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Characterisation of Gas and Particulate Phase Organic Emissions (C₉-C₃₇) from a Diesel Engine and the Effect of Abatement Devices

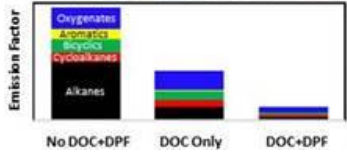
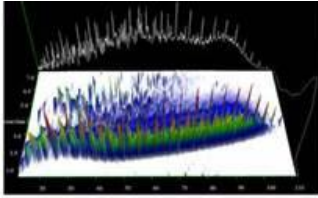
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24 **ABSTRACT**

25 Particulate and vapour phase emissions in the diluted exhaust of a light duty diesel engine designed
26 for Euro 5 application have been sampled. The engine was operated in three modes, and samples
27 were collected from exhaust without aftertreatment but also with aftertreatment by an exhaust
28 oxidation catalyst and particle filter. The samples were analysed by 2-dimensional gas
29 chromatography with Time-of-Flight mass spectral detection. The results show overall removal
30 efficiencies for organic compound mass by the combination of oxidation catalyst and particle filter
31 of 50%, 56% and 74% for the high speed/high load, low speed/low load and high speed/low load
32 conditions respectively. The results are clearly indicative of substantial repartitioning of the
33 particulate and vapour components within the abatement devices and show an apparently reduced
34 efficiency for removal of high molecular weight alkanes under high speed/high load conditions
35 relative to lower molecular weight compounds, although this may be due to alkane formation by
36 thermocracking of other species. A notable feature is the presence of oxygenated compounds in the
37 emissions which are not present in the fuel. These are increased under high speed/high load
38 conditions and the results suggest formation in the aftertreatment devices as well as in the combustion
39 process.

40 INTRODUCTION

41 Diesel vehicles are an important source of atmospheric pollutants, particularly in urban
42 environments¹. Numerous studies have investigated diesel exhaust generated particulate matter (PM)
43 due to the associated adverse health and environmental effects^{2,3,4,5}. Diesel exhaust PM consists
44 mainly of agglomerated solid carbonaceous material and ash, together with organic and sulphur
45 containing compounds⁶. The organic fraction is mainly sourced from unburned/partially-oxidised fuel
46 and lubricating oil while their contribution to emitted particles varies with engine design, operating
47 conditions and fuel formulation, and can be between <10 to >90% by mass^{6,7}.

48

49 Traditional studies of organic species emitted in diesel engine exhaust have focused on volatile
50 organic compounds (VOC) and primary organic aerosol (POA)^{8,9,10,11}. More recently, the focus has
51 been on the measurement of intermediate-volatility organic compounds (IVOC)^{12,13,14,15,16} and semi-
52 volatile organic compounds (SVOC)^{17,18,19} which have effective saturation concentrations (C*) of
53 10^3 - 10^6 and 1 - 10^3 $\mu\text{g m}^{-3}$, respectively²⁰. This typically corresponds to hydrocarbons in the range C₁₂-
54 C₂₂ and C₁₅-C₃₅ for IVOC and SVOC in engine exhaust, respectively. SVOC include any compound
55 with >1% of its mass in both the condensed and vapour phases, while IVOC are found almost
56 exclusively in the vapour phase but have a high potential to generate lower volatility products after
57 reaction²¹. Henceforth, in this study, S/IVOC will be taken to include both SVOC and IVOC. The
58 emissions of S/IVOC can lead to the formation of ozone and secondary organic aerosol
59 (SOA)^{13,22,23,24}. A full understanding of the composition of POA from diesel emissions and its
60 contribution to SOA formation still remain elusive, as many uncertainties exist relating to the semi-
61 volatile component of the particles¹⁸.

62

63 Emissions inventories such as the National Atmospheric Emissions Inventory (NAEI) in the UK (or
64 NEI in the US) report many fuel based emissions factors (EF), including EFs of non-volatile
65 particulate matter and volatile organic compounds <C₁₂ in the vapour phase. EFs of S/IVOC from

66 diesel vehicles, however are scarce and are usually reported only for individual species such as PAH
67 or n-alkanes^{25,26,27}. Recent literature has reported IVOC and SVOC emissions from diesel
68 vehicles^{11,14,15,28}.

