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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Time-resolved characterization of primary and secondary particle emissions of a modern gasoline passenger car" *by* P. Karjalainen et al.

Anonymous Referee #2

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Tailpipe emissions from a Euro 5 gasoline passenger car were either analysed directly, or aged in a PAM chamber prior to analysis. Ageing measurements were time-resolved, contrasting with previous smog chamber studies. The authors observe SOA formation was significantly higher than the primary emission, and that most SOA was formed from the cold start emissions. The authors conclude that legislation to limit SOA precursor emissions is necessary to improve air quality. The time resolved ageing aspect of this work is of interest to the community. This has only partly been investigated before, for example, Gordon et al. (1) examine SOA formation from different phases of a US driving cycle, albeit with a smog chamber, which lacks the resolution of a PAM chamber. For this reason, the ability of the PAM chamber to realistically simulate

the ageing of emissions in the atmosphere is of central importance. Unfortunately, a number of details about the PAM and the experiments are missing from the article, but which must have been used in analysing/ interpreting the results presented. This is a serious omission. I also do not believe that experiments on one vehicle with a new and unestablished (and in this work, undescribed) methodology are sufficient to recommend changes to current emission legislation.

Therefore, while this paper is broadly consistent with recent work, I believe major revision is required.

With additional work it might be possible address the problem areas, broken down as follows:

Major issues:

The authors do not describe how background CO2 is corrected for in the AMS. This can be important given the very high CO2 in the exhaust. If CO2 Is highly variable and not accounted for correctly, this would lead to variations in the organic aerosol mass which are merely an artefact.

In the materials and methods section a single reference is given for a description of the chamber, Lambe et al., which I assume is a general reference for this kind of set up. This is not enough, and a more detailed description should be given, e.g. material, emission spectrum etc. A schematic of the experimental set-up should be shown in the main text.

How well do the authors believe the PAM chamber simulates 'real' atmospheric chemistry, given the extremely rapid photochemistry? Some of the recent work by the Jimenez group may be of help (2-4) in understanding and discussing PAM chambers. Some of this work should also be referenced in the main text.

SOA formation depends largely on OH concentrations (or rather, OH exposure, time integrated OH, see also Barmet et al. (5)). Yet, the OH exposure in the chamber is unknown/ unreported. How then, are we to know whether the last part of the driving cycle produces less SOA because there is less OH, or because less precursors are emitted? OH exposure is a function of photon flux, residence time, H2O concentration and OH reactivity (which may depend on VOC concentration). Given that all of these parameters are known, or can be estimated (from typical concentrations and OH reaction rates), it may be possible to estimate the extent to which OH exposure varies during the experiments, even if it cannot be quantified. The author's statement that the relative humidity was 'typically 60%' appears insufficient in this context.

On interactions with the chamber walls. The surface to volume ratio in the PAM chamber is presumably much higher than a traditional smog chamber (though dimensions are not given in the text). It is therefore important to take interactions with the walls into account. Since particle losses to the walls depend exponentially on suspended matter concentrations, some attempt to estimate these losses is required. Are gas phase SOA precursors lost to the walls? This can artificially surpress SOA formation (6). There is strong evidence that at least the 'sticky' gases e.g. ammonia are lost. This is because I note that the ammonium nitrate/ SOA ratio is low compared with both Nordin et al. (7) and Platt et al. (8). To what extent do vapour losses to the walls suppress SOA formation in the PAM chamber? How was the PAM chamber cleaned between tests? A blank test should have been performed/ reported (lights on, and measurement without sampling emissions).

The author ran each test twice, once with and once without a PAM, to establish a baseline for SOA formation. However, what was the time interval between the tests? It takes hours for an engine to cool (which is why regulations stipulate a 24h soaking time at ambient temperature before all tests). If insufficient time between tests was given, this can produce very large discrepancies in the emissions, particularly in the cold start period.

Only one car was studied, but changes to legislation are recommend by the authors. Such assertions may appear to enhance the importance of this study, but in fact serve

to highlight the study's limitations. Furthermore, even if we are to accept that this one vehicle is truly representative of all other gasoline passenger cars, there are many factors to consider e.g. should we worry more about SOA or other pollutants such as NOX? What if reducing SOA could be achieved by increasing NOX e.g. by increasing the fuel air ratio in the engine, would this be helpful? Such considerations are clearly beyond the scope of the paper. Given that the paper could still be published without suggestions for changes in policy I recommend that all such discussions be removed from the text.

Minor comments:

One disadvantage with sampling directly at the tailpipe is that while exhaust flow is variable, the sampled flow is constant. A different fraction of the complete exhaust is sampled as the flow rate varies. In theory, this could lead to a sampled composition different from that emitted, if composition and flow rate do not co-vary. As an example Zardini et al., assess this effect in the supplementary material of their article (Fig. S3) (9).

