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# SUPPLEMENTARY INFORMATION

## Mapping and quantifying isomer sets of hydrocarbons ( $\geq C_{12}$ ) in diesel fuel, lubricating oil and diesel exhaust samples using GC $\times$ GC-ToFMS

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## 26 **Section S1: Chromatography Methodology**

27 Exposed adsorption tubes were spiked with 1 ng of deuterated internal standard mix for  
28 quantification, and desorbed onto the cold trap at 350 °C for 15 min (trap held at 20 °C). The trap  
29 was then purged onto the column in a split ratio of 102:1 at 350 °C and held for 4 min. An initial  
30 temperature of 90 °C of the primary oven was held for 2 min and then increased at 2 °C min<sup>-1</sup> to  
31 240 °C, followed by 3 °C min<sup>-1</sup> to 310 °C and held for 5 min. The initial temperature of the  
32 secondary oven of 40 °C was held for 2 min, and then increased to 250 °C by 3 °C min<sup>-1</sup>, followed  
33 by an increase of 1.5 °C min<sup>-1</sup> to 315 °C and held for 5 min. The modulation period was 10 s. The  
34 complete run time was approximately 105 min.

35

36 Diluted lubricating oil samples and particulate phase filters were spiked with 50 µL of 1 ng µL<sup>-1</sup>  
37 deuterated internal standard mix for quantification. Filters were immersed in dichloromethane  
38 (DCM) and ultrasonicated at 20 °C for 20 min. The extract was then concentrated to 50 µL under a  
39 gentle flow of N<sub>2</sub> for analysis on the GC×GC-ToF-MS. 1 µL of the extracted sample was injected in  
40 a split ratio 100:1 at 300 °C. An initial temperature of 120 °C of the primary oven was held for 2  
41 min and then increased at 2 °C min<sup>-1</sup> to 210 °C, followed by 1.5 °C min<sup>-1</sup> to 325 °C and held for 5  
42 min. The initial temperature of the secondary oven of 120 °C was held for 2 min, and then increased  
43 to 200 °C by 3 °C min<sup>-1</sup>, followed by an increase of 2 °C min<sup>-1</sup> to 300 °C and a final increase of  
44 1 °C min<sup>-1</sup> to 330 °C, ensuring all species pass through the column efficiently. The modulation  
45 period was 13 s.

46

47 1 µL of diluted (1:1000) lubricating oil was injected in a split ratio 100:1 at 300 °C. An initial  
48 temperature of the primary and secondary ovens were kept the same (175 °C) held for 5 min. The

49 primary oven temperature was increased by  $1^{\circ}\text{C min}^{-1}$  to  $325^{\circ}\text{C}$ , while the secondary oven  
50 temperature was increased by  $1^{\circ}\text{C min}^{-1}$  to  $330^{\circ}\text{C}$ . A modulation time of 8 s was used, while a total  
51 run time of each sample was 120 min. The transfer line and ion source temperatures were  $325^{\circ}\text{C}$   
52 and  $320^{\circ}\text{C}$ , respectively and were kept consistent for all sample analyses. Helium was used as the  
53 carrier gas at a constant flow rate of  $1\text{ mL min}^{-1}$ .

54

55

## 56 **Section S2: Computer Language for Identification of Chemicals (CLIC qualifiers)**

57 Language functions: See Reference 2 (below) for more details on selection language functions.

58

59 *Ordinal* – Returns the ordinal position of the indicated channel (m/z in a mass spectrum) in the  
60 intensity-ordered multi-channel array of the current object (blob)

61

62 *Retention* – Returns the retention time of the current object (blob) with respect to the  
63 chromatographic column indicated by the dimension parameter. Retention time for dimension 1 is  
64 expressed in minutes and dimension 2 is expressed in seconds.

65

66 *Relative* – Returns the intensity value of the indicated channel (m/z in a mass spectrum) in the  
67 multi-channel intensity array of the current object (blob) as a relative percentage of the largest  
68 intensity value of the array.

69

70 See Reference 2 (below) for more details on selection language functions.

71 Some examples of CLIC qualifiers are shown below:

72 C2-Alkyl Benzenes  
73 =(ordinal(91)=1)&(ordinal(106)=2);  
74

75 C3-Alkyl Benzenes  
76 =(ordinal(91)=1)&(ordinal(120)<=3)&(retention(1)<30))|((ordinal(105)=1)&(ordinal(120)<=3)&(r  
77 etention(1)<30));  
78

79 C4-Alkyl  
80 Benzenes=((ordinal(91)=1)&(ordinal(134)<=3))|((ordinal(105)=1)&(ordinal(134)<=3)&(retention(  
81 1)<80))|((ordinal(119)=1)&(ordinal(134)<=3)));  
82

83 C5-Alkyl  
84 Benzenes=((ordinal(92)=1)&(ordinal(148)<=3))|((ordinal(105)=1)&(ordinal(148)<=4))|((ordinal(11  
85 9)=1)&(ordinal(148)<=4))|((ordinal(133)=1)&(ordinal(148)<=3)));  
86

87 C6-Alkyl  
88 Benzenes=((ordinal(92)=1)&(ordinal(162)<=4))|((ordinal(105)=1)&(ordinal(162)<=5))|((ordinal(11  
89 9)=1)&(ordinal(162)<=5))|((ordinal(133)=1)&(ordinal(162)<=5))|((ordinal(147)<=2)&(ordinal(162  
90 )<=5)&(retention(2)<6))|((ordinal(106)=1)&(ordinal(162)<=4))|((ordinal(91)=1)&(ordinal(162)<=4  
91 )));  
92

93 C7-Alkyl  
94 Benzenes=((ordinal(105)=1)&(ordinal(176)<=4))|((ordinal(133)=1)&(ordinal(176)<=4))|((ordinal(1  
95 61)=1)&(ordinal(176)<=4)&(Retention(2)<5.5))|((ordinal(91)=1)&(ordinal(176)<=3))|((ordinal(147  
96 )=1)&(ordinal(119)<=4)&(ordinal(176)<=4))|((ordinal(106)=1)&(ordinal(176)<=4))|((ordinal(119)  
97 =1)&(ordinal(176)<=5));  
98

99 C1-Alkyl NAP=(ordinal(141)<=3)&(ordinal(115)<=3)&(ordinal(142)<=3);  
100

101 C2-Alkyl  
102 NAP=((ordinal(141)=1)&(ordinal(156)=2)&(ordinal(115)=3)&(relative(141)>90)&(relative(156)>5  
103 0))|((ordinal(156)=1)&(ordinal(141)=2)&(ordinal(155)=3)&(relative(156)>90)&(relative(141)>50))  
104 ;  
105

106 C3-Alkyl NAP  
107 =(ordinal(155)=1)&(ordinal(170)=2)&(Relative(155)>80)&(Relative(170)>25))|((ordinal(170)=1)  
108 &(ordinal(155)=2)&(Relative(170)>80)&(Relative(155)>60))|((ordinal(141)=1)&(ordinal(170)=2)  
109 &(ordinal(115)=3)&(Relative(141)>80)&(Relative(170)>25)&(Relative(115)>15));  
110

111 C4-Alkyl  
112 NAP=((ordinal(155)=1)&(ordinal(184)=2)&(Relative(155)>80)&(Relative(184)>15))|((ordinal(141  
113 )=1)&(ordinal(184)=2)&(Relative(141)>80)&(Relative(184)>15))|((ordinal(169)=1)&(ordinal(184)  
114 =2)&(Relative(169)>80)&(Relative(184)>30))|((ordinal(184)=1)&(ordinal(169)=2)&(Relative(184)  
115 >80)&(Relative(169)>50));  
116

117

118 **Section S3: Quantification of compounds with no authentic standards**

119 The authentic standard mixture contains 74 standard compounds including 9 internal standards (see  
120 Section 2.3 for more details). These standards were chosen in order to cover as much of the overall  
121 chromatogram as possible and are used for obtaining a calibration for quantifying groups of isomers  
122 with the same molecular ion and functionality. For example; the response for C<sub>11</sub> (undecane, m/z  
123 156) was used to quantify all C<sub>11</sub> alkane isomers which were positively identified in the analysed  
124 samples (and have the same molecular mass and retention times in all sample runs). Using retention  
125 times for C<sub>11</sub> alkane isomers as well as mass spectra, only those C<sub>11</sub> isomer peaks were selected that  
126 were observed using the SIC for m/z 156 (or the respective CLIC expressions). Isomer sets were  
127 comprehensively identified in the analysed samples using mass fragmentation at 70eV and  
128 molecular masses at lower ionisation energies (10-15eV); the methodology of identifying individual  
129 isomers has been published elsewhere (Alam et al. 2016). The total ion current within each polygon  
130 (C<sub>11</sub> isomer sets in this case) was then integrated and the isomer set abundance was estimated using  
131 the response ratio of the closest structurally related deuterated standard (dodecane-d<sub>26</sub>) to the  
132 corresponding compound class natural standard with the same carbon number (C<sub>11</sub> in this case).