69

70 At present relatively little is known about the chemical composition and magnitude of IVOC and
71 SVOC from diesel engine emissions, largely because of the scarcity of analytical techniques that
72 accurately resolve the complexity and allow quantification of speciated organic emissions.
73 Conventional gas chromatography (GC) techniques have been used to identify S/IVOC in diesel
74 exhaust^{14,26,27}. The species identified/quantified in these studies are typically polycyclic aromatic
75 hydrocarbons (PAH), n-alkanes, hopanes and steranes; and 80-90% of the S/IVOC composition
76 remains uncharacterised because it is unresolved by traditional GC, forming a large hump in the
77 chromatogram referred to as 'unresolved complex mixture' (UCM)²⁹. With significant advancements
78 in analytical techniques, studies have reported more comprehensive S/IVOC compositional
79 information for diesel fuel^{19,22,30,31}, lubricating oil^{19,32,33,34,35} and S/IVOC from diesel
80 emissions^{15,16,19,36}. Recently, Alam et al.¹⁹ comprehensively characterised diesel fuel, lubricating oil
81 and diesel exhaust emissions in the gas and particulate phases. The majority of diesel and lubricating
82 oil is comprised of acyclic and monocyclic alkanes (76% and 59%, respectively). This is reflected in
83 the gas and particulate phase emissions which were also largely comprised of these compounds.
84 Diesel exhaust gas phase emissions were remarkably similar to diesel fuel (with the exception of an
85 increased number of monocyclic aromatics in the emissions), whereas particulate emissions had an
86 organic composition similar to lubricating oil. Emissions in the particulate phase, however, were
87 comprised of few compound groups that were not identified in the lubricating oil including, PAH,
88 biphenyls, oxygenates and FAMES (see Table S1 in Alam et al.¹⁹).

89

90 The majority of studies have investigated diesel emissions using a dynamometer rig, averaging
91 emissions over a particular vehicle driving cycle (e.g. NEDC, WLTP, FTP-75, etc.) and thus

92 attempting to simulate real world driving conditions^{10,37}. Although the use of an engine or chassis
93 dynamometer permits tight control of engine and abatement device parameters, these studies offer
94 limited information with regard to combustion processes and specific engine conditions that play a
95 crucial role in the emissions of S/IVOC, particularly when averaging data over an entire cycle. A
96 limited number of studies have therefore investigated S/IVOC emissions under steady-state engine
97 conditions (constant engine torque, speed, etc.) with and without emission control technologies^{15,16,17}.
98 The fraction of vehicles with diesel oxidation catalysts (DOC) and diesel particulate filters (DPF) is
99 relatively smaller in developing countries³⁸, and so it is important to comprehensively characterise
100 the composition of S/IVOC emissions from diesel engines both with and without abatement devices.
101 The global on-road light duty diesel fleet includes older vehicles with no exhaust aftertreatment,
102 vehicles of intermediate age with a DOC, and in countries where the fuel quality is adequate, vehicles
103 with both a DOC and DPF. This study therefore includes measurements of all such configurations.

104

105 In this study we use thermal desorption coupled to comprehensive two dimensional gas
106 chromatography time-of-flight mass spectrometry (TD-GC×GC-ToFMS) to characterise and
107 quantify the composition of S/IVOC, both in the gas and particulate phases, from a light duty diesel
108 engine under different steady-state operating conditions with and without exhaust aftertreatment
109 systems. We investigate compositional changes and emission factors with varying engine speed/load,
110 with and without DOC and DPF. Detailed chemical speciation based on structure and functionality is
111 reported using an established mapping and quantification technique for isomer sets of S/IVOC¹⁹. The
112 results aim to shed light ultimately on the atmospheric fate of emitted S/IVOC and to better
113 understand the sources of emission which include unburned and partially burned fuel and lubricant,
114 as well as products of pyrolysis of fuel/lubricant or products of catalysis.

