

Interactive comment on “Gas phase composition and secondary organic aerosol formation from gasoline direct injection vehicles investigated in batch and flow reactors: effects of prototype gasoline particle filters” by Simone M. Pieber et al.

Anonymous Referee #2

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This paper describes measurements of primary emissions and secondary organic aerosol from four modern gasoline direct injection (GDI) engine equipped vehicles. The market share of GDI vehicles is rapidly increasing in the US and other countries, displacing the more traditional port fuel injection engine equipped vehicles. This paper represents probably most systematic study of SOA formation from GDI vehicles to date. The paper also investigates the impact of adding a retrofitted gasoline particulate filter (GPF) to two of the vehicles. While others have investigated the effect of this technology on primary emissions, I am not aware of previous studies that have investigated

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its impact on SOA formation. The paper also uses an oxidation flow reactor (OFR) and a smog chamber to investigate SOA formation, comparing the results between the two systems and with measurements made with individual compounds.

The paper shows SOA formation dominates primary PM emissions (consistent with previous studies, though the SOA/POA ratio seem much larger than previous studies). The paper demonstrates that the majority of SOA formation is formed from cold-start emissions, which is not surprising but I have not seen it demonstrated before. The paper shows that somewhat more than half of the SOA formation appears due to 8 single-ring aromatics. Finally the paper shows GPF reduces primary PM emissions but does not reduce the SOA formation (or non-methane organic compound emissions).

Overall the paper is well written and very comprehensive. The experiments appear to have been carefully conducted (though I agree with the other reviewer's concerns on treatment of wall loss), with results from repeated experiments shown (it would be nice to describe the precision a bit more). I think this paper makes a nice contribution and recommend that it be published in ACP after addressing the following comments.

Specific comments:

Abstract and a few other places “a large fraction (>0.5)” These statements refer to the mass closure of the SOA production based on measured precursors. 1 is greater than 0.5. The authors need to be more quantitative; e.g. give a range (or some other metric such as median and interquartile range). Figure 6 suggests that this ratio likely varies with OA concentrations. Figure 5 suggests poor closure for 100% and 70% OFR conditions, but good closure for 50% OFR. SC has better closure at short timescales. The authors need to be more quantitative about the mass closure.

Retrofitted GPF – How was this done? How representative is it of how a true OEM designed and installed GPF-system would operate? It is hard to simply add a control system to a vehicle for which it was not designed (I have seen tests with a retrofit GPF hanging off the back of a car!), therefore I am always concerned about how represen-

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tative the performance of researcher retrofitted system versus what might be done by a vehicle manufacturer. This is not to say that they are not seeing some effect of the GPF but it may be (much) less than the performance of bottom up engineered system. For example, I was surprised that the catalyzed GPF did not further reduce the NMOC emissions – what was the operating temperature of the GPF? Anyways I think the GPF results are interesting, but a bit more detail on how the retrofit was done, specifically limitations of researcher retrofitted systems should be acknowledged. Unless they can document that the retrofitted is representative of OEM designed and installed systems the conclusion section (~line 10 on page 25) is too strong.

The dramatically higher NMOC emissions and SOA production from cold start is important. Can the authors quantify how much more important it is than hot start (e.g. using an analysis similar to that Saliba et al. EST 2017 10.1021/acs.est.6b06509 to compare hot and cold start emissions).

The conclusion section largely repeats conclusion from earlier in the paper. The paper would be improved if they put the results in context with the growing literature in this area. In particular I was interested if the results are consistent with the existing body of knowledge on SOA formation for PFI vehicle exhaust. My sense is that it is.

You tested the vehicles using two different cycles? Were there any cycle dependencies or was cold start just dominant?

Figure 2 – The y-axes are five orders of magnitude. This illustrates large changes, but changes of a factor of 2 or 3 can also be interesting. For most tests it does appear that the GPF is reducing the POA emissions, but not as dramatically as the EC. I did not get that impression reading the text but it does appear in the figure. More attention needs to be paid to these trends.

Figure 2 – The SOA production seems surprisingly high. For GD11 the total NMHC (most of which are not SOA precursors) is around 1000 mg/kg (Figure 2a). The SOA production is between 200 and 600 mg/kg (Figure 2a) – the SOA production from the

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GPF equipped experiments with GD11 seem incredibly high. This suggests an effective of SOA of 20-60% of the total NMHC emissions of which less than half is aromatics (Figure 4b is misleading because the NMOC measured by PTR is only 65% of NMHC measured by FID). The SOA production seems higher than previous studies of modern vehicles (they are more similar to 25 year old vehicles). I guess Figure 6 suggest SOA yields are “reasonable”, but I was confused looking at Figure 2 (maybe it is just the log scale with 5 orders of magnitude). Are there background issues?

Figure 2c – There is a lot of vehicle to vehicle variability (2+ orders of magnitude). Are the reductions between cold and hot start consistent across vehicles? Plotting ratios may be more informative. What is up with the experiments with an NMHC emission rate of 0.1 mg/kg? Are those valid data?

Figure 2 is very busy (especially panel d). It is basically impossible to sort out the trends. Pick the key points you want to make and plot just that data. The SOA production appears surprisingly close to the NMHC emissions (it even exceeds it for some vehicles).

Additional ArHC (page 23). The analysis in Zhao et al. (EST 50(8): 4554-4563 2016) suggests some of the IVOCs are alkylated single ring aromatics larger than those included in the analysis here. How does including IVOC component measured by Zhao et al. change the analysis? His analysis suggests that IVOCs contribute somewhat less than half of the SOA in gasoline vehicle exhaust.

Page 3 “diesel PM emissions have been greatly reduced.” – This is true for new diesel particulate filter (DPF) equipped vehicles but there are a lot of old diesels on the road, especially in Europe so human exposure to diesel particles has probably not yet been greatly reduced. Eventually it will be when the fleet is completely turned over. May want to refine this statement.

Page 4 “modern diesel vehicles” Modern is too generic. You should be more precise catalyzed-DPF equipped diesel vehicles. I don’t necessarily think modern = DPF.

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Page 8 “experiment. Control experiments were conducted regularly in the SC to estimate the contribution of the SC background to SOA formation.” Please provide another sentence or two here that describes results from control experiments. How much SOA was formed in controls and how does it compare to what is measured in an experiment with vehicle exhaust. Did you run control experiments with the OFR – what were the background levels in that system?

Section 2.2.6 – I am pretty sure that you are calculated yields using the reacted aromatic mass in the denominator however this statement is confusing “the ratio of the SOA mass to the reacted SOA-forming mass, $\Delta_{\text{NMOCreacted}}$ ” My understanding is that $\Delta_{\text{NMOCreacted}}$ is not the same as the reacted aromatic mass. This needs to be cleaned up to avoid confusion. May also want to state this in the caption for Figure 6 to reminder reader of how yields are calculated.

Using “NMOC” to describe the sum of the PTR measurements is confusing as it is measuring less than 2/3rds of the organic gas emissions as measured with FID. This limitation needs to be stated more clearly (it is in the intro but the reader will likely forget – e.g. adding to caption of Figure 4 would be good and in other places in the main text when you discuss NMOC).

Emissions data from tests in mg/kg-fuel needs to be provided in tables in supplemental.

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