133

134 To assess the uncertainty of this method, we estimated known concentrations of compounds for  
135 which authentic standards were available. Table S3-1 shows the difference between  
136 concentrations estimated with the generic standard and the authentic standard. The overall  
137 uncertainty is difficult to estimate. This depends upon both the uncertainty associated with  
138 quantifying an individual compound (U), and the number of compounds in a polygon (n). Then

139 
$$U(\text{polygon}) = (U_1^2 + U_2^2 + U_3^2 + \dots + U_n^2)^{1/2}$$

140 where  $U_1, U_2 \dots U_n$  are the uncertainties associated with individual compounds. There were  
 141 three polygons for which calibration standards were available for all compounds. These gave  
 142 collective uncertainties calculated as above of 13.9%, 18.9% and 39.3% (mean = 24%). Although  
 143 statistically rigorous, we feel that this overestimates the uncertainty as the mass closure figures for  
 144 the samples as a whole appear realistic and none deviates appreciably from 75-100%, including  
 145 samples not described in this paper.

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 147

148 **Table S3-1.** Comparison of true calibrated concentrations and estimated concentrations using this  
 149 methodology.

150

<b>Compound</b>	<b>True Calibrated Concentrations in sample (ng/<math>\mu</math>L)</b>	<b>Concentration using TIC and n-alkane calibration (ng/<math>\mu</math>L)</b>	<b>% difference</b>
Pristane	9.9	9.3	-6%
Phytane	10.0	10.4	4%
Cyclohexane, pentyl-	3.1	3.3	6%
Cyclohexane, hexyl-	15.2	18.1	19%
Cyclohexane, heptyl-	14.0	16.5	18%
Cyclohexane, octyl-	11.1	12.5	13%
Cyclohexane, nonyl-	8.9	10.0	12%
Cyclohexane, decyl-	10.0	9.5	-5%
Cyclohexane, undecyl-	3.8	4.0	5%
Cyclohexane, dodecyl-	4.1	3.8	-7%
Cyclohexane, tridecyl-	3.7	3.7	0%
Cyclohexane, tetradecyl-	3.1	2.5	-19%
Cyclohexane, pentadecyl-	3.0	2.8	-7%
<b>Compound</b>	<b>True Calibrated Concentrations in sample (ng/<math>\mu</math>L)</b>	<b>Concentration using TIC and n-alkylcyclohexane calibration (ng/<math>\mu</math>L)</b>	<b>% difference</b>
naphthalene, 1-methyl-	20.0	24.0	20%
naphthalene, 1-ethyl-	15.0	13.0	-13%
naphthalene, 1-propyl-	12.0	10.0	-17%
naphthalene, 1-hexyl-	32.0	35.0	9%

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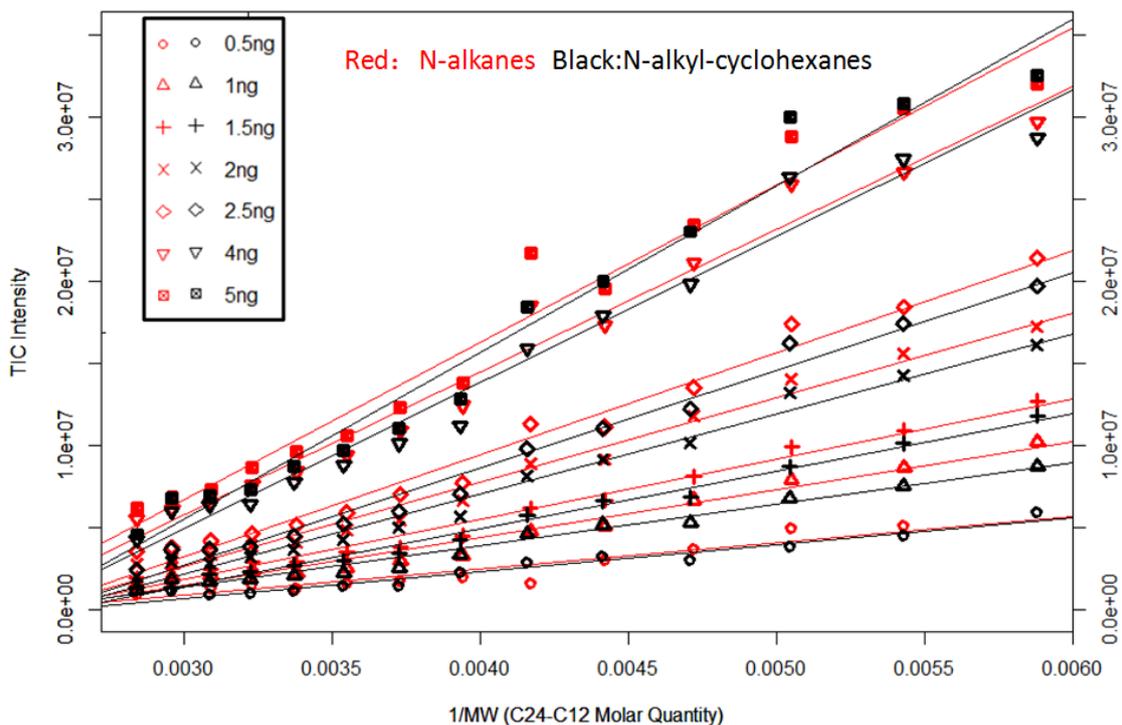
153 **Section S4: Scaling ion current to molar quantity for <C<sub>25</sub> and mass for >C<sub>25</sub>**

154 Previous work shows that the total ion current (TIC) signal can be scaled to molar quantity  
155 (depending on saturation and effective vapour pressure).<sup>1</sup> The TIC intensity of the individual  
156 authentic n-alkane standards (C<sub>12</sub>-C<sub>34</sub>), with seven injected concentrations covering 0.5ng/μL,  
157 1ng/μL, 1.5ng/μL, 2ng/μL, 2.5ng/μL, 4ng/μL and 5ng/μL were investigated. Below C<sub>25</sub>, the TIC  
158 intensity of alkanes increased linearly as the molar quantity (Figure S1, red curves). The TIC molar  
159 quantity of alkyl-cyclohexane (C<sub>12</sub>-C<sub>34</sub>) are also plotted here to compare with the curves of  
160 n-alkanes (Figure A, black curves). The curves of the n-alkyl-cyclohexanes overlap with those of  
161 the n-alkanes in the same injection, illustrating that n-alkyl-cyclohexane and n-alkanes have a very  
162 similar response per mole. This is also found to be the same for other species with increasing alkyl  
163 chain length (e.g. alkyl benzenes and alkyl naphthalenes). However, as the carbon number  
164 increases > C<sub>25</sub>, the TIC response is linearly related to the compound mass, which is plotted in  
165 Figure B as an illustration. The perfect overlap of the curves also demonstrates that the TIC  
166 intensity was almost unaffected by the individual chemical structures under the same injection mass.  
167 (For the high molecular weight alkyl-cyclohexanes, only C<sub>25</sub> and C<sub>33</sub> were investigated due to the  
168 limitation of the available authentic standards).