115

116

117

118 **EXPERIMENTAL**

119 **Sampling**

120 Experiments were conducted with a light-duty 2.2 L, 4-cylinder inline compression ignition diesel
121 engine (designed for Euro 5 applications); equipped with a common rail direct injection system, a
122 variable-nozzle-turbine turbocharger, a diesel oxidation catalyst (DOC) and a diesel particulate filter
123 (DPF). The open engine control unit (Open-ECU) allowed full control over the engine operating
124 parameters. 30 min samples were collected at steady-state engine operating conditions at three
125 different load/speed combinations (see Table S1). Each experiment type was performed before, and
126 in some experiments after, the DOC, and after the DPF to assess the performance of the abatement
127 devices installed. The DPF fitted to the test engine is believed to be catalysed as it oxidised
128 unconverted exhaust CO and HC leaving the upstream DOC during the experiments. It also depends
129 upon the production of nitrogen dioxide in the upstream DOC which is able to oxidise the deposited
130 carbonaceous particles at a much reduced temperature compared to oxidation by molecular oxygen.
131 Hence the DPF is continuously regenerating but exhaust pressure before and after the DPF is
132 monitored to use an active regeneration strategy if the exhaust back pressure becomes excessive. This
133 did not occur during our experiments and therefore the results represent the conditions occurring only
134 during continuous regeneration.

135

136 A pilot+main fuel injection strategy was used for all of the engine operating conditions. Exhaust gas
137 recirculation (EGR) and fuel injection pressure were fixed at approximately 55% and 500 bar,
138 respectively, for 1.4 bar BMEP and 1000 RPM, 33% and 600 bar for 1.4 bar BMEP and 1800 RPM,
139 17% and 1000 bar for 5.9 bar BMEP and 1800 RPM. Sampling was started after ensuring that the
140 engine was fully warmed-up and thermally stable. Standard European, EN590 specifications, ultra-
141 low sulphur diesel (ULSD, S < 10 ppm) and 5W-30 part synthetic engine lubricating oil were used
142 for the experiments. Comprehensive details regarding the engine test rig is described in a companion
143 paper³⁹. For S/IVOC characterisation, engine exhaust was diluted (1:50) using a modified TSI 3302A

144 diluter described in detail elsewhere¹⁸. Briefly, the undiluted hot exhaust sample was delivered via a
145 heated line maintained at 191°C (minimising sampling wall losses) and mixed with cleaned (moisture
146 free) compressed air, at ambient temperature, by utilising a high flow rate moisture trap and two
147 HEPA filters. The diluted sample was divided into two streams. Stream 1 was fixed to a flow rate of
148 9 L/min and was used to collect samples on 47mm quartz fibre filters (Whatman, Maidstone, UK).
149 Stream 2 demonstrated a fixed flow rate of 2 L/min and was utilised to collect gas phase constituents
150 using stainless steel thermal adsorption tubes packed with 1cm quartz wool, 300mg Carbograph 2TD
151 40/60 (Markes International) downstream of a polypropylene backed PTFE 47 mm filter (Whatman,
152 Maidstone, UK) to remove any particulates. The temperatures at the sampling points were 25 ±5°C.
153 A schematic representation of the experimental setup is presented in Figure S1. The sample collected
154 via stream 1 (onto the quartz fibre filters) was classed as particulate, while samples collected via
155 stream 2 (on the adsorption tubes) were classed as gas phase. The deposit collected on the PTFE filter
156 upstream of the adsorption tube was also analysed for particulates and compared to the results
157 obtained from the quartz filters. The results obtained between the two types of filters in these
158 experiments were in good agreement and within ±10% across the entire carbon range (C₉-C₃₇), apart
159 from C₁₃ compounds where quartz filters exhibited up to 14% larger concentrations than PTFE filters.

