

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 #1

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Review of “Secondary organic aerosol formation from gasoline passenger vehicle emissions investigated in a smog chamber” by E. Z. Nordin et al. (MS No.: acp-2012-891)

Sorry for the very late review.

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

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organic aerosol formation, greatly exceeding the direct primary particle emissions. The 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 NO_x) dominated. This is different than typical running emissions of light duty gasoline vehicles, which are frequently NO_x dominated. In addition, the experiments were performed under relatively cold ambient conditions (~0°C). 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.

Page 31735 – The paper discusses the VOC/NO_x ratio of the experiments. These

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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 NO_x 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/NO_x ratios are (ppbC/ppb) and compare them to typical urban ratios. If there are differences, what are the implications for interpreting the data?

Following from the previous comment, what were the VOC/NO_x 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.

Table 1 provides absolute concentrations of light aromatics, total VOC, and NO_x. Were these measured in the chamber? Are the total hydrocarbons reported as ppmC? These data suggest that the VOC/NO_x ratio is likely greater than 10:1 ppbC/ppb. So these experiments were conducted in the low NO_x 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?

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.

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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.

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 NO_x performed with HONO?

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?

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

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

How consistent were your estimates of OH exposure for the different light aromatic tracers.

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

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