169

170 The TIC molar quantity responses of deuterated standards are also shown in Figure S4-3 to further  
171 support the above view. Additionally, the TIC versus molar quantity for the alkane and  
172 alkyl-cyclohexane series are shown in Figure S4-2. This has been explored in more detail in Liang  
173 et al. (2017, in prep).

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176 **Figure S4-1.** TIC intensity response to the molar quantity of individual n-alkanes and  
 177 n-alkyl-cyclohexanes (C12-C24).

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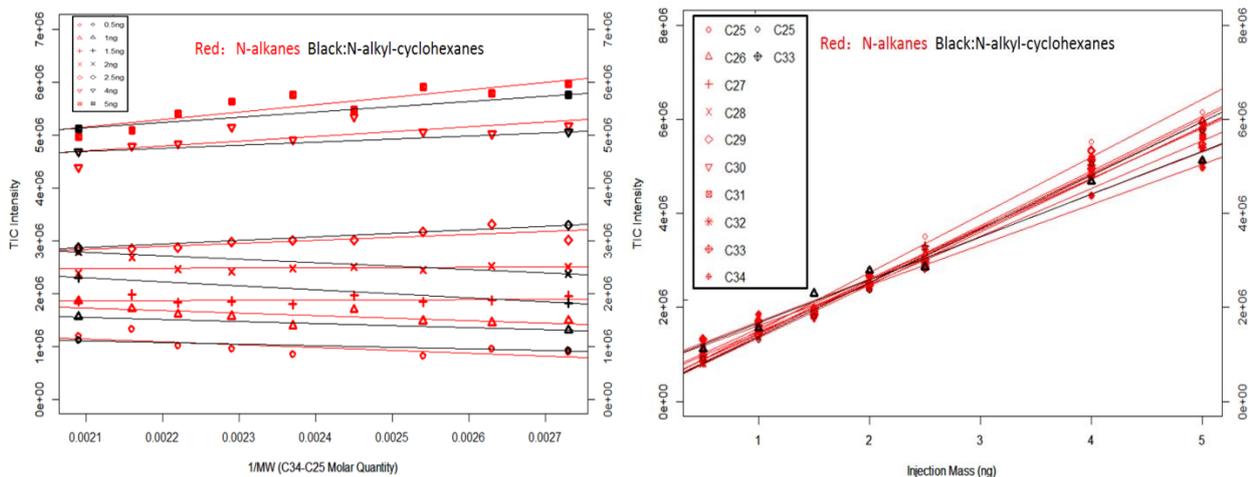
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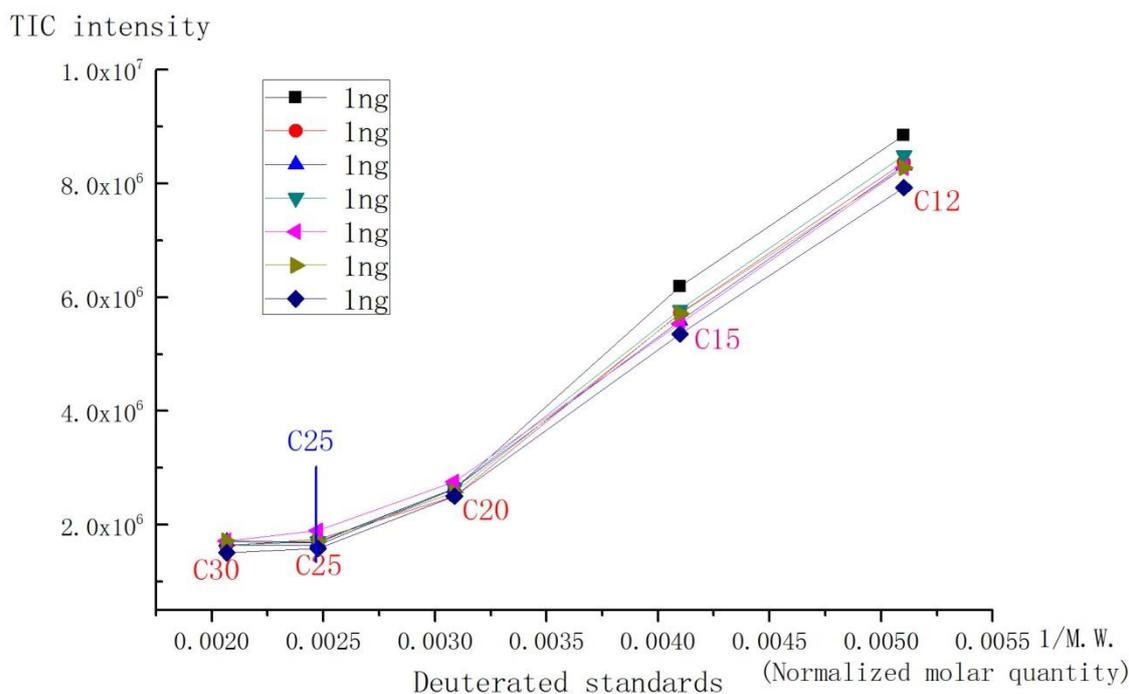
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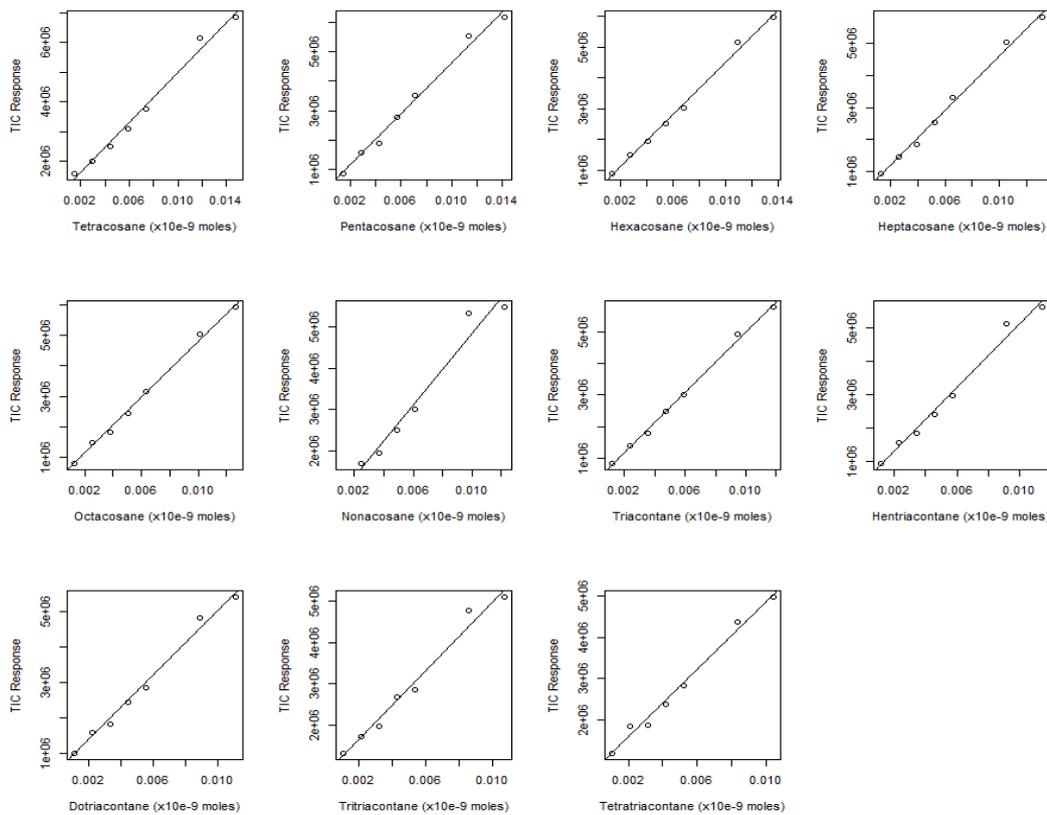
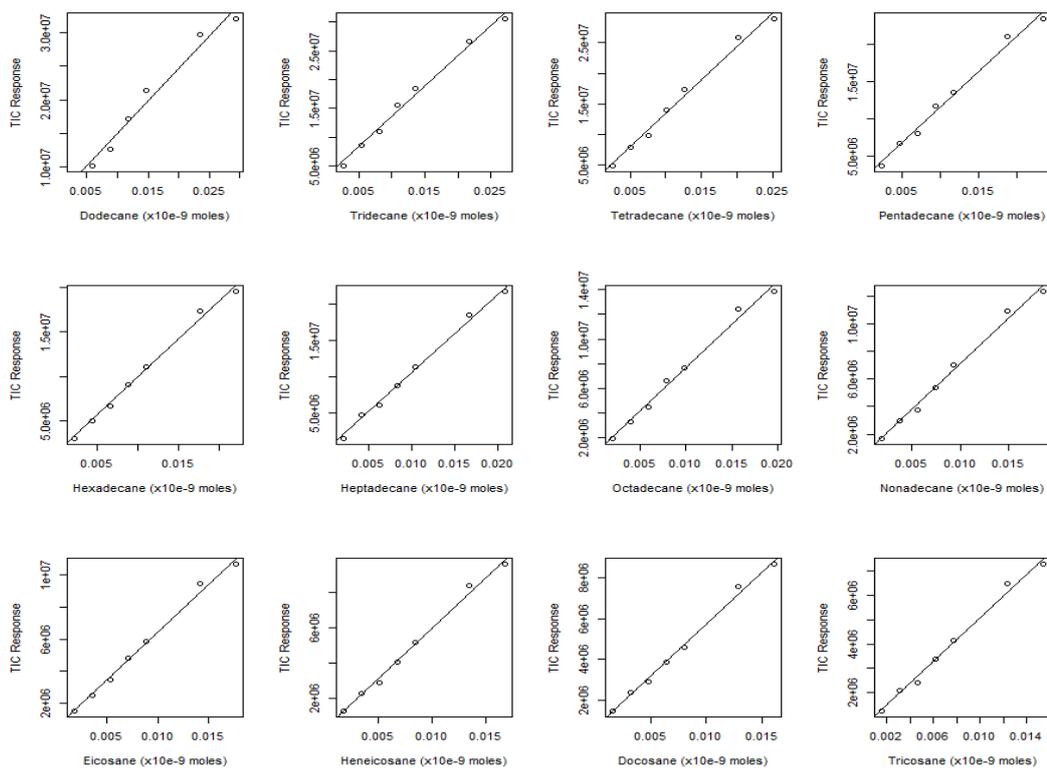
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**Figure S4-2.** TIC intensity response to the molar quantity (left) and mass(right) of individual n-alkanes and n-alkyl-cyclohexanes (C<sub>25</sub>-C<sub>34</sub>).



