

## ***Interactive comment on “Quantification of diesel exhaust gas phase organics by a thermal desorption proton transfer reaction mass spectrometer” by M. H. Erickson et al.***

**Anonymous Referee #1**

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This manuscript describes a method by which alkanes (C12-C17) can be preconcentrated and detected using a PTR-MS instrument. Most alkanes don't produce a response in the PTR-MS because their proton affinities are less than that of water, but the authors have demonstrated through the use of standards that large n-alkanes (> C8) produce a weak response within the PTR-MS. These large n-alkanes fragment extensively where they produce a series of ions characterized by the formula,  $C_nH_{2n+1}$ . Based on the similarity of PTR-MS mass spectra of the n-alkane standards with features in the PTR-MS mass spectrum of diesel fuel, the authors propose that PTR-MS can be used to provide a measure of the diesel exhaust alkane concentration in the ambient environment.

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This manuscript provides an interesting and novel approach to the determination of a very challenging and important set of compounds, referred to as the intermediate volatile organic compounds (IVOCs), in ambient air samples. At some level this work deserves to be considered for publication, but it is very difficult to support this manuscript in its current form. It has some nice sections, like those related to the laboratory studies of the n-alkanes and the liquid fuels. However, the manuscript has some major problems in the description and interpretation of the field measurements. It is not clear exactly what is being reported to have been measured with the desorption system. With some significant study of the manuscript it appears that the quantity reported reflects the sum of the C9 – C17 normal and branched alkanes. Many different terms are used throughout the manuscript to describe this quantity such as; IVOC alkanes, alkanes, diesel alkanes but these terms are neither adequately defined nor consistently used. I also have concerns about the quantification procedure. The one important comparison that is presented, dodecane versus diesel fuel, wasn't done using the desorption system. The tenax trap as operated in this project retains the n-alkanes C18 or greater. It would seem to be important to know how the retention of this higher molecular weight material affects the measured signal at  $m/z$  85 in the diesel fuel experiments. The results presented in Figure 5 of Vendeurve et al. 2005 suggest that a significant fraction of the total n-alkane and branched alkane mass fraction will not be recovered from the tenax trap. Finally, the manuscript needs a more objective tone and surprising results should be critically evaluated rather liberally interpreted. The technique is unproven, carefully presented arguments need to be crafted which show support within the literature for the observations and/or conclusions that are presented. Interpretations should carry the proper caveats and be left for the summary section.

Other specific comments:

Page 2 Line 1 – change C12 and above to C12-C17.

Page 2 Line 8 – drift field strength reflects  $V/cm$ , it is the ratio of electric field to number

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density E/N that is the relevant parameter.

Page 2 Line 16 – find a different term for “total diesel exhaust alkane”. Your experiment only measures a fraction of diesel exhaust alkanes and strictly speaking the measured species don’t even represent the majority. According to Schauer et al. ES&T (33) 1999, 1578. The C12-C17 alkanes (normal and branched) only represent ~ 20% of the alkanes (normal and branched) within the exhaust.

Page 2 Line 18 – express the concentration as dodecane equivalents.

Page 2 Lines 18-20 – revise this sentence with new term for “total diesel exhaust alkane”.

Page 3 Line 4 – consider replacing pyrogenic with pyrolysis.

Page 3 Lines 5-6 – Reference this statement if one exists. This diesel exhaust composition published by Schauer et al. ES&T (33) 1999, 1578 does not support this statement.

Page 3 Lines 10-13 – fix this sentence . . .”and are useful to assess their relative abundances.”

Page 3, Line 8 – “n-alkane to toluene” specify exactly which n-alkanes are being included.

Page 3, Line 19 – specify exactly which n-alkanes are being included.

Page 3, Line 21 – “While n-alkanes are among the most abundant individual components of diesel exhaust. . .” is not referenced. Additionally, this statement does not appear to be correct.

Page 20, Lines 23-30 – your method provides a measure of some IVOC species. The current section infers a total measurement. Fix this section to provide a more accurate description.

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Page 6, Lines 20-30 – This section describes results and should be moved to that section.

Page 6, Line 34 – Describe what is being reported as the “n-alkane sensitivity” shown in Figure 4. Is the sensitivity the sum of all of the ions, the response measured at m/z 85?

Page 7 Line 3 – What mass or masses are used in defining the normalized sensitivity for dodecane?

Page 7 Lines 7-8 – How did you arrive at the factor of 1.6? The ratio of the 120 Td/80 Td suggests an increase in sensitivity of 1.5 due to the longer reaction time at 80Td.

Page 7 Lines 15-17 – Why is there discussion of ion signals <C7 alkanes when none is reported?

Page 7 Section 2.4 – In most cases liquid fuel is a poor surrogate for engine exhaust, and there are large compositional differences between diesel fuel and diesel exhaust. While it may be logical to argue that the high molecular weight component of diesel exhaust will look just like fuel, you need to build an argument to justify this assumption.

It would helpful to restructure this section where the mass spectra are described first followed by the interpretations.

Page 7 Line 24 – “It appears possible to determine the total alkane, aromatic and alicyclic hydrocarbon content in air by measuring a few key species.” This statement needs to be substantiated. It seems more appropriate to make this assessment after you have finished the discussion of the mass spectra of the different fuels.

