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Interactive comment on "The Effect of Varying Engine Conditions on Unregulated VOC Diesel Exhaust Emissions" *by* Kelly L. Pereira et al.

Anonymous Referee #2

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General Comments

This manuscript presents diesel exhaust measurements of from a light-duty diesel engine using an engine dynamometer. The study investigated the effects of engine load and use of diesel oxidative catalyst (DOC) on emissions of volatile and intermediate volatility organic compounds (VOCs/IVOCs) in diesel exhaust. The exhaust emissions were diluted in an atmospheric chamber and online sampling was conducted to measure speciated VOCs and grouped VOCs using a TD-GCxGC-FID system. The study results showed that VOC/IVOC emission rates and VOC profiles were greatly impacted by engine load and DOC efficiency. Intermediate volatility organic compounds (IVOCs) are quite difficult to sample and quantify accurately, and speciated IVOC emissions measurements are rare, particularly online measurements. Therefore, the publication

of results from this work will be of significant benefit to the emissions research community to improve our understanding of IVOC emissions from a diesel engine and how they are impacted by engine conditions. However, there are several important issues raised below that must be addressed before this work is accepted for publication in ACP.

One major issue is that the rationale behind selection of the engine, fuel, experimental conditions was not articulated in the manuscript. Why was the particular engine with retrofitted DOC selected, and why was the goal to mimic Euro 4 emissions standard? I would imagine this engine/technology must be outdated compared to current and near future European light-duty vehicle fleet adhering to Euro 5 and 6 standards. Therefore, are these emission rate results at all relevant to the current European vehicle fleet?

Why were the specific experimental conditions chosen: specific engine loads, dilution ratios, speeds, multiple fuel batches? Based on the experiments listed on Table 1, the research strategy behind these measurements is very difficult to tease out. For example, in Section 3.1 the effects of engine load were discussed. However, because the DOC was also included, the results reflected the coupled effects of engine load and DOC that were interdependent. This is not ideal for a mechanistic study such as this work. Was it intended to study the effects of both simultaneously or was this an unintended consequence of the experimental design? Either way, no explanation was given. The rationale behind the experimental design and study conditions needs to be clearly described in order for the reader to interpret the results.

The second major issue is that a large portion of the discussion in the supplementary information is extremely important and should be provided in the main text. I believe some discussion points brought up in the SI are actually more scientifically relevant and impactful than some of the extended discussion about engine load and DOC effects in the main text that have been previously studied by others.

Experimental reproducibility is vital experimental information; this information (e.g.

measurement replicates, test replicates) needs to be clearly detailed in the main text in order for the reader to assess the data quality and statistical power of the results. In Table 1, which experiments were meant to be replicate tests, and are the numbers in parentheses the measurement replicates or something else? Also, the origins of the error bars and emission rate standard deviation values need to be explained in the main text. If they are from the calibration propagation of error uncertainty calculations in SI Section 3.1, then how were measurement and test replicates included in the errors?

The discussion in the SI indicated that dilution ratio had a substantial impact on IVOC emissions between two similar experiments. Given the wide range of dilution ratios used in this study, this issue warrants further discussion in the main text, particularly how this issue may have influenced the results. Furthermore, a discussion of the observed differences in emission rates for the two different fuel batches and linking them to fuel composition by 2DGC-TOF fuel analyses was very interesting and should be included in the main text.

The third major issue is that in Section 3.4 the comparison between these engine dynamometer emission rates with California tunnel measurements is misleading and not scientifically relevant. While I understand the desire to link these results to real world measurements, I don't see the scientific merit or rationale for making this particular comparison. This study used an engine, aftertreatment technology, and fuel that are not at all relevant for these CA on-road measurements. What I believe would be of much greater scientific benefit to the mobile source emissions research community is a thorough literature comparison of speciated IVOC measurements that are so rarely measured for at least light-duty diesel engines and vehicles from engine and chassis dynamometer studies. Are these measurements consistent with other light-duty (and perhaps also medium/heavy duty) diesel vehicles and how to they compare with Euro5 and Euro6 compliant engines/vehicles/fuels? If the IVOC data is lacking for modern vehicles with newer emission standard, how are the emissions expected to change from Euro 4 to Euro 5 and 6. Finally, how will the engine operation and other effects on

VOC/IVOC emissions impact SOA formation from vehicle exhaust?

Specific Comments

Section 1. Introduction: there are some repetitive statements (Page 2, Lines 17-20; Page 3, Lines 34-36; Page 4, Lines 1-2, 5-7). The introduction could be made more concise by removing the repetitive text.

Page 4, Lines 10-12. The introduction referenced research that has previously studied the effects of DOC and engine operating parameters on vehicle exhaust composition, e.g. Chin et al. 2012. Other studies have also investigated these effects on diesel vehicles/engines (e.g. Ballesteros et al. (2014), Zhu et al. (2013)). Can this statement be further clarified so that it is more accurate?

Page 4, Line 28. Please provide hygrometer vendor information.

Section 2.2. Section title is misleading. This section not only describes the engine but also exhaust sampling system. Please provide more detailed information on the engine specifications and about DOC usage status (mileage or rapid thermal aging hours) as this can significantly impact the emissions. Provide rationale behind the selection of the specific engine, aftertreatment and why Euro 4 emission control was approximated. Please provide a schematic of the dynamometer and sampling system (this may be included in the SI). Please describe all engine operating conditions including driving scenarios and include rationale behind the experimental design.

