

(1) Page 28353, lines 4-18: Here the authors outline the reasons why they added ozone and propene to the chamber containing the primary emissions. However, I am not fully convinced by their explanation and since the addition of these species clearly influences the reaction conditions and hence the amount of SOA formation, further clarification is required. Firstly, the addition of ozone in the dark will result in the conversion of NO to NO₂, with the total amount of NO_x remaining largely unchanged. Unfortunately, the amount of ozone injected into the chamber is not provided and it is therefore unknown if any NO is remaining at the start of the photolysis. The ozone mixing ratio shown in Figure 4 also does not help since it has missing data from this part of the experiment.

The addition of propene and its effects is also discussed in detail in the answer to Anonymous Referee #1 question 5. Briefly, the main reason for the addition of propene here was to increase the rate of photochemistry in the chamber (please see response to Anonymous Referee #1, Fig. 6).

C13498

Regarding concerns that conditions are “low NOX” inside the chamber it must be pointed out that several hundred ppbv (~ 600) of NOX are inside the chamber during aging. Given that “low NOx conditions” in e.g. Ng et al., (2007) refers to NO concentrations below detection (<1 ppb), and given that there was a source of NO via NO2 photolysis it cannot be said that conditions were truly low NOX. NO. That is, even if the NO concentration is really low, its concentration is orders of magnitudes higher than that of RO2 radicals. The regime is therefore high NOX. Furthermore, there are many factors influencing SOA formation, not just NOX, but also other conditions such as light levels (night or day), temperature etc. Terminology will therefore be adjusted to reflect this: a SOA emission factor (EF) in the text will be termed a “potential SOA formation factor” to reflect the fact that the SOA observed in this study is but one of many possible outcomes from the aging of the exhaust.

Ozone was added to the chamber as previous observations have demonstrated that conversion of most NO to NO2 is required before SOA production occurs. This effect has been seen by e.g. Nordin et. al., (2013). Conversion to NO2 therefore shortens delay time before SOA formation and shortens overall experiment time. It is of course unfortunate that for Experiment 2, the O3 monitor was not working until some time after lights on. However, the amount of O3 added may be inferred from the decrease in NO concentrations in the chamber, assuming all O3 is consumed in the oxidation of NO to NO2, as 350 ppbv. Furthermore, Fig. 1 shows data from Experiment 1 where data before lights on are available for O3. From Fig. 1 it is clear that an excess of O3 is not present before lights on. We accept that during injection of O3 some alkenes present in the chamber may have reacted with the O3 plume. This point will be addressed in the revised manuscript. We assume the effect to be minor as no SOA production was observed before lights on.

(2) The procedure outlined for derivation of $J(\text{NO}_2)$ appears to be oversimplified. It relies on the assumption that a photostationary state is achieved. However, there are other possible processes that may need to be taken into account including the

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formation of NO3 and its subsequent reactions, as well as wall loss of NO2 and O3 (Wang et al., 2011). Is a photostationary state really observed? i.e. do the measured mixing ratios of NO, NO and O3 remain unchanged for a sufficient amount of time?

The procedure used to determine $J(\text{NO}_2)$ is identical to that used by Paulsen et al., (2005). Figure 2 shows that a stable reading of NO2 and ozone was attained for calculations. No decrease in O3 after the assumed steady state is reached is observable and therefore wall losses of O3 are neglected. Further oxidations to NO3 are neglected and this point will be discussed in the text as it may give rise to error.

(3) The section describing the photolysis of HCHO (page 28360, lines 1-10) and its subsequent use in the validation of predicted photolysis rate constants is difficult to understand. It seems that the terms rate constant and loss rate (and their units) are mixed up and the numbers shown in Figure S3 do not appear to match those in the text. This section needs to be revisited.

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. Additional validation of the equations of atmospheric photochemistry, as presented in this section, is beyond the scope of this article.

Other minor comments and suggested orthographical changes to the text are addressed:

(1) Page 28344, line 3: Should this be “emission” or “emissions”? This also appears at numerous points throughout the manuscript.

This should generally be “emission” and will be corrected.

(2) Page 28344, line 8: Change to “-7 to 25C”. This also appears at numerous points throughout the manuscript.

This will be corrected throughout for the revised manuscript.

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(3) Page 28344, line 9: The units for J(NO₂) are incorrect and should simply be s⁻¹

This will be corrected throughout for the revised manuscript.

(4) Pages 28344-28345: The Introduction section is a little repetitive and could be improved.

Any repeated statements will be removed for the revised manuscript.

(5) Page 28345, line 13: Change to “: : or directly emitted, primary organic aerosol (POA): : :”

This will be corrected for the revised manuscript.

(6) Page 28345, line 26: Change to “: : of 3.4 and 0.16 g kg⁻¹ were observed: : :”

This will be corrected for the revised manuscript.

(7) Page 28346, line 3: Change to “: : of 25.61 and 0.25 mg km⁻¹ were observed: : :”

This will be corrected for the revised manuscript.

