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Atmospheric
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Discussions

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 1 for taking the time to read the paper and to provide us with valuable comments that we feel will make the paper better

This paper describes an experimental study of the secondary organic aerosol formation from idling gasoline vehicle exhaust and mixtures of light aromatics. Dilute exhaust from three different vehicles was injected into a small, temperature-controlled smog chamber and then photo-oxidized with black lights. The experiments were performed under cold start and cold-idle conditions. The experiments found substantial secondary organic aerosol formation, greatly exceeding the direct primary particle emissions. The

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paper estimated an apparent yield based on the decay of light aromatics. They compared this apparent yield estimates to comparable data from experiments performed with simple mixtures of light aromatics conducted under similar experimental conditions. This was a nice comparison. They concluded that about 60% of the SOA formed in the dilute vehicle exhaust could be explained by light aromatics. They also performed extensive analysis on HR-AMS data that reached a similar conclusion.

The paper is well written and the experiments appear to be carefully conducted. The paper interesting and it makes a valuable contribution to the ongoing discussion of the SOA formation in urban area. I recommend that it be published in ACP after addressing the following comments.

A major shortcoming of the experimental design is that they were only performed on cold start and cold idle conditions. There are very high emissions under these conditions, but it is not clear how much these operational modes contribute to the overall emissions from motor vehicles in an urban area. (Most of the gasoline is not burned at idle). The data in Table 1 suggests that the emissions are VOC (but not NOx) dominated.

This is different than typical running emissions of light duty gasoline vehicles, which are frequently NOx dominated. In addition, the experiments were performed under relatively cold ambient conditions (_0oC). As pointed out in the paper this further enhances the VOC emissions. However, it is not clear how representative these conditions (operating and ambient) are for, for example, the summer time conditions of LA during the Bahreini experiments (which the authors claim the new data support). Furthermore, under these cold (wintertime) conditions there likely will not be that much photochemistry in the atmosphere (likely much less than in the chamber). These limitations (only cold start and idle under relatively cold conditions) mean that one must be careful at drawing overly broad conditions from the work. This needs to be pointed out.

-Clearly emissions of VOCs including SOA precursors vary with driving mode, temperature, engine and catalyst type etc. This is particularly true for the absolute emission factors of the precursors. For example, Clairotte et al. (2013) examined the temperature dependence on emissions from gasoline vehicles. The vehicles were cold started and then driven according to the UDC cycle. The emissions of toluene were elevated a factor 6 at -7 °C compared to +22 °C.

However, as shown in the paper the distribution of light aromatics from the idling case is similar to tunnel measurements. In our experiments light aromatics consisted 10-15% of the total VOC emissions, this figure and the fraction of naphthalene are both similar to what was found in the most extensive characterization of gasoline exhaust known to us (Schauer et al. 2002). The data by Schauer et al. are for older vehicles but are consistent with newer data of the main emitted VOCs reported for the European driving cycle by Montero et al. (2010) for Euro 3 and 4 gasoline vehicles. Thus the composition of the exhaust for our idling case is of relevance for gasoline emissions in the atmosphere. Guo et a.l (2011) examined the emissions from different driving speeds and idling for gasoline vehicles. The emission factors (mg h-1) for idling are in the same range as the emissions factors for driving (converted from mg/km to mg/h using the driving speed).

The following text has been added: “It is important to note that the reported SOA production factors only relates to cold idling and cold start operating modes (this study) and a single vehicle (Platt et al. 2012). Clearly there is need for more data to systematically investigate a larger set of operating modes, engine types and exhaust after treatment systems at well-defined oxidant levels in parallel with field observations of gasoline SOA formation in the atmosphere.”

We used the Master Chemical Mechanism version 3.2 (MCMv3.2) to simulate the gas-phase chemistry in the urban plume downwind the city of Malmö in southern Sweden (∼300.000 people), during a typical clear sky winter and early spring day in southern Sweden. The actinic flux used to calculate the photolysis rates in MCMv3.2 was esti-

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mated with the radiative transfer module from the ADCHEM model (Roldin et al., 2011). From the modeled daytime OH concentration profile we calculated a winter and early spring daytime cumulative OH exposure of ∼106 and ∼3.5x106 molecules cm-3 hr, respectively. Hence, the cumulative OH exposure during the smog chamber experiments corresponds to ∼3-6 winter days or 1-2 early spring (or autumn) days in northern Europe. Thus the SOA formation time scales are longer at wintertime conditions (low temperatures) with litter solar irradiance. Still the main degradation of for example light aromatics occurs in the atmosphere initiated by reactions with OH, thus they will still contribute to SOA formation, although further away from the source.

