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"Secondary organic

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

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We thank reviewer 2 for taking the time to read the paper and to provide us with valuable comments that we feel will make the paper better

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 Most experiments were performed with a car meeting Euro 2 standards, outdated as of January 2000.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



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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. -From Euro2 to Euro5 the total HC legislative emission limits have been reduced by a factor of 3-4. Between Euro4 and Euro5 the total hydrocarbon limit is the same, but there is now in addition a new limit on non-methane hydrocarbons. The variability of gasoline exhaust composition is often larger between vehicles within each legislative class than between legislation classes (Clairotte et al. 2013). This is due to differences in the type of engine and catalyst and due to differences in operating parameters (rich vs lean etc) between different vehicles of the same class. Thus the composition of the exhaust and thereby the conclusions should be valid also for the newest vehicles. The impact of operation mode on VOC emissions are further addressed in our answers to reviewer #1. The following text has been added: "The legislative VOC emissions have been reduced a factor of 3-4 from EURO2 to EURO5. The composition of gasoline exhaust (for example VOC/NOx ratio) varies strongly between gasoline vehicles within the same emission class (Clairotte et al. 2013)." 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 PTRMS, should be given (even if it suggests only small contributions) as it would be especially useful to the scientific community. -According to Gentner et al. (2012) gasoline contains compounds with carbon numbers (Cn) up to about 12. Alkanes and cycloalkanes are dominated by carbon number up to 9. The expected yields of those relatively small alkanes and cycloalkanes are low. We quantified selected alkanes including 2-methylpentane, hexane, heptane and octane. Assuming a mass yield of 0.01 these alkanes would contribute to ~ 0.5 % of the SOA mass in experiment I2. Styrene was also guantified, assuming a yield of 0.05 would give a minor contribution of \sim 0.5 % to the SOA. The

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concentration of quantified compounds with Cn>12 in the exhaust is about two orders of magnitude lower than the light aromatics according to Schauer et al. (2002). Quantification of alkanes with the PTR-MS is complicated due to fragmentation, further we only measured at selected m/z channels. Thus quantification of for example alkanes from these data is not possible. Conclusions on the importance of alkanes to SOA in gasoline exhaust can also be drawn from the SOA mass spectra. For example, SOA from alkanes is rich in CxH2(x+1) fragments. We found very low concentrations of such fragments, in contrast to diesel exhaust SOA where these fragments are common. The following text was added to the article: "SOA from alkanes is rich in CxH2(x+1) fragments e.g. m/z=43, 57, 71 etc. (Miracolo et al., 2010). The SOA formed from gasoline exhaust had low contribution of these fragments, which suggests that alkanes are of minor importance as SOA precursors in the gasoline exhaust experiments."

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 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 collection efficiency (CE) for the AMS is given as the ratio between the (uncorrected) mass concentration measured by the AMS and the volume concentration measured by the SMPS multiplied with the density (CE = CAMS/(CVOL SMPS*Ro), where the aerosol density is derived from the chemical composition. The collection efficiency typically increased from about 0.25 to 0.40 when organic material condensed on the ammonium sulfate seeds, due to less bouncing on the vaporizer. The wall loss correction method also correct for a change in CE, if we assume that we have internally mixed condensation. The SMPS volume concentration is in this case only used as an initial value for the wall loss correction. Since the aerosol in the smog chamber at start of each experiment almost to a 100 % consists of ammonium sulfate, ammonium sulfate density (1,769 g cm⁻³) is used, in

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experiments were the POA was non negligible, the seed density was corrected using a POA density of 1.0 g cm⁻3. We have added the following text "This method also accounts for an increase in collection efficiency (CE) of the AMS, most likely due to decreased bounce when the seed particles become coated with SOA. A typical change in CE was from 0.25 for ammonium sulfate before exhaust in. to 0.40 at the end of the experiment. AMS and SMPS size distributions at the beginning and end of experiment I2 are given in Figure S4. It should be pointed out that uncertainties originating from wall loss correction are likely small when comparing the experiments reported here to each other. But there may be larger uncertainties when extrapolating our results to other chambers and experimental conditions. Clearly wall loss correction methods merit further investigation." and "For ammonium nitrate and SOA we used densities of 1.72 g cm⁻³ and 1.40 g cm⁻³, respectively." The black carbon concentration measured with the SP-AMS was negligible in the idling experiments and consisted about 20% of the mass concentration before lights on during cold start. We did not explicitly take the black carbon concentration into account in the wall loss correction. It would have a small effect if the CE for soot and seed cores is different and if the condensation on the soot cores were markedly different from that on the seed particles. A figure (fig. S4) showing SMPS and AMS distributions for both beginning and the end of the experiment has been added to the supplement. More than 80% of the particle volume and mass is contained within 100-600 nm, which is within the SMPS measurement range and the efficient part of the AMS lens transmission window. 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