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**Figure S4-3.** TIC intensity response to the normalized molar quantity of individual deuterated standards (C<sub>12</sub>, C<sub>15</sub>, C<sub>20</sub>, C<sub>25</sub>, C<sub>30</sub>).



**Figure S4-4.** Plots of total ion current vs. molar quantity for the individual alkanes with carbon number from C12-C34.

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## 222 Section S5: Representative Mass Spectra for diesel and gas phase hydrocarbon identification

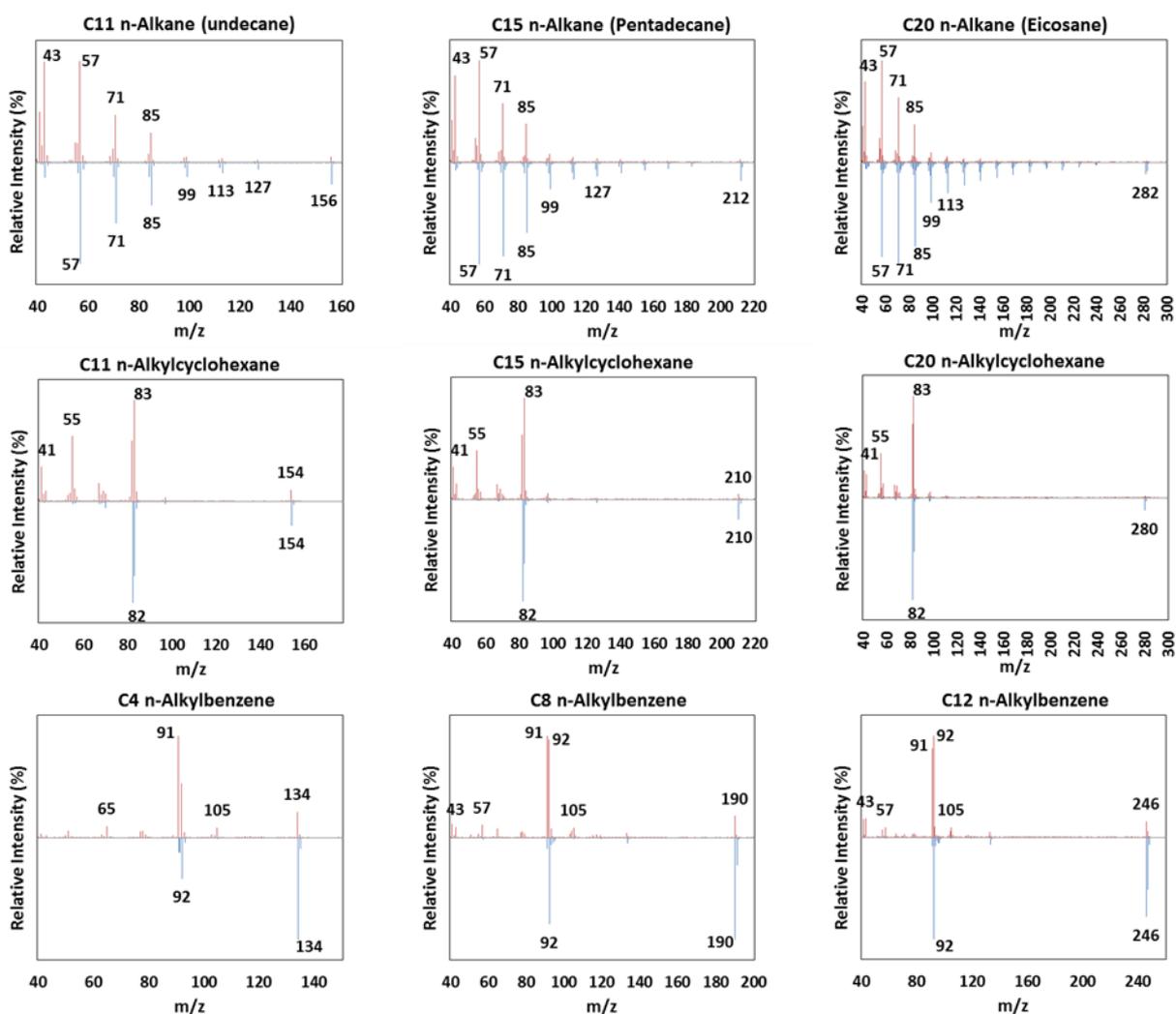
223 Representative mass spectra at 70eV and 12eV ionisation are shown below. These mass spectra

224 were identical at their respective retention times in different samples. Mass spectra at the bottom

225 panel (blue peaks) are from 12 eV ionisation, while the top panels (red peaks) are from 70eV

226 ionisation.

227



228

229 **Figure S5-1.** Representative mass spectra of n-alkanes, n-alkylcyclohexanes and n-alkylbenzenes.