The following text has been added to the manuscript: “The elevated emissions due to cold starts at reduced temperatures will typically be accompanied by lower OH concentrations in the atmosphere. So these emissions will therefore contribute to SOA formation for a longer time period. “

Page 31735 – The paper discusses the VOC/NOx ratio of the experiments. These were adjusted by adding NO to a target range based on the measured concentration of light aromatics. I found it strange that they were controlling this ratio just based on the light aromatics as opposed to total VOC. The light aromatics were only a small fraction (15%) of the total VOC emissions. It is the total VOC to NOx ratio that influences the important radical branching channels such as the fate of organoperoxy radicals (RO2). The paper needs to state what the overall (not just light aromatics) VOC/NOx ratios are (ppbC/ppb) and compare them to typical urban ratios. If there are differences, what are the implications for interpreting the data?

-Controlling the LA/NOx ratio was done due to practical reasons, as the LA concentration in the chamber was available on-line from the PTR-MS. We agree that a fraction of the remaining VOCs in the gasoline exhaust contributed to the atmospheric chemistry in the chamber (exceptions being methane and other low reactivity compounds). We do not give the VOC/NOx ratios in ppbC/ppb as we do not know the molecular weight of most of the VOC’s. In terms of ppb/ppb our gasoline exhaust experiments span ratios

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between 8 and 70 (where the VOC concentration includes methane). This can be compared to recent emission measurements by Clairotte et al. (2013) for Euro4 and Euro5 gasoline vehicles using the urban driving cycle who found ratios of 2-8 using the same units. In urban environments the VOC to NOx ratio is 0.5-1 and the figure increases downwind the urban area as a function of photochemical age. Clearly there is a need for future pure high NOx experiments on the SOA formation of gasoline exhaust.

The following text has been added: "Our gasoline exhaust experiments were carried out at relatively high total VOC to NOx ratios. The ratios were 8-70 (in ppb VOC per ppb NO), compared to $\sim$7 for the precursor experiments. This is higher than that found in gasoline exhaust emission tests and urban areas (typically 0.5-10). However, still the NO-pathway for RO2 strongly dominated in the first 45-60 minutes (longer in experiment I3) of each experiment. It is important to note that SOA formation starts at a higher NO 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 μg m-3 SOA formed at NO>20 ppb as shown in Fig. S7). So while a majority of the SOA formation in the gasoline exhaust experiments may have occurred via the HO2 pathway, we suggest that gasoline exhaust may contain precursors (for example naphthalenes) that have a high NOx yield that is larger than that of for example m-xylene."

Following from the previous comment, what were the VOC/NOx ratios for the precursor (not dilute exhaust) mixture experiments? Were these different than for the gasoline vehicle exhaust experiments? The data in Table 1 suggests they were quite different. It appears that they were setting these ratios based only on light aromatics and not the total VOC burden. This seems a bit problematic since in the mixture experiments the entire VOC burden is light aromatics but this was not the case in the gasoline vehicle exhaust experiments. If there are differences, what are the implications for Figure 5? Would this alter conclusions about the relative contribution of light aromatics to the

SOA formed in the chamber.

-The VOC/NOx ratio was ~7 (ppb/ppb) in the precursor experiments. It is correct that the total VOC/NOx ratios are higher in experiment I1, I2 and I5 compared to P1, P2. On the other hand the VOC/NOx ratio is similar or only slightly higher in experiment I3 and I4. According to Song et al. (2005), the yield for m-xylene is independent of VOC/NOx in this range. This suggests that the impact of the varying VOC/NOx between experiments on the comparison between gasoline exhaust and precursor SOA formation may be only minor. If anything the remaining NO-concentration in the period when the majority of SOA formation took place was slightly higher in the idling experiments compared to the precursor experiments, which would suppress LA SOA formation in the gasoline exhaust. However measurements of NO at such low levels (<2 ppb) are highly uncertain. Previous studies (Song et al. 2005) have added propene to increase the VOC/NOx level in precursor experiments, this has led to a slight decrease in LA based yield.

