

Interactive comment on “Secondary organic aerosol formation from gasoline passenger vehicle emissions investigated in a smog chamber” by E. Z. Nordin et al.

Anonymous Referee #2

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This paper presents results from the aging of gasoline exhaust emissions from three vehicles at a smog chamber. Emissions, which included a mix of light aromatic and other hydrocarbons, from cold start or from idling were injected into the chamber and irradiated to produce secondary organic aerosol (SOA). Further experiments were also performed in the smog chamber with mixtures of pure light aromatic hydrocarbons. Comparing the two sets of experiments shows that 1.7 times more SOA was produced per reacted aromatic in the gasoline exhaust than in the case of pure aromatic, suggesting that up to 60% of SOA production from gasoline exhaust is from light aromatic oxidation. The authors also give a SOA formation factor from gasoline cars significantly higher than that previously reported for diesel cars.

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The article is generally well written and the study of vehicle emissions aging is of interest to sections of the scientific community dealing with atmospheric aging processes and also specifically with vehicle emissions. This being the case care must be taken to avoid misleading statements. Furthermore some points need more clarification while others could be expanded upon. Therefore I recommend the paper be accepted on ACP once the following issues are addressed:

Major points:

The vehicles used in this study do not comply with current Euro 5 legislation. Most experiments were performed with a car meeting Euro 2 standards, outdated as of January 2000. Specifically, hydrocarbon emissions have been lowered in the intervening period. The results of this study are only atmospherically relevant if they apply to the current vehicle fleet. Therefore can the authors provide assurances, from for example literature or their own analyses that emissions have been reduced in a way that would not affect their conclusions? I.e. have emissions been reduced without altering exhaust emission composition? Furthermore the authors must make clear throughout that the results they present are based on study of emissions from the most modern vehicles.

The authors argue convincingly that aromatic oxidation explains a major fraction (60%) of the SOA from gasoline. Why stop there? Although some discussion of possible contributions from PAHs is presented, this leaves half of the story unexplained. More information on VOCs is available to the authors and therefore some estimation of SOA production from any other compounds e.g. alkanes, measured with GC-MS or PTR-MS, should be given (even if it suggests only small contributions) as it would be especially useful to the scientific community.

An SMPS was used to correct for collection efficiency (CE) of the AMS. This is very briefly mentioned in the text and it is not clear how exactly this was done. Specifically: what density was assumed, how was non refractory (black carbon) accounted for, were the particle mass distributions within top and bottom size cut-offs for both instruments

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throughout all experiments? What was the CE and is it constant throughout an experiment? CE and density should be mentioned in the text, relevant size distributions can be shown in the supplementary.

The conclusion that gasoline SOA is from light aromatics relies on the comparison between different datasets after aging, and the paper also compares emissions from different vehicle emissions after aging. Given that OH exposure is known, why were yields calculated and compared for the time at the end of experiment and not at a common OH exposure? Would the difference between SOA produced from gasoline and from pure aromatics then still be a factor of 1.7 when compared at the same photochemical age? SOA production factors should also be given at the same OH exposure. Throughout the text comparisons between vehicles, experiments etc. should be given at a fixed photochemical age as a time after lights on is arbitrary.

Generally, very little movement on the f43/f44 space or on Van Krevelen diagrams is observed with OH exposure. Time resolved data in Fig 7 b) show that gasoline POA has an O:C significantly higher than the 0.04 reported in Aiken et al., (2008). How do the authors explain the high starting O:C and only small movement in the space?

Minor points:

Over what period are POA emissions quantified? is an average concentration used, if so is a wall loss correction applied over this averaging time? According to section 2.5.3 POA is taken immediately after injection. However this may lead to error as some time is required to achieve a homogeneous mixing of the aerosol inside the chamber.

Vehicles were all run in idle. To make sure that the article does not mislead the reader the article title must reflect the conditions under which experiments were performed, i.e. include the words "idle" (or idling) and "cold start"

Vehicles normally emit NO_x even in idle. Can the authors show that absence of NO_x is typical for gasoline vehicles operating in idle? If not, the vehicles were outside of

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normal operating conditions and the results less relevant.

UV black lights do not significantly photolyse NO₃. Discuss the possibility that in the case of the gasoline experiments some of the extra 40% SOA could come from NO₃ chemistry (reaction with exhaust alkenes).

SOA formation is delayed until NO is converted to NO₂. This has been observed previously, but do the authors have an idea why is this the case?

Why were decay curves of C7 and C8 aromatics used to calculate OH concentrations when the same calculation could be done with toluene (only one KOH required)? Was the decay of the C7-C8 aromatics so slight as to produce significant uncertainty in the OH concentration? Assuming toluene could be measured what would the OH concentration be if toluene were used as a tracer, as in Barmet et al., (2012)?