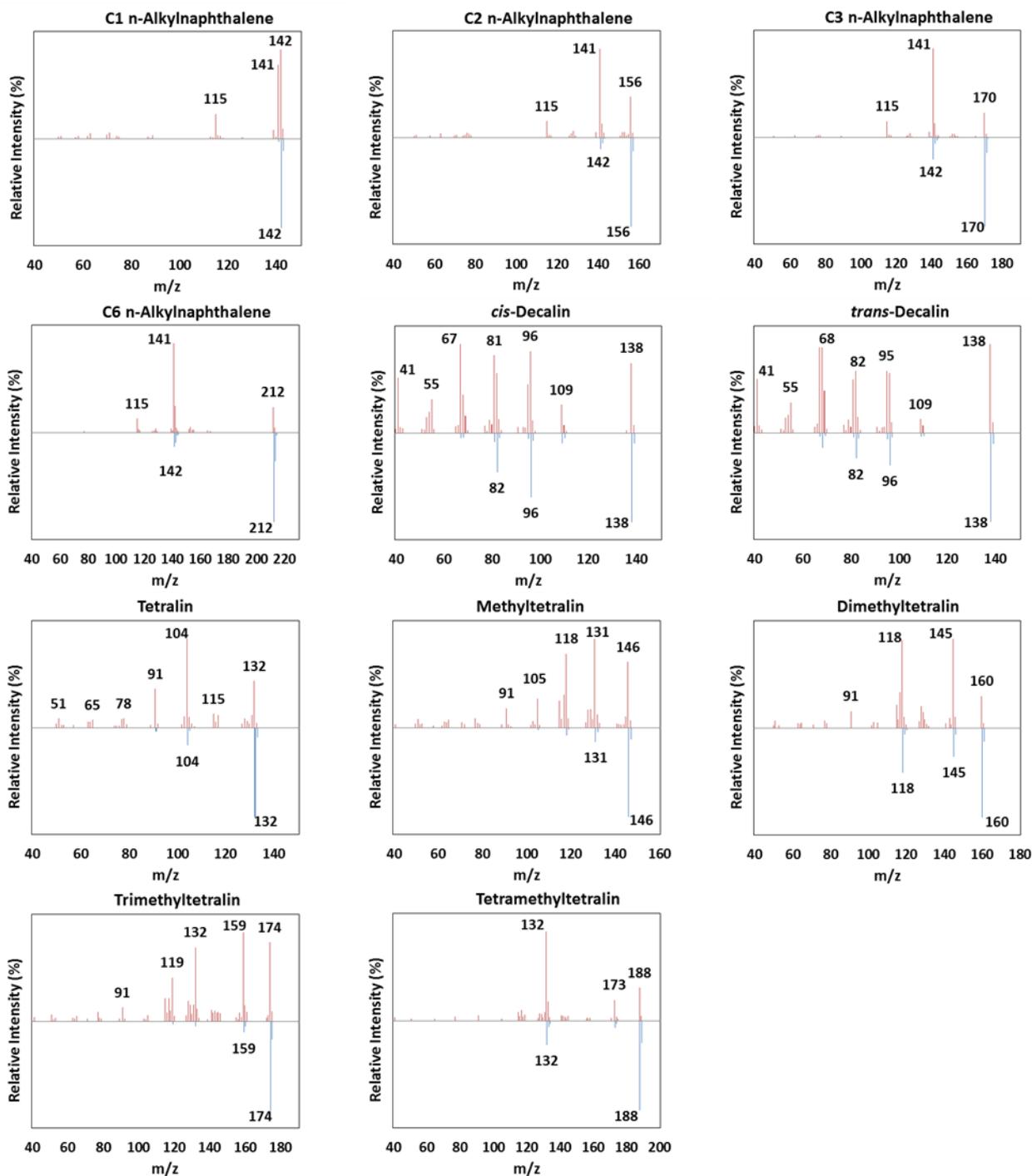
230 Top graphs with red peaks are 70eV ionisation mass spectra, while bottom graphs with blue peaks

231 are 12eV spectra.

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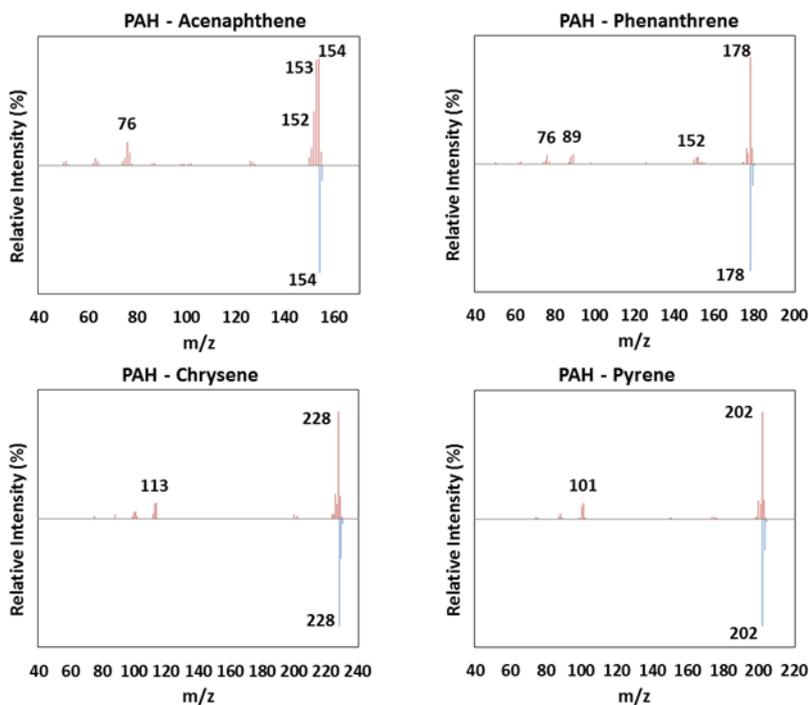
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**Figure S5-2.** Representative mass spectra of n- alkylnaphthalenes, cis and trans-decalin, tetralin, methyl-, dimethyl-, trimethyl-, and tetramethyl tetralins. Top graphs with red peaks are 70eV ionisation mass spectra, while bottom graphs with blue peaks are 12eV spectra.

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251 **Figure S5-3.** Representative mass spectra of four PAH. Top graphs with red peaks are 70eV  
252 ionisation mass spectra, while bottom graphs with blue peaks are 12eV spectra.

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254

255 When two compounds co-elute, it is often possible to quantify each by using the low ionisation  
256 energy mass spectrum. The molecular ion of the higher molecular weight component is used to  
257 provide an ion current which is scaled upward to include the other peaks in the mass spectrum to  
258 give a total ion current due to the component. The second component can be determined by  
259 difference. The molecular ions for a C<sub>11</sub> and a C<sub>12</sub> cycloalkane are at m/z 154 and 168, respectively.  
260 These peaks would be present in the mass spectrum of co-eluting compounds, but can be separated  
261 by isolating the ion current attributed to a peak by assessing the mass spectrum that contains only  
262 the molecular ion of one of the compounds. This avoids the issue of co-elution of some compounds.

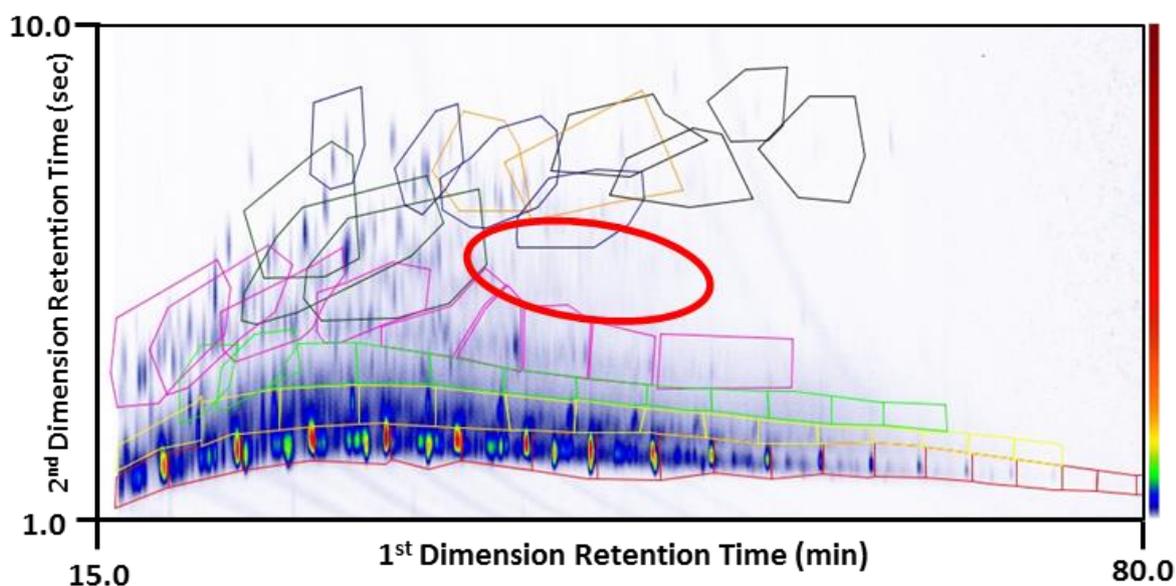
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265 **Section S6: Unresolved peaks**

266 For the diesel fuel 90% of the total mass injected was accounted for. We suspect that a significant  
267 amount of the mass that was unaccounted may be  $<C_{10}$  and/or any unresolved peaks that we were  
268 unable to measure and/or identify using our technique. There were 123 unresolved peaks in the 2D  
269 chromatogram and their positioning is shown in Figure S6-1. The intensities of the peaks, however,  
270 are relatively small and thus suggest a small contribution to the overall mass. Representative mass  
271 spectra of some of these unresolved peaks are shown in Figure S6-2.