160

161 **Quantitative and Qualitative Analysis**

162 Sample deposits were extracted from the filter after addition of deuterated standards by using
163 dichloromethane (DCM), ultrasonicated and concentrated to 50 µL under a gentle flow of nitrogen
164 for subsequent analysis using a 2-dimensional gas chromatograph (GC, 7890A, Agilent
165 Technologies, Wilmington, DE, USA) equipped with a Zoex ZX2 cryogenic modulator (Houston,
166 TX, USA). Samples collected on adsorption tubes were desorbed using thermal desorption (Unity 2,
167 Markes International, Llantrisant, UK) and subsequently analysed using the GC×GC which was
168 interfaced with a BenchTOF-Select, time-of-flight mass spectrometer (ToF-MS, Markes
169 International, Llantrisant, UK) with a scan speed of 50 Hz and a mass range of 30 to 600 m/z. Electron

170 impact ionisation energies were tuned between 10 and 70 eV, the former retaining the molecular ion
171 and the latter causing extensive fragmentation and allowing comparison with standard library
172 spectra³⁴. All data produced were processed using GC Image v2.6 (Zoex Corporation, Houston, US).
173 Individual compounds were identified on the basis of retention times (in two dimensions) and mass
174 spectra, and were aggregated into compound groups according to their location in the 2D
175 chromatogram. Quantification was on the basis of ion current after calibration with appropriate
176 standards. Further details are provided in the Supplementary Information. In depth details regarding
177 sample preparation, instrumental parameters, identification and quantification methodologies are
178 presented in detail elsewhere^{18,19}.

179

180 **RESULTS AND DISCUSSION**

181 Over 500 compounds were identified and quantified, and aggregated into eight groups in the vapour
182 phase and six groups in the particulate phase. On average 83% and 72% of the total ion current was
183 accounted for in the gas and particulate phase sample chromatograms, respectively; in agreement
184 with our previous work¹⁹. The EFs calculated in this study for the three steady state conditions with
185 and without after-treatment devices are shown in Table S2, for the gas and particulate phases of all
186 measured groups of compounds in the range C₉–C₃₇. The calculation method for the reported EFs in
187 this study is described in S3 and further details are available in a companion paper³⁹. Briefly, the EFs
188 are emission concentrations normalised to the actual (measured) engine fuel consumption (kg.fuel)
189 at each engine operating condition.

190

191 **Gas Phase Emission Factors – Speeds and Loads**

192 The eight groups with their relative contributions to the total identified organic compounds for all the
193 conducted experiments included; normal (n-) and branched (i-) alkanes (40 – 63%), monocyclic
194 alkanes (17 – 33%), bicyclic alkanes (5 – 11%), monocyclic aromatics (7 – 24%), bicyclic aromatics
195 (2 – 7%), tetralins (1 – 7%), aldehydes and ketones (<1%) and PAH (<1%). Figure 1 illustrates the

196 EF of compounds from the diesel engine in the gas phase before the diesel oxidation catalyst (DOC)
197 and after the diesel particulate filter (DPF) at different speeds and loads. The most abundant
198 compound class was the n- and i-alkanes accounting for 37-60% and 46-68% of the total identified
199 organic compounds between C₁₁-C₁₈ before DOC and after DOC+DPF, respectively. The majority of
200 C₁₉ compounds (90%) were n- and i-alkanes and C₂₀-C₂₆ compounds were exclusively n-alkanes,
201 although present in relatively low concentrations. This is because the majority of compounds in this
202 volatility range would be expected to be in the particulate phase. The largest total EF of C₁₁ – C₂₆ gas
203 phase compounds were in the order of HS/LL > LS/LL > HS/HL (for both before DOC and after
204 DOC+DPF). This general trend was only observed for the n- and i-alkanes and monocyclic alkanes
205 (the two most abundant compound classes). For all other compound classes the largest EF were
206 observed in the order LS/LL > HS/LL > HS/HL. Some bicyclic alkanes (C₁₁ and C₁₅) were
207 significantly larger in LS/LL conditions, factors of 1.8–10.2 larger than other conditions before DOC
208 and after DOC+DPF. Bicyclic alkanes have been shown to be both thermally stable and endothermic
209 fuel components for advanced jet fuels which may give rise to the larger EF for bicyclic alkanes for
210 LS/LL⁴⁰. The presence of bicyclic alkanes in diesel fuel can reduce smoke emissions without
211 sacrifices in brake specific energy consumption⁴¹. The longer ignition-delay of some bicyclic alkanes
212 makes it possible to complete fuel injection early in the combustion stage and thus decreases the
213 quantity of fuel directly injected into the hot flame zone which leads to reduced smoke emissions⁴¹.