Table 1 provides absolute concentrations of light aromatics, total VOC, and NOx. Were these measured in the chamber? Are the total hydrocarbons reported as ppmC? These data suggest that the VOC/NOx ratio is likely greater than 10:1 ppbC/ppb. So these experiments were conducted in the low NOx regime. The text seemed to imply otherwise. How do the VOC and NO concentrations listed in Table 1 compare to typical ambient levels. What are the implications for translating the data to ambient conditions?

-Total VOCs were measured with the FID near the tailpipe. NOx was primarily measured in the chamber. The total VOCs are reported as ppm (not ppmC). It is correct that the VOC/NOx ratio was larger than 10:1 ppbC/ppb in the experiments. However as pointed out above, from a more fundamental perspective the NO pathway for reactions of RO2 dominated over the first 45-60 mins of each experiment. Just as essentially every published smog chamber data set, the concentrations are higher than those under ambient conditions. This is particularly true for the VOC concentrations.

A clarification has been added to table 1 that the total VOC levels were measured before primary dilution.

Page 31749 line 5 The paper states the large amounts of SOA formation in dilute gasoline vehicle exhaust support the conclusions of Bahreini. The paper also suggests that the majority of SOA in gasoline vehicle exhaust can be explained by light aromatics. However, analyses by de Gouw (JGR 2008) and others (e.g. Volkamer GRL 2006, etc.) suggests that there are large gaps between the observed SOA in urban areas and the amount of SOA predicted to be formed by light aromatics. This seems like a disconnect that should be pointed out in the paper. -This is a good point. We changed the text to the following: "It should be pointed out that the results of this study when combined with the conclusions by Bahreini et al. (2012) that gasoline exhaust dominates anthropogenic SOA production in urban areas is not fully consistent. We found that 50-60% of the gasoline SOA is formed by light aromatics, while de Gouw et al. (2008) showed that a dominating fraction of urban SOA is formed from other precursors than light aromatics, thus more research is needed on SOA formation in urban areas." How do the apparent SOA yields from the simple mixtures compare to predictions" based published yield data? This was briefly mentioned on page 31742 (line _17).Figure 5 suggest reasonable agreement with Song (is that correct?). It would be nice to have some quantitative comparisons – how much lower were the yields in these experiments. Weren't the Hildebrandt data high NOx performed with HONO? - This section has been expanded, it now reads: "The mass yield for experiment P1 and P2 is 2-3 times lower than other pure precursor experiments presented in the literature (Hildebrandt et al., 2009; Ng et al., 2007). Those experiments with significantly higher yield have been performed using H2O2 as OH-precursor. The experiments presented in this paper were performed without added OH-precursors. 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 radical concentration used here (Ng et al. 2007), thus explaining the observed delay in SOA formation. For the H2O2 “high NOx” experiments in the literature NO was converted to NO2 within minutes. Thus SOA formation for that case and in the case without added NOx may have been dominated by the HO2 pathway throughout the majority of the experiment which may explain the higher yields found in these studies.”

Clarifications Page 31742 line 26 – This conclusion about 1.7x more SOA than light aromatics. This based on comparison with your mixture experiments (i.e. not some sort of modeling with published yields)? How would using published yields change your conclusions here?

-Using the data reported by Song et al. (2005) carried out under similar conditions and assuming a density of 1.4 g cm-3 for their data, the factor 1.7 would change to 1.55. However, as pointed out above the yield for light aromatics are dependent on the experimental set-up, added oxidants, OH level, wall-loss correction method etc. Therefore we believe the accuracy of the ratio of SOA formed for gasoline to that formed by pure precursors becomes more uncertain if comparing with yields carried out under less comparable conditions.

Equation (2) – DeltaHC was directly measured or calculated based on the OH concentration.

-We used the directly measured DeltaHC (sum of all measured C6-C9 light aromatics) from GC-MS measurements before lights on and at the end of the experiment. This has been clarified in the text.

Page 31743 line 9 – these percentages correspond to the fraction of the initial mass of each compound that reacted? (E.g. 0.9% benzene)

-No, these ratios are the fractions of the sum of total reacted light aromatics. The text has been modified to: ”The percentages of the total reacted light aromatic compounds in the idling gasoline exhaust were for each light aromatic on average 0.9 % benzene. . ...”

How consistent were your estimates of OH exposure for the different light aromatic tracers. -Typically within 20% with the highest variability for toluene. This is further addressed in the answer to reviewer 2.”

The following text has been added: “OH exposures were typically within 15% when comparing analysis based on C8 and C9 aromatics.”

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