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lights on is arbitrary. -An alternative version of the yield graph (fig. R1) is provided at the end of this response, where we have plotted the mass yield of all experiments at a cumulative OH exposure of 3*10⁶ h cm⁻3. That OH-exposure figure was chosen as it was the lowest final exposure amongst the experiments (experiment I1). The trend that the precursor experiment has lower apparent mass yield remains, at 20 μ g m-3 the factor is 1.9. The estimation of the yield at 3*10⁶ h cm⁻³ has uncertainties associated with the estimate of cumOH in the experiments that didn't use PTR-MS. We then had to estimate the time for CumOH=3*106 h cm-3 from a limited number of time points by GC-MS (for the P2 experiment there were only two time points, before lights on and at the end, making this experiment especially uncertain) due to lack of continuous measurements. The slightly higher ratio of gasoline exhaust to precursor SOA production at a low photochemical age is consistent with naphthalenes being important SOA precursors in the early part of the experiments when the NO pathway dominates further reactions of RO2. Thus, the design of the experiments makes it difficult to present the results with high precision at a fixed photochemical age. The new figure will be added to the on-line supplement. The SOA production factors at idling vary between 0.005-0.05 g kg⁻¹ fuel at cumulative OH exposure of \sim 5*106 h cm⁻³. These numbers have been added to the text. The following text has been added to the main article: "At a low cumulative OH exposure of 3*10⁶ the ratio was 1.9 (Figure S5) consistent with a slightly earlier onset of SOA formation in gasoline exhaust compared to light aromatic precursors."

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? -The POA concentration in experiment I3 was so low that we could not quantify O:C and H:C in a reliable way. The starting point in figure 7 is taken when the SOA concentration becomes larger than \sim 4 μ g m-3. At this point the SOA dominates the OA, thus the low f43 and high f44 at the starting point and the following movement during the experiment

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is rather a measure of variations in the SOA composition and contains information related to the SOA precursors. For example: these results are consistent with a higher SOA fraction from naphthalenes at the start of the experiment. This has been clarified in the figure text to fig. 7.

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.

-The concentration of POA is determined using the ratio between POA and SO4 when the concentration (POA) was stabilized (typically 15 mins). Since the exhaust air was hot (\sim 100 °C) when entering the chamber, the mixing in the chamber occurs rapidly. POA to our definition is not being produced over time, so there is no wall loss correction applied. The POA/SO4 ratio was essentially constant over time after achieving mixing. An average over 5 mins was used to determine the POA concentration.

The following text was added to the article: "The POA to sulfate seed ratio is determined during a 5 minute period about 15 minutes after exhaust injection to allow the exhaust to mix in the smog 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" -This is a valid point, we have included idling in the title. The title is now "Secondary organic aerosol formation from idling gasoline passenger vehicle emissions investigated in a smog chamber"

Vehicles normally emit NOx even in idle. Can the authors show that absence of NOx is typical for gasoline vehicles operating in idle? If not, the vehicles were outside of normal operating conditions and the results less relevant. -Most vehicles operate at a lambda either slightly above or below 1 at idle. This results in either high NOx and low HC or

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Low NOx and high HC. There was quite a large difference in NOx emissions between the vehicles. The emission factors for NOx (mg/h) varied between 0.1 for the Euro4 vehicle (30 at cold start) and was on average 2.1 for the euro 2 and 5.0 for the euro 3 vehicle. We examined the exhaust from several other cars in pre-experiments, there were other cars than those presented in the paper that also had "low" NOx emissions.

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). -It cannot be ruled out that NO3 chemistry contributes to SOA formation. Simulations using the Master chemical mechanism v3.2 (MCMv3.2) estimated the cumulative NO3 concentration to 5.5x106 molec cm-3 hr while the simulated OH exposure was 7x106 molec cm-3 hr for the P2 experiment with lights on (using only the measured UV-spectrum, thus an upper limit). These simulations showed that reactions between NO3 and either m-xylene and RO2 would be negligible. We do not expect reactions between NO3 and the rather small alkenes present in gasoline exhaust to produce significant amounts of SOA, but it cannot be ruled out. The following sentence has been added to the manuscript "It cannot be ruled out that reactions with NO3 (which is not effectively photolysed by black lights) was contribution to SOA formation. However the SOA yields of NO3 reactions for example with the short alkenes (C<10) occurring in gasoline exhaust are expected to be low.". 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? -In the initial oxidation step the light aromatic compounds react with OH. A large fraction of the formed products are peroxy radicals (RO2). E.g. according to the master chemical mechanism (MCMv3.2) >50 % of the products formed by the m-xylene + OH reaction are RO2. The formed RO2 mainly react with NO or HO2 and form different non-radical organic compounds. In the beginning of the experiments the RO2 + NO reaction pathway strongly dominates (high NO pathway). The reaction products from these reactions generally tend to be more volatile than the products formed from the RO2 + HO2 pathway (e.g. Ng et al. (2007)). Most likely the concentrations of the reaction products of the RO2+NO compounds do