8. Page 28346, line 4: As far as I can tell, Chirico et al. did not use EURO 4 fuels

There exist different regulations for “diesel passenger cars” and “gasoline passenger cars.” That is, even at one “Euro” standard there are different requirements, hence the need to differentiate by fuel type.

9. Page 28346, line 5: Chirico et al. was published in 2010 and not 2012.

This will be corrected for the revised manuscript.

10. Page 28347, line 13: Should be “chamber”

This will be corrected for the revised manuscript.

11. Page 28349, line 26: What is meant by “: : :emissions’ hydrocarbons and aerosols”?

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This should read “emissions of hydrocarbons and aerosols” and will be corrected for the revised manuscript.

12. Page 28350, line 14 and 15: Was the NO gas 1000 ppmv in nitrogen?

This is ppmv of NO.

13. Page 28350, line 16 and 17: How much ozone was injected?

Please see answer to major comment #1.

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

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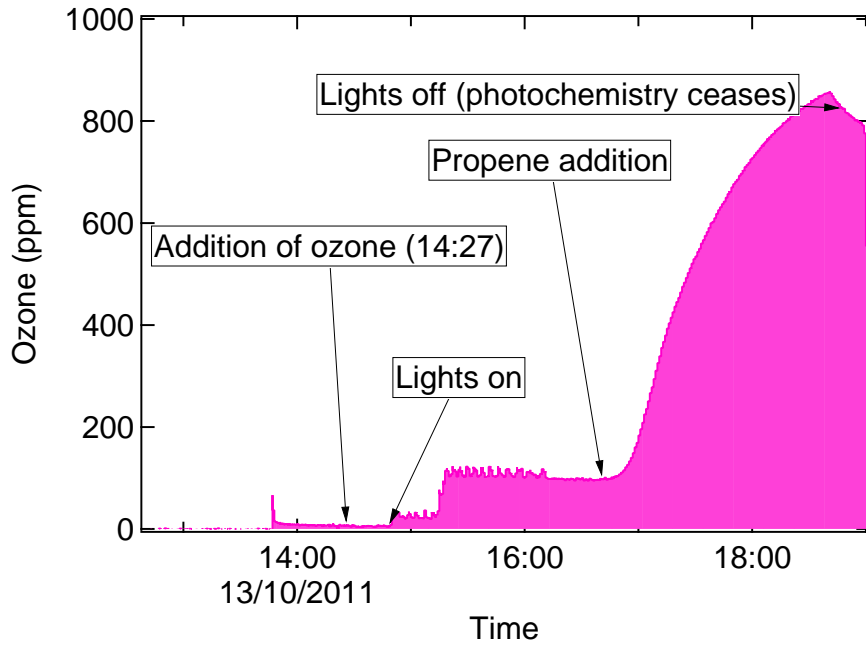


Fig. 1. : Ozone concentrations during aging of gasoline light duty vehicle emissions. The addition of ozone before lights on to partly react NO to NO₂ doesn't produce excess ozone.

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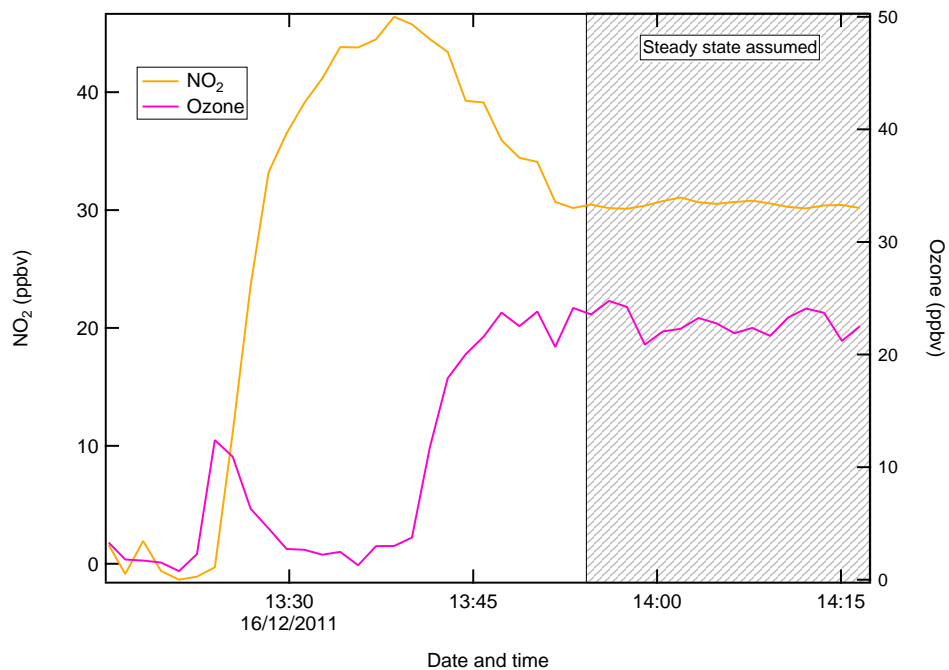


Fig. 2. Concentrations of ozone and NO₂ inside the mobile smog chamber during actinometry experiments. A steady state was assumed after a stable concentration was attained (shaded region).

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