

## ***Interactive comment on “Measuring long chain alkanes in diesel engine exhaust by thermal desorption PTR-MS” by M. H. Erickson et al.***

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Thank you for your time and helpful comments to make this paper more clear.

Reviewer comment 1. The authors used a comparatively unusual injection technique of neat chemicals via extremely low flow syringe pumps. It would be of interest to readers why this technique, which according to the authors showed some difficulties, was chosen instead of injecting calibration standard diluted samples, e.g. in pentane (which would have remained undetected), which are commercially available.

Response. The technique works well enough; we are able to make VOC test mixtures that agreed with 15% of compressed gas standards we use in the lab. Typically buying neat compounds is less expensive than commercial standards and allowed us to make

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test mixtures of a wide range of compounds, many of which could not be purchased as standards. The approach also allowed us to continuously inject a sample over many hours to perform replicate experiments with the thermal desorption system in an automated way (ie. overnight. That would not have been possible by manual injections of liquid standards directly onto the trap (although this was also done).

We have changed the sentence on page 6010, line 7 to reflect these points. “The syringe pump was used to continuously deliver low flow rates of a neat liquid into a dilution flow of air or nitrogen to produce stable and accurate test mixtures that could be analyzed for many hours for instrument testing.”

Reviewer comment 2. Sampling lines need to be heated and are ideally made from inert materials when transporting low vapor pressure compounds. The authors identified using electropolished stainless steel and Sulfinert tubing, but did not identify the temperature (“heat traced”, line 24, page 6009m also line 25, page 6011) used, unless it is the same mentioned later, namely 80 deg C (line 24, page 6010). Please clarify. In addition, explain why 80 deg C was chosen. Our experience is that much higher temperatures are generally needed for quantitative transmission of >C12 species through inert tubing, and that a significant “tubing lag” to the signal can be expected at temperatures below 100 deg C.

Response. We acknowledge that higher temperatures would be better for transporting these hydrocarbons. We were restricted by how hot we could heat the drift tube and did not want to have the drift tube act as the “cold spot” in the system which might then become contaminated. For IVOC analysis having a high temperature drift tube would be desired, such as used by Thornberry et al., (2009) but constructing such a drift tube was outside the scope of this project. We don't feel that this prevented us from our purpose which was to investigate the potential of PTR-MS analysis of long chain alkanes. Tubing losses (fraction of mass absorbed to tubing walls compared to total mass flow) can be minimized by increasing the mass flow of analyte (ie. through higher flow rates or concentrations) and/ or by using humidified air and this is the approach

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we took to condition the system.

The heat traced sample line temperature is now clearly noted in the text as 80 °C on page 6009 and 6011. We have changed the text on page 6009 to explain the temperature used.

“The drift tube was thermostated to 70 °C using the thermoelectric drift tube heater supplied by Ionicon. For analysis of heavier organics a high temperature resistive glass drift tube would be preferred such as used in Thornberry et al. (2009). Because of limitations on drift tube temperature, the sampling lines, either electropolished stainless steel tubing (UHP Cardinal) or silica coated stainless steel tubing (Sulfinert, Restek Corp), were heat traced to a similar temperature (80 °C), so that the drift tube didn't act as a cold spot and become contaminated.”

Reviewer comment 3. Connected to 2., please specify more PTR-MS operational parameters, particularly pressure and temperature. At too low drift tube T, again, the low vapor pressure species are expected to show memory and carry over effects. These have to be characterized in order for ambient measurements to be time resolved and the data be quantitative.

Response. On page 6010 we now list the drift tube operating conditions: “For the experiments and measurements described, the PTR-MS was operated at 80 Td with a drift pressure of 2.08 mbar, drift temperature of 70 °C, and a drift voltage of 325 V.” We experienced no problem with carry-over as evidenced by collecting zero air blank samples on the Tenax trap and have modified line 9 on page 6010 to note this: “Zero air was collected on the trap in the same manner as a sample and peak responses above the zero air signals were determined; no carryover effects from previous samples were observed in the zero air desorptions.”