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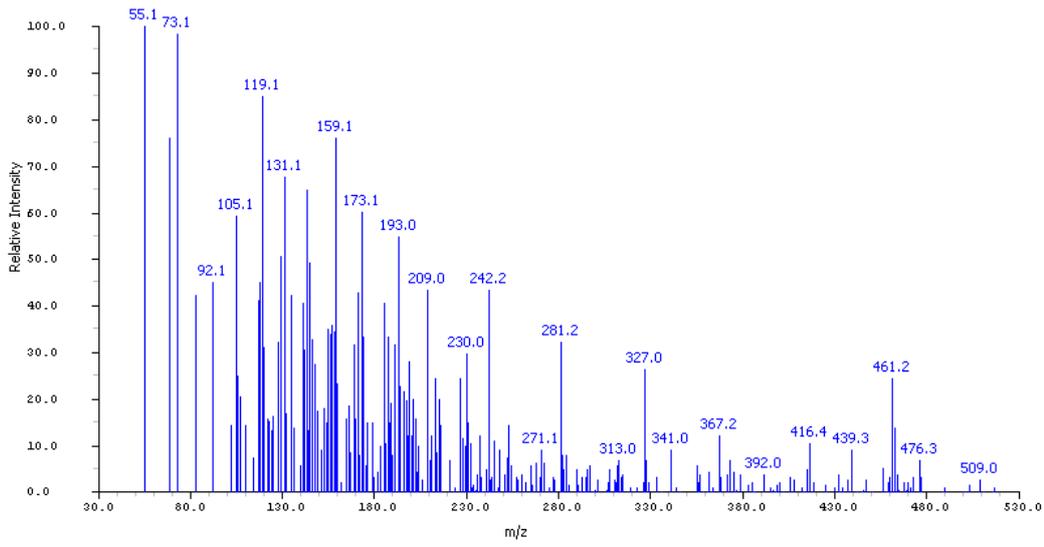
274 **Figure S6-1.** A 2D chromatogram showing the positioning of unresolved peaks (red oval).

275

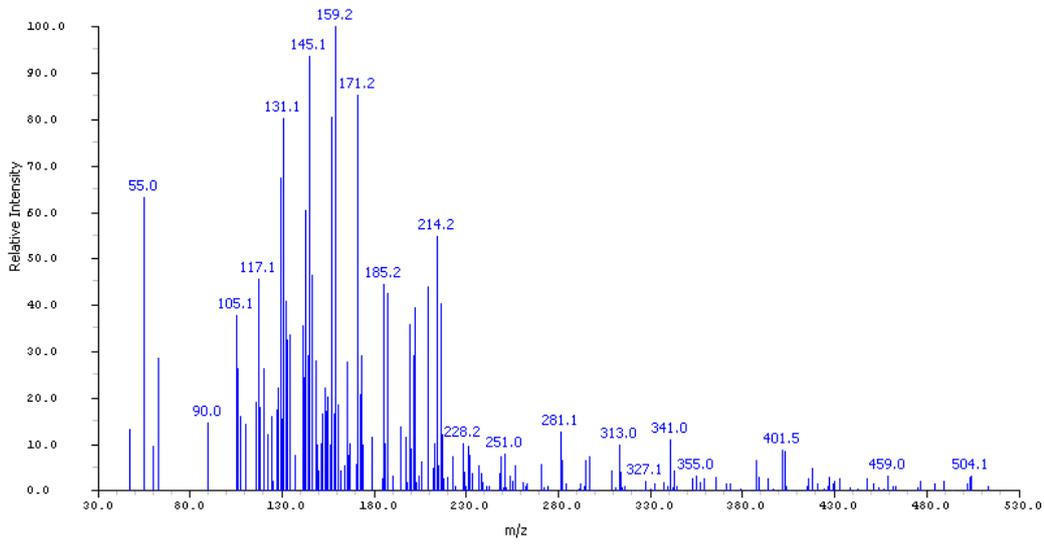
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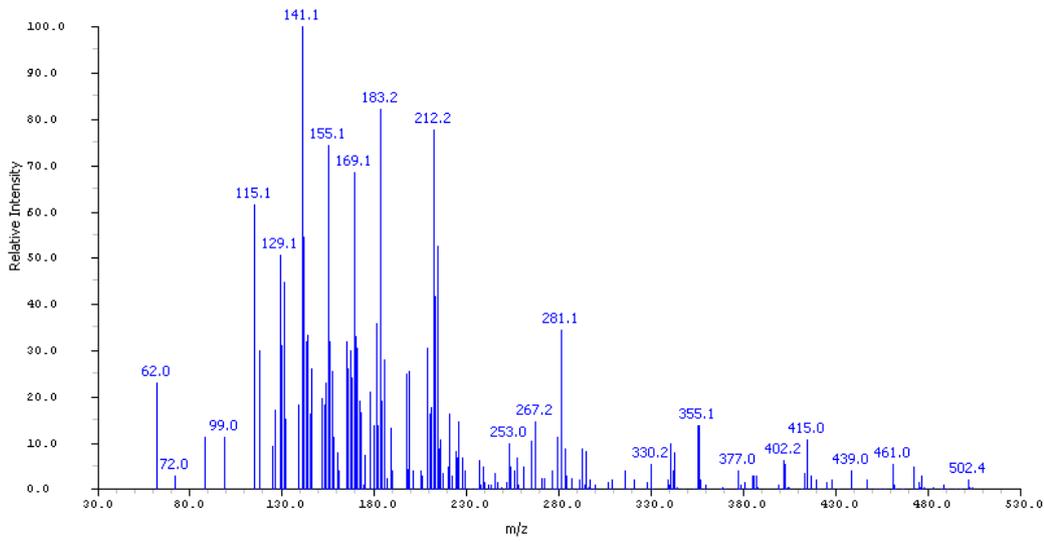
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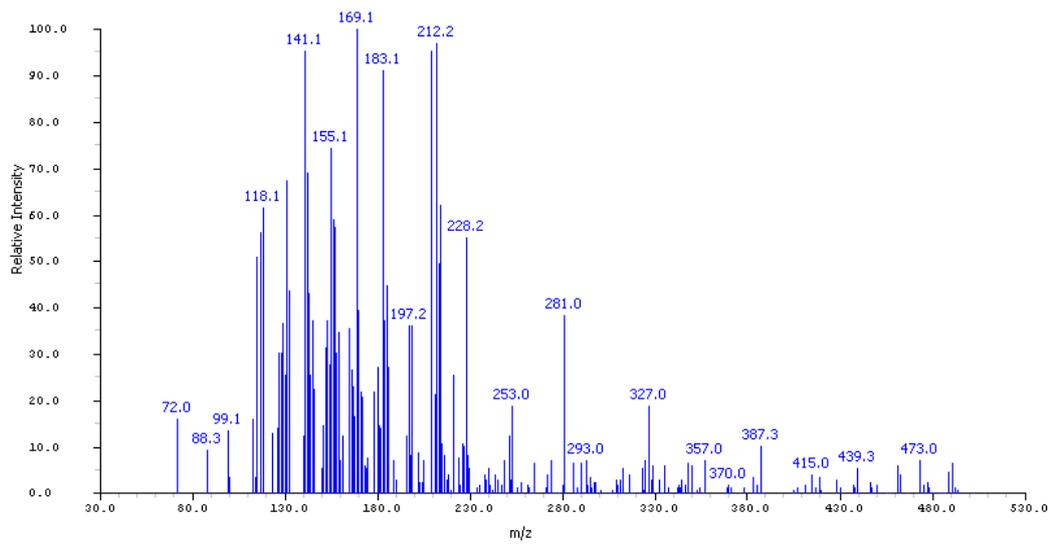
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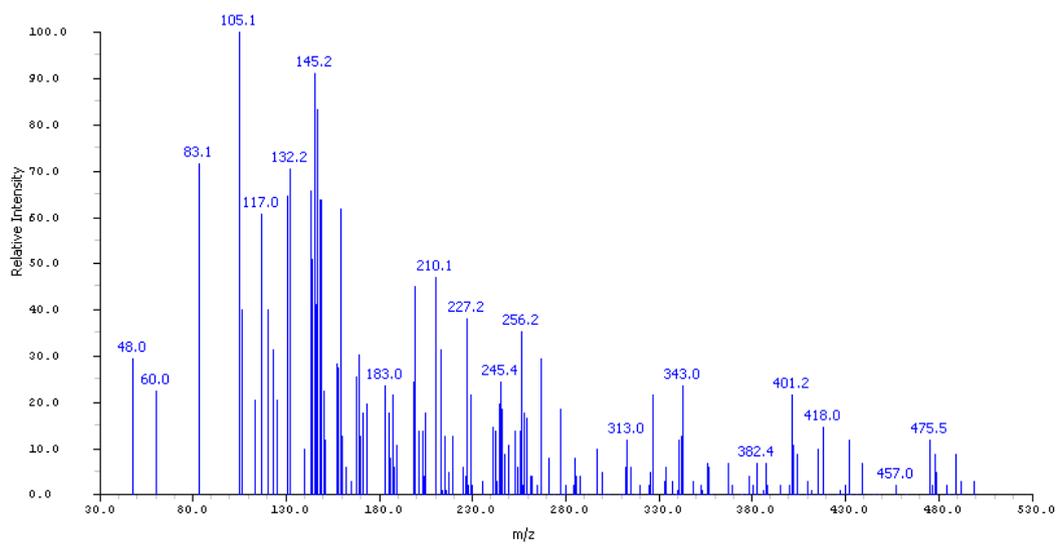