Page 5, Line 12-13. Was the MAC filled before exhaust was introduced? How were the dilution ratios decided upon and why did they vary from experiment to experiment? How long was the diluted exhaust allowed to equilibrate before sampling took place and were there any apparent losses in IVOCs over time?

Page 5, Line 18. Please explain why two batches of diesel fuel were used. Please include any fuel composition or fuel property analyses that were conducted. What was the sulfur content of the two batches? Do both batches of the diesel fuel meet Euro 4

or Euro 5 specifications? Please discuss differences in fuel composition here. What is meant by “standard”?

Page 5, Line 25. What temp was the line heated to?

Page 6, Line 17. How often was the calibration checked by a standard? Were MDLs determined? If so, explain how and provide MDL values for all compounds. This can be provided in the SI.

Page 7, Line 1-4. The engine operating conditions should be described in detail in the experimental as well as justification for why these specific conditions were chosen.

Page 7, Line 9. Not enough evidence has been provided to identify the grouped VOCs “branched aliphatics”, particularly because these were not GC/MS measurements. These would be better labeled as unspeciated or unresolved organics. The grouped VOCs should also not be called speciated VOCs because they are not individually speciated. Therefore, sum of SpVOC is a misleading term and should also be changed to minimize confusion. Also, please discuss why this narrow range of VOCs was studied? Was it intentional to focus on IVOCs or was this due to sampling/instrumental limitations?

Page 7, Line 11. How often were the retention time windows confirmed? Were any internal standards used?

Page 7, Line 23-24. Both reproducibility and dilution effects are important enough to merit detailed discussion in the main text. Please see general comments above.

Page 7, Line 29-30. While similar sets of conditions have been compared in the discussion, emission factors are all presented for every experiment, allowing the reader to freely compare between experiments without fully understanding the impacts of differing dilution ratios unless they read the SI in detail. This is why a full discussion of the effects of dilution ratios is needed in the main text.

Section 3.1 Why were these loads chosen? Please state clearly whether these ex-

periments (and for each subsection in the Results section and in all figure captions) are from tests with or without DOC? This section title is also misleading because the combined effects of engine load and DOC were studied simultaneously.

Page 8, Line 7. Is this statement suggesting that engine load is the most important factor that controls VOC emission rates, whereas other factors, e.g. aftertreatment and fuel, are less important? If not, please clarify. Also, please state clearly that the assumption was made that engine load is linearly related to engine combustion efficiency or provide ancillary measurements to confirm combustion efficiencies for each experiment.

Page 8, Line 18, 20. Should the reference be Chin et al. (2012)?

Page 9, Lines 16-22. This text contradicts what is shown in Figure 2a, 2b and previous discussion on Page 8.

Page 10, Lines 16-17. Did Alam et al. use the same type of DOC or was it different from what was used in this study? It may also be interesting to compare the results of Liu et al. (2010) with this work.

Page 10, Lines 26-30. Please show how the conditions of these three scenarios change in a diagram in the experimental section or SI.

Page 11, Line 17-18. Relative abundances discussed here?

Page 11, Line 18-22. It is not clear why the effect of the DOC are brought up here. It does not logically fit with the rest of the discussion in this paragraph.

Section 3.4. Please see general comments on this section. It would be extremely useful to conduct a literature comparison to assess whether the emission factors from this study are consistent with similar studies. The comparison with Gentner et al. (2013) is misleading and should not be included.

Page 12. Line 32-33. Aldehydes are not at all mentioned here and represent arguably

the most important air toxic/hazardous VOCs emitted from modern diesel vehicles.

Page 13. Lines 3-7. Please discuss differences between Euro 5 and Euro 6 emission standards in relation to the approximated Euro 4 emission standards simulated here and how modern vehicles and their aftertreatment technologies are specifically changing. How are these changes expected to impact VOC emissions? Emission control technologies targeting other pollutants may still have significant effects on VOC emissions. This is where the literature comparison of emission factors from this study with emission studies with Euro 5 and Euro 6 vehicles would provide insight (see general comments).

Page 13. Lines 7-8. Please see general comments about this comparison.

Page 13. Lines 11-13. Please see earlier comment on the veracity of this statement.

Table 1. Please clearly indicate which tests were replicate tests and which tests had replicate measurements.

Figure 1. What are the compounds below B and above G? What is the peak above #8? Why does benzene elute after toluene – are those labels correct? Have any attempts been made to quantify the lighter compounds and to assess total unspeciated organics?

Figure 2. What do error bars represent? Are these tests with or without DOC? Toluene and benzene colors are difficult to distinguish.

Figure 4. Evidence was not provided to speciate into aliphatic and aromatic components.

Figure 5. See general comments on this comparison.

Supplementary Information

Page 4, Lines 13-14. Why was toluene used and not an n-alkane?

References:

Ballesteros, R., Guillen-Flores, J. Martinez, J. D.: Carbonyl emission and toxicity profile of diesel blends with an animal-fat biodiesel and a tire pyrolysis liquid fuel, Chemosphere, 96, 155–166, 2014.

Liu, Z. G., Berg, D. R., Vasys, V. N., Dettmann, M. E., Zielinska, B., Schauer, J. J.: Analysis of C1, C2, and C10 through C33 particle-phase and semi-volatile organic compound emissions from heavy-duty diesel engines, Atmospheric Environment, 44 1108-1115, 2010.

Zhu, L., Cheung, C.S., Zhang, W.G., Fang, J.H., Huang, Z.: Effects of ethanol–biodiesel blends and diesel oxidation catalyst (DOC) on particulate and unregulated emissions, Fuel, 113, 690–696, 2013.

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