Page 7 Lines 26-29 – The reference list needs to be divided into fuel references and exhaust references. Why isn’t the Schauer reference included?

Page 8 Line 7 – this sentence indicates that the alkylbenzenes represent 75% of the non-ethanol total ions, but Table 2 reports 48% (gasoline) and 43 % (diesel). Correct

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this statement accordingly.

Page 8, Lines 15-23 – Vendeuvre et al. J. Chromatogr. A, 1806 (2005) 21 indicates the presence of naphthenic aromatics of which includes species like tetrahydronaphthalenes and indane. Seems appropriate to reference that the tetrahydronaphthalenes have been previously identified in diesel fuel.

Page 9 Line 3 – Why don't the response sensitivities vary in proportion to ion abundances reported in Table 2?

Page 9 Lines 6-9 – These sentences are contradictory. One indicates that you divide the area response by the sensitivity the other claims that you multiply the area response by the sensitivity.

Page 9 Lines 10-12 – The last sentence needs to be referenced. Check the reported percentage. This 88% number appears to be too high based on Vendeuvre et al. J. Chromatogr. A, 1806 (2005) 21.

Page 9 Line 17 – The assumption of 70% of mass is alkane is not correct in your case because the 70% reported by Vendeuvre includes the alicyclic compounds which are not amongst the compounds detected at m/z 85.

Page 9 Line 21 – "... thought make up a large fraction of the overall fuel alkane composition" Are you referring to the fuel or the exhaust composition? This statement needs a supporting reference.

Why not consider calibrating with diesel fuel. Seems more straightforward and defensible than using dodecane.

Page 9 Line 33 – Indicate that the 2 $\mu$ m refers to the filter pore size.

Page 9 Line 35 – Please explain in more detail why the trap temperature is raised to 100°C for the last three minutes. Using the trapping conditions employed please indicate which compounds are retained and which are not. Is Benzene retained? Please

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provide some details about the range of compounds that are measured with the thermal desorption system.

Page 10, Line 10 – Specify which ions were measured as well as their dwell times.

Page 10 Lines 10-30 – It is not obvious why the measurement of toluene at m/z 93 would not be similarly affected by fragmentation of the larger alkylbenzenes. My first thought about the observed discrepancy with the C3 and C4-benzenes was that these substrates are lost on the -30°C ice trap. The authors' previous paper where they describe the ice trap shows that this is probably not the case. So what is the important chemical property that dictates whether a compound will or will not be retained by the ice trap? Provide some details on which compounds (alkanes and aromatics) are efficiently transmitted through the ice trap and which are not.

The lack of agreement with m/z 121 must be of some concern. This result is not well explained by the fragmentation argument. Other groups have examined the C3-benzenes using the m/z 121 signal with respect to traditional GC based methods and these studies have not observed large discrepancies, certainly nothing on the order of a factor of 3. Since cold traps were not used in those studies one can assume that the full range of aromatic compounds were delivered to those instruments.

Page 10, Lines 26-30 – I don't think there is sufficient evidence presented to draw this conclusion.

Page 10 Line 31 – Rather than asserting that these ions are indicative of the alkanes, consider a more cautious approach, such as: These ions were considered or were evaluated as potential markers for the presence of the large alkanes. I think one needs to first consider which ions are logical choices and then consider whether there are other compounds present in the ambient atmosphere that would interfere.

Pages 10 -11 – General discussion of Figures 7 and 8. If your assertion is that the C<sub>n</sub>H<sub>2n+1</sub> ions reflect the unburned component of diesel exhaust (ie diesel fuel) then

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correlation scatter plots should provide similar ratios as what was observed in the study of the liquid fuels. A plot versus CO would be useful. In addition to providing evidence that the ion(s) are related to roadway combustion, you might be able to provide an emission ratio. It is hard to judge the degree of correlation from simple time series.

Page 11 – Discussion of Figure 9. Figure 9 provides some very compelling evidence that diesel exhaust is the major source of the low volatility compounds analyzed by the thermal desorption system.

Page 11 line 28 – Discussion of “ average alkane to alkylbenzene ratio”. Your result should be discussed with respect to the literature before drawing any conclusions. Schauer et al. *ES&T* 33, (1999) 1578 and Presto et al. *Atmos. Environ.* 45 (2011) 3603 both report alkylbenzenes and quantities related to the semi-volatile or intermediate volatility compounds that could be evaluated and discussed. These studies suggest that semi-volatile or IVOC to alkylbenzene ratio of 4.3 – 3.0 for diesel and jet aircraft exhaust. The reference to jet exhaust might be a stretch but jet fuel (kerosene) and diesel fuel are quite similar in composition. Given that only a fraction of the semi-volatile material would be registered as the normal and branched alkanes suggests that a 10/1 ratio is too high.

Page 11 line 34 – The previous comment also applies to the discussion of the “alkane to toluene” ratio.

Page 12 lines 1-11 – Based on the number of assumptions in your study, the uncertainty in your final measurements will be much greater than 10% value associated with calibration factor for dodecane. Please provide some estimate of the uncertainty for the reported “total alkane” measurement. This would be a good section to summarize your assumptions and any potential sources of error.

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