Reviewer comment 4. Quantification is an issue. If the response factor (“sensitivity”) can be reproduced for a certain set of PTR-MS parameters and tubing temperatures etc., an ambient measurement under identical conditions should be quantitative if the

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sensitivity is representative of the ambient mix. This was not demonstrated in the manuscript with some actual ambient data. Could that be included? If the sensitivity is not representative for whatever reason, a more sophisticated approach would be necessary, which would then have to include, e.g., transmission efficiency of the PTR-MS (possibly the reason for the mass response cutoff observed by the authors).

Response. We have indeed applied the TD-PTR-MS sampling approach to ambient measurements in a 2010 field experiment in Sacramento California and those results are the subject of another paper. In that paper we evaluating if the measurements of TD-PTR-MS alkane mixing ratios make sense given the measured abundances of monoaromatic compounds and predicted emission inventories rates for monoaromatic and alkane compounds as provided to us by the California Air Resources Board. In the absence of another method to compare to, we feel this is the simplest initial approach to using our diesel fuel based sensitivities to quantify the IVOC alkane signal. A more sophisticated approach may be required, and could be applied if the community knew more about the speciation of C12-C18 alkanes in ambient air and exhaust. In our view the sampling of the exhaust is our “ambient” test for initial testing of the method. This allowed us to make useful comparisons to expected abundances of exhaust compounds from published work as described in section 3.6. The exhaust analysis literature is much more comprehensive for heavier organic compounds than ambient measurements. For ambient measurements there is really no information on total abundances of C12-C18 alkanes or aromatics to compare to. What is reported from GC methods is the abundance of n-alkanes. Most GC measurements report the C2-C12 compound range so the literature is very limited on IVOC abundance. Even in the published engine exhaust work, alkane analysis is limited, typically only reporting n-alkanes for the C12-C18 range. The problem we face with ambient measurements is what to compare to; how do we know if the measured abundance by TD-PTR-MS is reasonable? For that reason we have separated the technical methods paper presented here from the applied ambient measurements paper – merging them is too complicated of a story.

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Reviewer comment 5. To which extent could the result in Figure 6 be caused by the fact that sampling was carried out through a chamber and Teflon filter (section 2.3, page 6011), which could have caused deposition of higher molecular weight species onto the chamber walls and filter surface ?

Response. Our result or point with Figure 6 is that the diesel and gasoline engine exhaust look very similar with PTR-MS measurements – most of the exhaust compounds are VOCs. The significant decrease in signal after  $m/z$  121 reflects both lower concentrations of these compounds in exhaust (Scahuer et al., 1999, 2002) and decreased ion transmission efficiency. We acknowledge the potential for line losses of heavier compounds in diesel exhaust in getting the material from the engine to the chamber and then to our instrument. Of course the biggest loss would likely be going through the -30 C cold trap which we noted on line 24 of page 6019. We have added text to page 6020, line 10 in the discussion of Fig 6 to acknowledge this line loss issue: “We can’t exclude the possibility that line losses of heavier organic compounds may occur in the ducting of the exhaust to the chambers and in the instrument sampling lines, making the exhaust appear more similar than in actuality.”

Reviewer comment 6. The engines used in the study are comparatively old. How may this have affected the results qualitatively and/or quantitatively? Are modern diesel exhaust particulate filters known to cause a significant reduction in higher MW (I)VOCs? A statement about representativeness would be helpful.

Response. We are not experts in diesel engine emission technologies but do recognize that emission standards imposed for heavy duty diesel engines in both the US and Europe mean that PM, NO<sub>x</sub> and NHMC emissions from heavy duty diesel engine vehicles should significantly decline over the next 20 years as the diesel fleet turns over. We have added the following sentence in the paragraph of section 2.3 to reflect this outlook: “The emissions output from these engines reflect older emission standards with the diesel generator simulating emissions from a medium duty diesel truck engine. Current US and Euro zone emission regulations for diesel truck engines are

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expected to significantly decrease diesel engine emissions of NO<sub>x</sub>, particulate matter, and non methane hydrocarbons over the next 20 years as the existing heavy duty diesel vehicle fleet is slowly replaced by newer vehicles with better emissions controls.”

Reviewer comment 7. I suggest removing some repetition from the manuscript, some times present within the same sentence.

Response. The manuscript was edited for repetition.

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