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285 **Figure S6-2.** Representative mass spectra of unresolved peaks by this methodology. These  
 286 unresolved peaks were present in the chromatographic space outlined in Figure S6-1.

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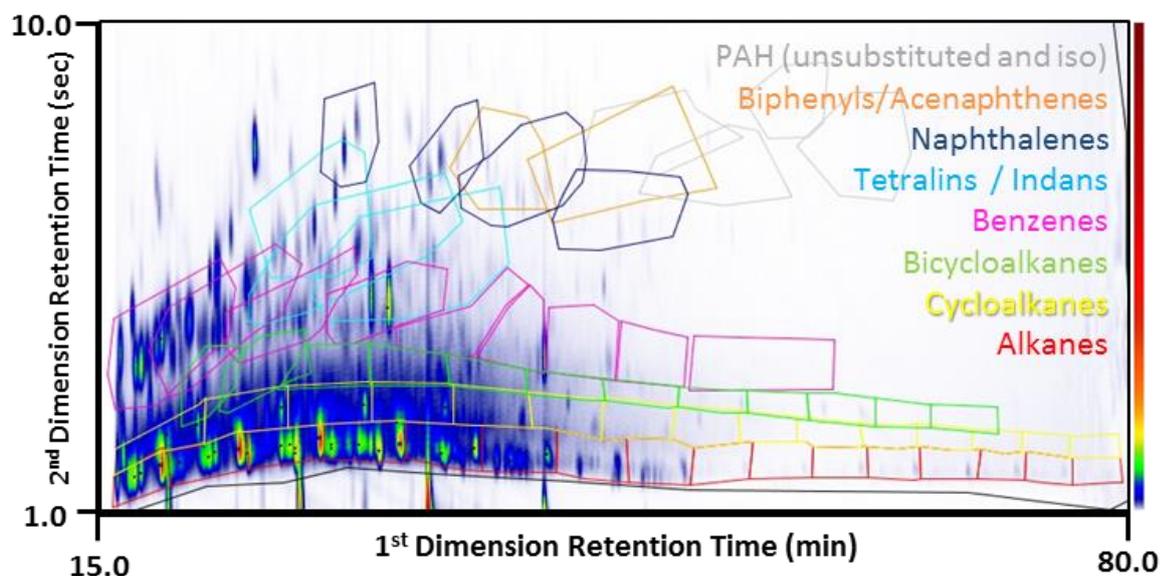
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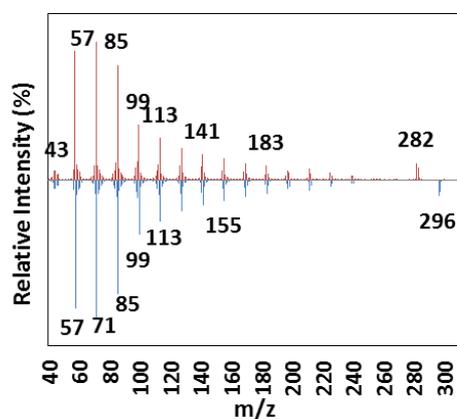


**Figure S7.** A chromatogram of diesel exhaust emissions in the gas phase collected on an adsorption tube and analysed via thermal desorption.

296

297 **Section S8 – Representative mass spectra for compound classes identified in the lubricating oil**

298 n + i-Alkanes were identified by the SIC of m/z 57 and selecting the corresponding molecular ion of  
299 the alkane. Figure S8-1 shows two representative alkanes with the molecular ions 282 (C20) and  
300 296 (C21).

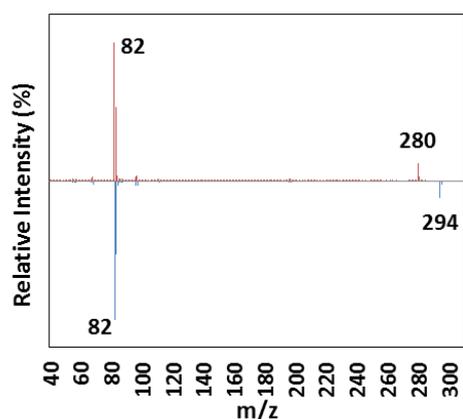


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302

303 **Figure S8-1.** n-Alkane mass spectra at 12eV for m/z 57 and the molecular ion 282 and 296 for C20  
304 n-alkane (top mass spectrum, red) and C21 n-alkane (bottom mass spectrum, blue), respectively.

305

306 Monocyclic alkanes were identified by the SIC of  $m/z$  82 and selecting the corresponding molecular  
307 ion of the specific monocyclic alkane. For example, Figure S8-2 shows two representative  
308 monocyclic alkanes with the molecular ions 280 (C20) and 294 (C21).



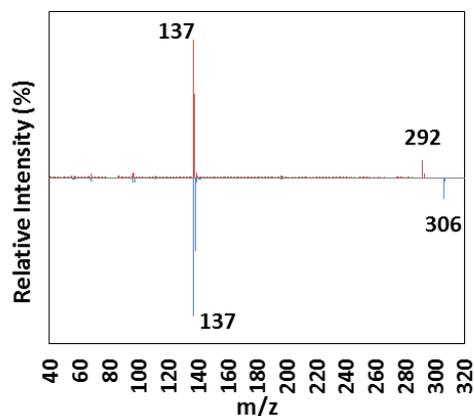
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310

311 **Figure S8-2.** Monocyclic alkane mass spectra at 12eV for  $m/z$  82 and the molecular ions 280 and  
312 294 for C20 monocyclic alkane (top mass spectrum, red) and C21 monocyclic alkane (bottom mass  
313 spectrum, blue), respectively.