In Fig. 3 it does not look as though a background reading of the gas phase (through a filter with the AMS) was taken. I assume that background CO₂ etc. was corrected for in all experiments?

Pg 31726, L2: Emissions are elevated during cold start yes, idling not necessarily, this statement may therefore be misleading.

Pg31726, L7: Arabic numerals (1, 2, 3, 4) should be used for "Euro" standards of light duty vehicles, not Roman (I, II, III, IV), which are for heavy duty vehicles. Correct throughout the article.

Pg31726, L8: "with" photo-oxidation, not "using"

Pg31726, L10: characterisation "instruments" not "methods"

Pg31726, L14: It would be preferable to give an OH exposure time here rather than simply "4h" which is only relevant to one smog chamber during one experiment, given how much OH can vary.

Pg31726, L25: Also important to health, include a reference.

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Pg 31727, L2: “dominant” not “dominating”

Pg 31727, L21: Potentially misleading. Because the catalyst is working only when hot, all gasoline vehicles emit significantly during cold start. However, cleaner, more modern, vehicles have efficient catalysts and thus must drive even further before they reach their equivalent cold start emission, i.e. they appear dirtier when using this metric. Make this clear or remove the statement.

Pg 31727, L17: Care must be taken in discussing results of Odum et al., 1997 as aerosol loadings were very high, affecting partitioning. This point should be mentioned.

Pg31730: Relative humidity during experiments should be given, include also in Table 2. If the chamber was not humidified prior to experiments then this point needs to be addressed in discussion as dry experiments may be less atmospherically relevant.

Pg31731, L18: State whether this fuel matches closely that in use in other countries.

Pg31730, L13 “may” can be deleted and HONO can be added to this list

Pg31735, L9: If the engine is warmed then this is “hot idling” not cold idling.

Pg31735, L9: What is a standardised circuit? Most likely this is fairly arbitrary and not “standardised” by anyone, and should be deleted, 3 minutes warm up would suffice.

Pg 31735, L10: Temperature is a hugely important parameter effecting emissions and so more detail should be given how and where the engine temperature was measured. I would suggest that Table S2 is sufficiently important to merit inclusion in the main text.

Pg31735, L21: Was the line to the FID heated and if so to what temperature? If not heated this can lead to error and should be mentioned in the text if this is the case.

Pg31736, L17: An additional assumption is that SOA production is constant over the period where the correction is applied.

Pg31737, L2: Was the sulphur content of the Swedish fuel also so low?

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Pg31737: Approximately what proportion of the SOA reported and shown in Fig. 4 comes from the wall loss correction factor?

31736, L2: The authors state “In experiment I4 O₃ was added to convert a major fraction of the emitted NO into NO₂” Why was this done? Furthermore, O₃ could react with alkenes in the exhaust or produce NO₃. Do the authors have any indication that this was the case?

Pg31739, L14: Since the catalyst temperature was not measured it is inappropriate to produce statements ascribing effects to low catalyst temperature. Low engine temperature is possibly OK (as it was in some way measured), low catalyst temperature should be removed.

Pg31740, L5: “As shown” not “as it can be seen”

Pg31740, L10: make clear at what point in the experiment the given O:C, H:C refers to.

Pg31742, L21: delete “do”

Pg31742, L22: What exactly is “towards zero”? what is the NO concentration, or is it below detection? Low NO_x in the case of for example Ng et al., (2007), was NO in the ppt range.

Pg31744, L24: Does “early aging” refer to a time after lights were switched on or low OH exposure. Even if experiments are compared “early” they can have very different photochemical aging times.

Pg31745: This section is important and makes a strong case for a contribution of higher aromatics to the remaining observed SOA. However, the discussion is a little ‘messy’ at times. Generally it should be clear to the reader that theoretical f₄₃ f₄₄ of SOA from aromatics is being referred to not, as is written, the “f₄₃ f₄₄ values. . .for light aromatic precursors” At a first reading it appears as though the authors have taken fragmentation patterns for precursors, not their SOA, and compared them to the real

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emissions.

Pg31746, L1: I do not understand “in-data”

Pg31746, L6: change “low f43 of ethyl benzene” to “low f43 of ethyl benzene SOA”, see above commentary on Pg31745

Pg31746, L23: change “has” to “have”

Pg31746, L24: change “have” to “has”

Pg31748, L19: Since catalyst temperature is not measured/ reported this conclusion should not be made here from this study.

Pg31748, L22: This is not true; driving is mostly driving and not idling. Furthermore that “the driving pattern in urban environments includes idling and shorter driving stints, which may hinder the engine and catalyst from reaching its optimum operating temperature” is not a conclusion that can be made from this study.

Pg31761, Fig 4 b). Here, SOA appears to grow exponentially. Can the authors give an assurance that this is real, not an artefact from an incorrect wall loss correction?

References

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