

## ***Interactive comment on “Mapping and quantifying isomer sets of hydrocarbons ( $\geq C_{12}$ ) in diesel fuel, lubricating oil and diesel exhaust samples using GC $\times$ GC-ToFMS” by Mohammed S. Alam et al.***

### **Anonymous Referee #2**

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This article describes a novel GCxGC-TOF-MS approach for the characterization of carbonaceous material (oil and aerosol emissions). The research is novel and worth publishing although it is not clear why this necessarily belongs in an atmospheric journal as most of the work and discussion is on oil. The only, but serious weakness is in the writing itself. The text looks more like being part of an extensive report or a thesis than a scientific manuscript with constant referring to 3 other papers by the authors as well as abundant references to the SI. In its current form it is a painful read, even for people interested in the topic, and I find that it is not really able to stand on its own without the information in these other sources. I think the manuscript should be substantially cleaned up to be more readable and tell a consistent and concise story, with

the critical information if really not in the paper itself then in 1 single place. For the least, some clarifications are needed and this being an atmospheric measurement journal, it would be useful to emphasize the atmospheric relevance by a clearer comparison to what is known in the field.

Major points:

Please review what is really necessary here as method vs what can be in SI and vice versa and in regards to the other manuscripts. Some critical info is lacking as example: what mass resolution is used for the quantification? In no place the resolution of the TOF is mentioned and some spectra in SI are at unity resolution while others are at .1 Da resolution? This would matter.

The text should be focused more on the atmospheric community. This starts with the abstract where quantitative info is only given for oil and goes through the text. It is quite unsatisfying to just point out that the results are different from e.g. Gentner's work but then not attempt at all is being made to explain why? the same is true for other places of the manuscript where the text leaves it at: we see more/less than these other people. . . These differences should be addressed.

In that regards too, there are the highly cited papers by the Cass group (Rogge et al papers) that discuss for 1D GC extractable vs elutable, resolvable, identifiable for oils and diesel emissions. . . given that these papers are extremely known and cited, may be data could be compared? To illustrate the advance of this methodology over the 20 year old work that is cited hundreds of times.

The methodology of the quantification should be clarified in the present manuscript. example~ L254-2" Therefore, out of the 8026 ng that was injected into the GC×GC, a mass of approximately 7200 (± 1728) ng was accounted for." It is unclear here. . . how the 8026 ng was determined? and why does it not have an uncertainty? Similarly how was the uncertainty for the 7200 obtained?

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Please clarify how some homologous series were quantified for which you do not list standards (hopanes and steranes etc)?

I am deeply confused also on the mass balance how any non organic/hydrocarbon species are handled? Especially synthetic motor oil could have a substantial fraction Si or other non HCO materials. Related also you refer to synthetic oil and contribution from crude. This is confusing as synthetic oil could be completely synthetic i.e. nothing in there has ever been seen crude.

Minor points:

The text needs some attention to detail. In the experimental section, please use a consistent form to refer to manufacturer, location etc.. also check for typos, USA not US etc Do states need to be included for USA?

I am not a native speaker but the English clearly seems off at times e.g. 187-190, two sub sentences starting with while.. reads really odd?

References cite in chronological and antichronological order in the text not random

Details: L129: Ref: EU. . . please write as citation

L153: "6"? number reference?

L253 I am not sure it is appropriate to label column bleed as contaminant plus there is no evidence that this is only column bleed. Siloxanes might well be present in synthetic oil or even ambient air.

L322.. this is experimental and does not belong in the results section

SI section:

Page 4: formatting issue

Page 7: Liang et al 2017 in prep?

Figure S4-1: legend X axis? What is 1/MW (C24-C12 Molar Quantity)? Explain clearer

and make legend text consistent with actual legend

S4-2 left panel idem to S4-1 plus straight unreadable (font size)

S4-3 make labeling consistent with other figures

All of the double MS plots, please make them look like the ones in the actual paper or I suggest that on one panel at least the eV are indicated as for MS community this way of showing spectra is typically how + and – ion spectra, so could be confusing

The model spectra, are they corrected for background ? how were they obtained? some have many peaks (PAH)?

S6 what is really the use of this if not even the position of one relative to the other are shown in fig 6

Please even in SI use a uniform formatting of references

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Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-366, 2017.

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