214

215 As previously reported the gas phase emissions are remarkably similar to diesel fuel while the
216 particulate phase emissions resemble that of the composition of lubricating oil^{18,19}. In this study the
217 S/IVOC gas phase composition between different speeds/loads does not differ much, in contrast to
218 previous studies of IVOC emissions by Cross et al.¹⁵ who reported IVOC EF and chemical
219 compositional changes over a wider range of engine conditions, using a medium duty diesel engine.
220 At low loads, IVOC emissions were dominated by saturated hydrocarbon species similar to unburned
221 fuel, but at higher loads the IVOC emissions became increasingly characterised by unsaturated

222 hydrocarbons and oxygenated species, possibly formed from incomplete combustion processes¹⁵. In
223 this study a larger relative proportion of classes of compounds other than alkanes contributed to the
224 overall EF for LS/LL in comparison to the HS/HL and HS/LL conditions. The largest gas phase EF
225 were present in low load conditions (LS/LL and HS/LL), but did not seem to vary greatly with speed.
226 This may suggest that the contribution of unburned fuel is larger for low load conditions, and
227 improved combustion efficiency is observed for the fuel for higher loads. In a diesel engine, for a
228 given speed, the equivalence ratio, defined as the ratio of the actual fuel/air ratio to the stoichiometric
229 fuel/air ratio, normally increases with load. CO, total hydrocarbon (THC) and organic gas phase
230 compounds would expect to typically increase with equivalence ratio; however, other factors such as
231 the in-cylinder gas turbulence and temperature, fuel injection timing and pressure calibration and/or
232 number of injection events can also play vital roles and differ depending on a particular engine.

233

234 **Effect of Abatement Devices on Gas Phase Constituents**

235 Figure 1 shows the effect of the presence of a DOC+DPF on the gas phase composition for three
236 steady state conditions. In all instances the presence of the DOC+DPF shows a decrease in the EF of
237 gas phase constituents. For HS/LL conditions, measurements were also made after the DOC to assess
238 the efficiency of the DOC and DPF separately. The DOC is expected predominantly to adsorb and/or
239 oxidise gas phase constituents, whereas the catalysed DPF is expected to mainly filter particulate
240 phase species and oxidise gas phase species at lower rates. The percentage decreases in the EF for the
241 sum of all species for the three conditions are shown in Figure S3 (before DOC to after DOC+DPF
242 for all conditions; and before DOC to after DOC for HS/LL only). For HS/HL, the low molecular
243 weight (LMW) monocyclic and bicyclic alkanes, tetralins and monocyclic aromatics compounds in
244 the vapour phase are more efficiently removed than high molecular weight (HMW) compounds;
245 however, as the acyclic alkanes represent the majority of the mass, this is not reflected in Figure S3.
246 Alam et al.¹⁸ reported a greater efficiency of the DOC for HS/HL engine steady state conditions for
247 LMW acyclic alkanes in the gas phase. This is not the case for HS/LL (after DOC), or for LS/LL and

248 HS/LL (both after DOC+DPF) in this study where a more uniform decrease in EF as a function of
249 carbon number is observed for acyclic alkanes. The average decreases in the total organic EF for
250 HS/HL, LS/LL and HS/LL are 50%, 56% and 74% using the DOC+DPF, respectively. DOCs have
251 been reported as typically reducing emissions of PM by 20-40% or more and gaseous emissions by
252 50-70%⁴². Figure S3 also shows the percentage decrease of organic vapour phase compounds for
253 HS/LL conditions after the DOC and after the DPF. The EFs of gas phase C₁₁-C₁₈ compounds were
254 reduced on average by 40% after the DOC and a further 34% after the DPF. The HMW gas phase
255 species (C₁₈-C₂₆) showed a modest 20% average decrease after the DOC and a further 53% after the
256 DPF. These results appear to reflect oxidation of vapour on the catalytic surfaces of the DPF.