Mass spectra from the HR-ToF-AMS can be useful for interpreting the results. I strongly recommend the authors include these, at least in the supplementary section. The very high SOA formation may be related to very high loading in the PAM (which is much above ambient values). This should be discussed/ acknowledged in the text. Did the authors check that the aerosol volume/mass distribuiton was within the size cut-off of the AMS over the course of each experiment?

Specific comments:

Pg. 33253: The title should be changed to reflect the fact that secondary particle are not emitted, but formed. Suggest: 'Time-resolved characterization of primary particle emissions and secondary particle formation from a modern gasoline passenger car' Pg. 33255, ln1: 'changes in traffic systems' I understand this as changes to roads and other traffic related infrastructure. . .do the authors mean this? This is not within the scope of the paper in any case, and I would suggest starting with something like 'Changes in vehicle after-treatment technologies have significantly affected traffic related emissions in urban areas' Pg. 33255, ln5/6: change to 'both primary (direct) particulate emission and secondary particle formation (from gaseous precursors in the exhaust emissions) need to be characterized. Pg. 33255, ln8: What is modern? State e.g. Euro standard and/ or vehicle age. Pg. 33255 Ln 9: No it doesn't. It is from tailpipe to atmosphere, quite a lot happens before the tailpipe (of course) and this is not investigated. Change to 'from tailpipe to atmosphere'. Pg. 33255 ln 19: Since this is a study on one vehicle only, 'strongly indicates' changes to any legislation is an overstatement. I suggest deleting this last statement. Pg. 33255, ln 27: This is misleading since-though I do not know about regulation everywhere-there are no particle mass (PM) limits for European or Californian gasoline cars. Particle number (PN) is limited only for direct injection gasoline. I suggest being clear here, and stating exactly what is limited for gasoline (since this is the focus of this study) with reference to sources. Pg. 33256 ln 10: Again, PM is not limited for gasoline cars. Therefore, gravimetric sampling is likely not done for type approval of gasoline passenger cars in Europe. The authors can point out that although not directly regulated, SVOCS are likely to be affected by THC/ NMHC limits. Pg. 33257 ln 20: Suarez-Bertoa et al. refers to a Flex-fuel (ethanol) vehicle. The authors may keep this reference (and Nordin et al. should be kept), but Platt et al., 2013 (8) and Gordon et al., 2014 (1) should be included. Pg. 33257 ln 21: In Suarez-Bertoa et al., emissions were sampled during a driving cycle, not at constant speed. Furthermore, although the smog chamber part of that study was not time-resolved many measurements e.g. of NOx and various VOCs were in fact time-resolved. The authors may refer to Chirico et al. (10) and Nordin et al. as examples of experiments lacking any time-resolved measurements/ sampling at idling or constant speed. Pg. 33259 ln 1: The authors should refer to their Figure 1a for the NEDC. Pg. 33259 ln 4: The NEDC has only two test phases (urban and extra urban). Pg. 33259: Please provide a schematic of the experimental set-up Pg. 33259 ln 9: What material is the transfer line? Was the transfer line heated? Pg. 33259 ln 21:

The authors provide the typical temperature and relative humidity, but over what range/ how much did these in fact vary? Pg. 33262 ln18: While the AMS community often uses 'Chl' for chlorine, this is in fact wrong, and it should be Cl. Pg. 33262 ln19: It should also read 'sulfate' in the figure, not 'sulphate' Pg. 33263 ln21: Missing full stop Pg. 33263 ln22: Secondary particles are not emitted Pg. 33265 ln27: How was the catalyst temperature measured? Pg. 33266 ln 11: Given that exhaust/ catalyst temperature do not seem to have been measured and that only one vehicle was tested, I do not feel that the evidence is strong enough to merit this conclusion. Pg. 33266 ln 19: I think this should be calculated and not calculative Pg. 33267 ln 21: Not enough evidence to suggest an influence on atmospheric pollutant levels, given that only one vehicle was tested Pg. 33268 ln 4: Suarez-Bertoa refers to a flexi fuel vehicle. The reference can be kept but Gordon et al 2014/ Platt et al., 2013/ Nordin et al., 2013 should be included in this comparison. Pg. 33268 ln 6: Secondary particles are not emitted. Pg. 33269 ln 22: These conclusions are all too strong given the limited sample size and should be removed. Figure 6: increase the size of the text in the axis labels/ legend. The caption should be written with the letters before the description, and the text clarified e.g. "(a) Chemical composition of primary emission (b) secondary formation…" Supplement figure 1: text is rather small, font size should be increased Table S1: Chl should be Cl. Numbers should be in subscript for chemical compounds

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