314

315 Bicyclic alkanes were identified by the SIC of  $m/z$  137 and selecting the corresponding molecular  
316 ion of the specific bicyclic alkane. For example, Figure S8-3 shows two representative bicyclic  
317 alkanes with the molecular ions 292 (C21) and 306 (C22).



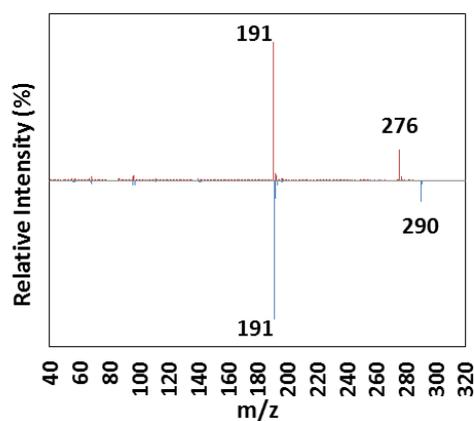
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320 **Figure S8-3.** Bicyclic alkane mass spectra at 12eV for m/z 137 and the molecular ions 292 and 306  
321 for C21 bicyclic alkane (top mass spectrum, red) and C22 bicyclic alkane (bottom mass spectrum,  
322 blue), respectively.

323

324 Tricyclic terpanes were identified by the SIC of m/z 191 and selecting the corresponding molecular  
325 ion of the specific tricyclic terpane carbon number. For example, Figure S8-4 shows two  
326 representative tricyclic terpanes with the molecular ions 276 (C20) and 290 (C22).

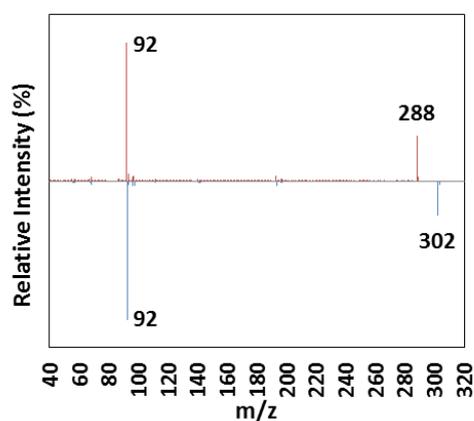


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328 **Figure S8-4.** Tricyclic terpanes mass spectra at 12eV for m/z 191 and the molecular ions 276 and  
329 290 for C20 tricyclic terpane (top mass spectrum, red) and C21 tricyclic terpane (bottom mass  
330 spectrum, blue), respectively.

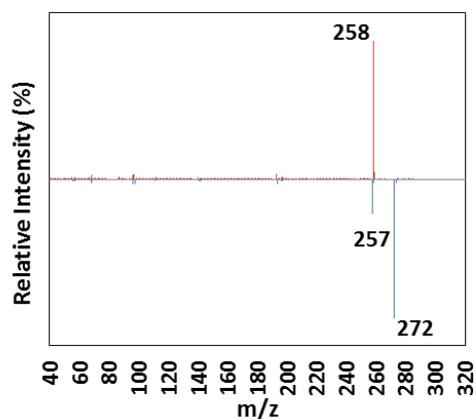
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332 This analysis was repeated for all the compounds shown in Table 1 and representative mass spectra  
333 are shown in Figures S8-5 to S8-7 below.

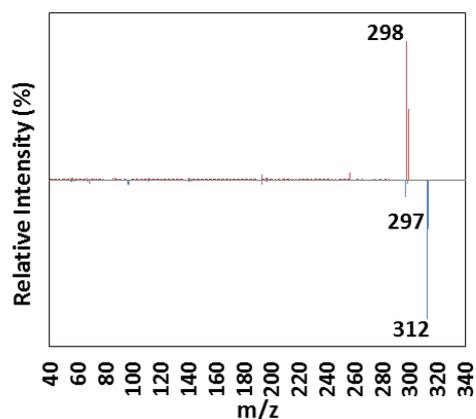


334

335 **Figure S8-5.** Monocyclic aromatics mass spectra at 12eV for m/z 92 and the molecular ions 288  
336 and 302 for C21 (top mass spectrum, red) and C22 (bottom mass spectrum, blue), respectively.  
337



338 **Figure S8-6.** Pentacyclic alkanes mass spectra at 12eV for the molecular ions 258 (top mass  
339 spectrum, red) and methyl pentacyclic alkane with molecular ion 272 and m/z 257 mass fragment  
340 (bottom mass spectrum, blue).  
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343 **Figure S8-7.** Hexacyclic alkanes mass spectra at 12eV for the molecular ions 298 (top mass  
344 spectrum, red) and methyl hexacyclic alkane with molecular ion 312 and m/z 297 mass fragment  
345 (bottom mass spectrum, blue).  
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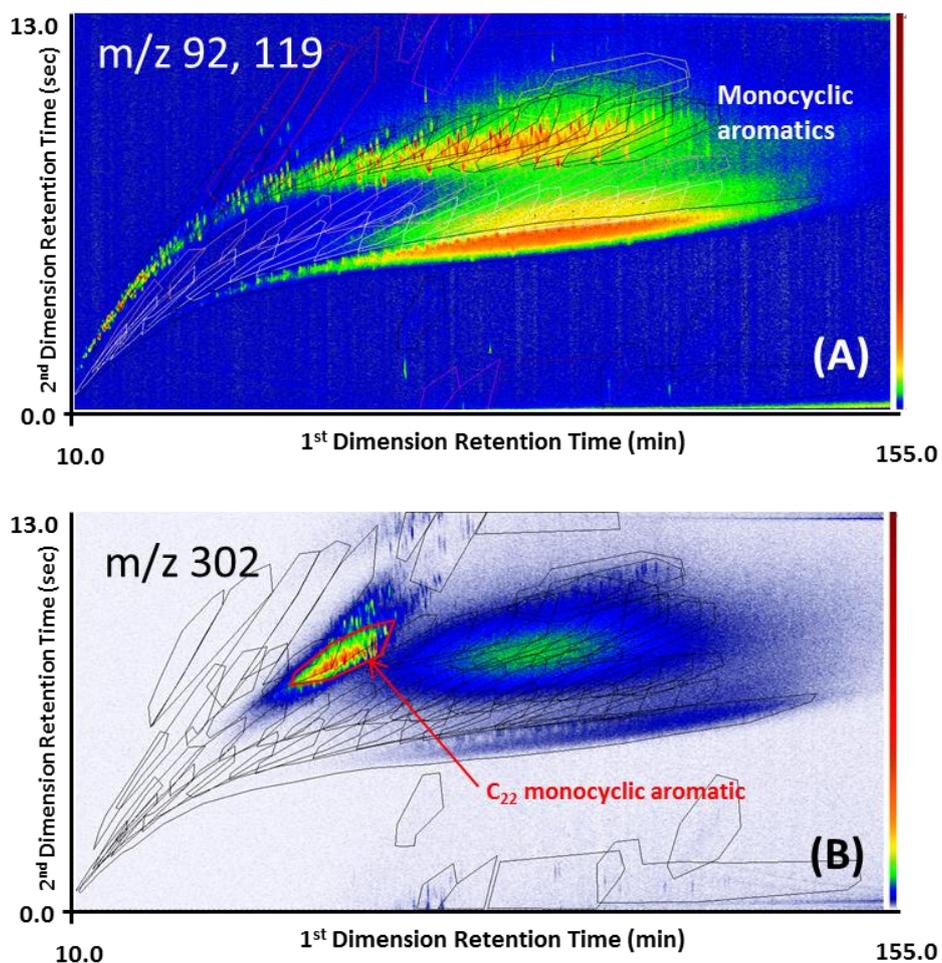
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356 **Figure S9**

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**Figure S9.** A selected ion chromatogram of lubricating oil (5W30) with mass fragments (A) m/z 92 and 119 signifying monocyclic and methyl-monocyclic aromatics and (B) m/z 302 signifying the M<sup>+</sup> for C<sub>22</sub> monocyclic aromatic isomers.

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