257

258 **Particulate Phase Emission Factors – Speeds and Loads**

259 The six groups with their relative contributions to the total identified organic compounds for all the
260 conducted experiments included; normal (n-) and branched (i-) alkanes (37 – 68%), monocyclic
261 alkanes (5 – 19%), bicyclic alkanes (3 – 10%), monocyclic aromatics (3 – 12%), oxygenated
262 compounds, including alkyl-3(2H)furanones, aldehydes and ketones (13 – 37%) and PAH (<1%).
263 Figure 2 shows the EF of compounds emitted in the particulate phase before the DOC and after the
264 DOC+DPF at the three studied steady state conditions. As for the gas phase, the most abundant
265 compound class was the n- and i-alkanes accounting for 63-65% (before DOC) and 37-68% (after
266 DOC+DPF) of the total identified organic compounds between C₉-C₃₇. The lower average abundance
267 of acyclic alkanes after the DOC+DPF must reflect the efficiency of the DOC+DPF in the removal
268 of these compounds. The majority (>83%) of particulate phase compounds \geq C₂₈ were n- and i-alkanes
269 and all measureable compounds \geq C₃₃ were exclusively n-alkanes. LMW particulate species with C₉-
270 C₁₃ were exclusively oxygenated compounds, present in modest concentrations relative to the
271 aliphatic alkanes for HS/HL (before DOC and after DOC+DPF) and HS/LL (after DOC+DPF), see
272 Figure 2. Some of the most abundant identified oxygenated compounds are presented in
273 Supplementary Information S4. In our previously published work, bimodal peaks were observed for

274 the particulate phase for HS/HL steady state conditions and 2D-chromatography of the particulate
275 phase indicated the presence of two unresolved complex mixtures¹⁸. The LMW UCM was attributed
276 to a diesel fuel component while the HMW UCM indicated emissions from the lubricating oil.
277 Previously published measurements using the same techniques have shown that the composition of
278 the same diesel fuel used for this study did not contain oxygenated compounds¹⁹. Thus, the origin of
279 the oxygenated compounds in this study is not from unburned fuel or lubricating oil, but more likely
280 from combustion products. Wagner and Wyszynski⁴³ showed how hydrocarbons from unburned fuel
281 are oxidised to aldehydes and ketones during in-cylinder mixing and in the exhaust manifold. The
282 formation of these oxygenated compounds, however, is dependent upon numerous engine parameters,
283 including speed and load, mixture composition, compression ratio, air-fuel ratio and heat losses to
284 the wall/in the exhaust. The larger EF of these oxygenated compounds for HS/HL and HS/LL suggest
285 that the engine parameters are such that they favour their formation in comparison to LS/LL, which
286 is a factor of 3-6 smaller (for before DOC). There is much debate whether diesel fuel composition
287 has a significant effect on the oxygenated hydrocarbon emissions. Some studies suggest low density
288 and low aromatic content diesel fuel produces minimal aldehyde emissions⁴⁴, and others show no
289 notable difference⁴⁵. In this study we observe a notable difference in the emissions of oxygenated
290 compounds with varying speed and load, but do not test the effect of different fuel formulation.

291

292 **Effect of Abatement Devices on Particulate Phase Constituents**

293 Figure 2 shows the effect of the presence of a DOC+DPF on the particulate phase composition for
294 three steady state conditions. In all instances the presence of the DOC+DPF shows a decrease in the
295 EF of particulate phase constituents and the largest decrease is observed for HS/LL. The percentage
296 decreases in EF of all species for the three conditions are shown in Figure S3 for before DOC to after
297 DOC+DPF and for before DOC, after DOC and after DOC+DPF for HS/LL. The average decrease
298 observed after DOC+DPF for the total organic EF, as a function of carbon number, for LS/LL, HS/HL
299 and HS/LL are 68%, 44% and 89%, respectively. The higher efficiency of the abatement devices for