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not reach above their saturation concentrations. When the NO concentration drops below ~1-2 ppb the reactions with HO2 starts to become important. Since these oxidation products generally are less volatile they will contribute with a main fraction of SOA formation in our experiments. It is important to note that SOA formation starts at a higher concentration in the gasoline exhaust experiments compared to the pure precursor experiments. Particularly in experiment I3 (which started from the highest NO level) there is evidence for sustained SOA production at elevated NO (for example 10 μ g m-3 SOA formed at NO>20 ppb). This observation is shown in a new figure in SI (Fig. S7).

The following text has been added: "The formed peroxy radicals (RO2) will in the beginning of the experiments predominantly react through the NO-pathway, while in the later parts of the experiments the HO2 pathway will be of increasing importance. Simulations with the Master Chemical Mechanism version 3.2 (MCMv3.2) showed that the fraction reacting in the HO2 pathway is about 5-7% at 2 ppb NO. Light aromatics which react via the NO pathway are likely to form products that are too volatile to end up in the particle phase, when oxidized at the OH radial concentration used here (Ng et al. 2007), thus explaining the delay in observed SOA formation."

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)?

-Using Toluene, similar results (within 20%) were found as for the C9 aromatics. The scatter was higher for toluene when compared with several other C8, C9 compounds. Thus, the decay of toluene was too slight to provide a good base for calculations of OH exposure, since the uncertainties in VOC measurements would have played a bigger role. C8 aromatics could be used, but we would still require multiple kOHs then.

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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?

-A 5 min filter measurement was performed several times in each experiment, to be able to correct for the CO2 gas phase contribution from the exhaust. However, we chose to connect the data points before and after the filter measurement when plotting, to make the graph more readable.

The following text has been added: "Gas-phase contributions (especially to CO2+) to the detected signals were subtracted using filtered air measurements carried out in 5 min periods several times in each experiment."

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

-The following text has been removed "have elevated emissions of volatile organic compounds during cold starts and idling and"

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.

-Corrections has been made throughout the article and supplement

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

-Correction has been made

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

-Correction has been made

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

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how much OH can vary.,

-The OH exposure range between experiments was $3-9 \times 106$ (mean 5.5) for gasoline exhaust and 6-7 $\times 106$ for precursor experiments (mean 6.2). The following text has been added: "After a cumulative OH exposure of $\sim 5 \times 106$ h cm-3" instead of 4 h.

Pg31726, L25: Also important to health, include a reference. -The following sentence was added "There is a lack of knowledge about how SOA affects public health, though the association between concentration of fine particles and mortality is stronger in the summer (Nawrot et al., 2007), which is also when the SOA production is increased (Hallquist et al., 2009)." Pg 31727, L2: "dominant" not "dominating"

-Correction has been made

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.

-The following text was added to the sentence: "(this figure is most likely even higher for newer vehicles, since the emissions during driving has been further reduced)"

Pg 31728, 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.

-The following text was added: ", it should be mentioned that the aerosol mass loadings in the study by Odum et al. were very much higher compared to other studies (including ours) which affects the partitioning between the particle and gas phase."

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.

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-RH has been added to table 1. "The following text has been added: The RH was around 5% in our study, it will also be important to investigate the effect of increased RH on gasoline exhaust SOA yield and composition in future studies."

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

-The fuel used in the study was classified according to the latest Swedish regulation, which complies with the latest EU standard (EN 228). The allowed concentrations of for instance aromatics and sulfur are identical.

-", which complies with latest EU standard (EN 228)." Was added to the text

Pg31733, L13 "may" can be deleted and HONO can be added to this list

-Corrections have been made

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

-We have changed "cold idling" to just "idling" throughout the paper.

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.

-The words "on a standardized circuit" have been removed

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.

-The engine temperature was given by a built in indicator for the Euro2 vehicle. The two other vehicles were driven the same way before the experiments but the exact engine temperatures are not known.

There are already two tables in this section of the paper, so we think it would be too much information. We have added more visible references to the table S2 in the main article.

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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.

-The sampling line to the FID was heated to 100 $^\circ\text{C},$ we have inserted this in the text

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

-This is correct.

Pg31737, L2: Was the sulphur content of the Swedish fuel also so low? -Yes, it is the standard in the European Union

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

-The non-wall loss corrected organic mass in experiment I2 is about 23 μ g m-3, the wall loss corrected mass is 44 μ g m-3. i.e. about half of the SOA comes from the wall loss correction factor. This has been added to the figure text.

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?

-This was done to investigate whether additional SOA formed upon addition of ozone down to a NO concentration of 20 ppb remaining. No SOA formation was found. NO3 can't co-exist with NO so NO3 concentrations were very low during this part of the experiment.

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.

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-Sentence revised accordingly

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

-Sentence revised accordingly

Pg31741, L10: make clear at what point in the experiment the given O:C, H:C refers to.

-Added "The O:C and H:C ratios were both similar for the gasoline exhaust and the precursor experiment (0.4 and _1.4, respectively) throughout the experiments.

Pg31742, L21: delete "do"

-Sentence revised

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

-See discussion above, the RO2+HO2 reaction pathway starts to become important at about 1-2 ppb NO.

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.

-We have removed the word "early"

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 emissions.

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-We have made some changes to clarify the text: the whole section is inserted below, changes are highlighted "The experimentally observed ÆŠ43, ÆŠ44 values from this study are compared with literature data for light aromatic precursors in Fig. 8. The precursor experiments reported here are in general agreement with previous studies of SOA from pure m-xylene and 1,3,5-TMB (Ng et al., 2010) both positioned to the right of the triangular plot. From known literature values of the fragmentation patterns of the dominating C6-C9 light aromatic compounds we calculated the theoretically expected fragmentation pattern of the gasoline exhaust assuming that only the C6-C9 light aromatic compounds were contributing to the SOA. It was assumed that the fragmentation pattern of the mixed SOA could be determined as the weighted sum of the fragmentation patterns of SOA from the individual precursors, the theoretically expected 43, ÆŠ44 values are also plotted in Fig. 8. The procedure and the literature data to this calculation are shown in more detail in the online supplement. It is found (Fig. 8.) that the theoretically expected ÆŠ43 for the gasoline exhaust experiments, calculated as described above, is slightly lower than for the pure precursor experiments, but still substantially higher than that experimentally found in the idling experiments. The small difference between the expected ÆŠ43 and the three component precursor mixture used in our experiment (P1) is due to the low ÆŠ43 of ethyl benzene SOA and slightly higher toluene content in the gasoline exhaust compared to experiment P1. From this analysis we can put constraints on the magnitude and composition of SOA from the additional precursors discussed above. If we subtract the expected ÆS43 and ÆS44 fractions (based on only C6-C9 aromatics) from the mass spectra at the end of each gasoline exhaust experiment, it can be shown that a maximum 50-60% of the mass would come from light aromatics, (Table S4 in the online supplement). At higher fractions of light aromatic precursors, the ÆŠ43 value of the SOA from unknown additional precursors would become below 0 (i.e. the precursor would have been positioned on the negative side of the x-axis in Fig. 8). In contrast, for the cold start experiment, the ÆŠ43/ÆŠ44 relationship assuming only C6-C9 precursors is almost identical to the experimentally found value, again supporting that the cold start emissions can be

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explained from essentially C6 to C9 light aromatics only."

Pg31746, L1: I do not understand "in-data"

-The in-data is the f43 f44 for the compounds included in this calculation, we have changed it to literature data.

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

-Corrections have been made

Pg31746, L23: change "has" to "have"

-Corrections have been made

Pg31746, L24: change "have" to "has"

-Corrections have been made

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

Statement removed

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.

-Statement removed

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? -The SOA growth is largely consistent with the OH concentration derived from the VOC measurements, slightly increasing with time in this experiment, which resulted in the described shape of the curve. Further, in this experiment the NO concentration reached

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below 2 ppb inly in the last hour which may further enhance SOA formation in the final part.

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 31725, 2012.

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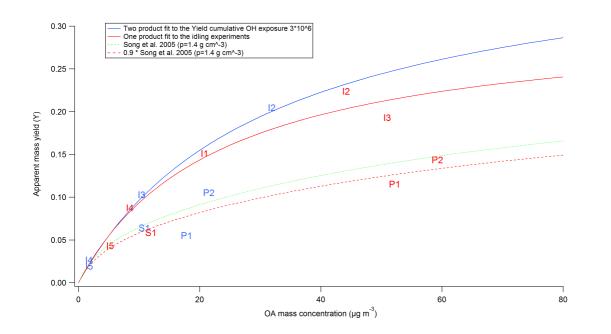
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Interactive Discussion





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Fig. 1. Fig R1: The apparent mass yield from the gasoline and precursor experiment. Blue

letters is the yield at a cumulative OH exposure of 3*106 molecules cm-3 hr. The letters is the

yield at the end of eac