300 HS/LL may reflect the composition and concentration of organics, as total EF for HS/LL were a factor
301 of 3.0 and 2.3 larger than HS/HL and LS/LL, respectively. The acyclic alkanes are the main
302 constituent in the organic particulate fraction and so the overall efficiency of the DOC+DPF is
303 dependent upon the removal of these species. For LS/LL the decrease in the total EFs of organic
304 species C₉ – C₁₈ (which are predominantly in the vapour phase, see Figure S4) was 54%, significantly
305 lower than compounds C₁₉-C₃₇ which was 75%. Although this observation is similar to HS/LL (albeit
306 to a lesser extent, see C₉-C₁₆ HS/LL, Figure S3), it is in contrast to HS/HL, where reductions in EFs
307 of species after the DOC+DPF was lower (38%) for HMW compound C₁₉ – C₃₇, see Figure S3. The
308 reduced efficiency of the abatement devices for removing the particulate phase HMW aliphatic
309 alkanes for HS/HL may reflect a shift in the volatility distribution or n-alkyl hydrocarbon
310 thermocracking. At elevated temperatures (~250°C) during engine operation n-alkyl substituted
311 naphthenic and naphthalene-aromatic compounds have been reported to undergo mild
312 thermocracking, preferably at the tertiary carbon atom, leading to the production of HMW alkanes,
313 even when the fuels/lubricants were originally deficient in those compounds^{8,46}. The EF of LMW
314 alkanes (C₉- C₁₈) for HS/HL are reduced by 56% and the overall EFs after the DOC+DPF are within
315 25% of LS/LL and HS/LL, indicating similar emissions for LMW alkanes for all steady state
316 conditions. This suggests that the efficiency of the DOC+DPF for removing HMW alkanes is
317 dependent upon driving conditions and is less effective for HS/HL conditions. However, it may also
318 indicate a shift in volatility distribution of the acyclic alkane emissions. Cross et al.¹⁵ did not observe
319 significant differences in IVOC volatility profiles when investigating different loads, and this was
320 attributed to the possibility of different types of IVOC being emitted at differing loads but with the
321 same volatility distributions. In this study, for HS/HL we observe a possibility of a volatility shift for
322 the acyclic alkanes, but in the presence of a DOC+DPF, which may most likely be the inefficiency of
323 DOC+DPF removal of these compounds. Williams et al.⁴⁷ reported that the survival rate of fuel
324 aliphatic components increases with molecular weight, when investigating the role of unburned fuel,
325 which gives rise to the larger relative EFs after DOC+DPF. However, unburned fuel is expected to

326 be a larger fraction of the emissions for lower exhaust gas temperatures and for conditions of low
327 speed/load¹⁷; thus the HMW aliphatic alkanes (C₁₉ – C₃₇) probably originate from unburned
328 lubricating oil rather than fuel^{18,32,35}. Alam et al.¹⁸ reported <25% particulate phase concentration
329 reductions of n-alkanes for HS/HL conditions in the presence of a DOC only, in agreement with the
330 small reductions in EFs observed in this study for the same conditions. Huang et al.¹⁷ reported large
331 reductions in concentrations (>99%) in PM including PAH, NPAH, hopane and sterane emission
332 rates, but also reported reductions of 83-99% during regeneration of the DPF in comparison to
333 emissions without a DPF. During regeneration, exhaust temperatures increase burning off PM
334 accumulated in the DPF, therefore it can possibly increase the emissions of PM and S/IVOC. We do
335 not believe that the reduced reduction of HMW alkanes is due to active regeneration in this study, as
336 exhaust back pressure was insufficient to trigger active regeneration.

337

338 The overall reduction in EF of monocyclic alkanes and aromatics for LS/LL, HS/LL and HS/LL are
339 between 60-94% using DOC+DPF. Although the overall decrease in EF for oxygenated compounds
340 is 59%, 61% and 82% for LS/LL, HS/HL and HS/LL, respectively, with DOC+DPF, there is an
341 inefficiency of the removal of this compound class by the DOC. An average of 15% reduction in EF
342 was observed for oxygenated compounds C₉-C₂₆, after the DOC, compared to >81% reduction for
343 other compound classes. This increased to 82% removal after the DPF for HS/LL. Thus 40% of the
344 total particulate organic composition, between C₉-C₂₆, after the DOC are oxygenated compounds.
345 This indicates a contribution of oxygenated compounds to primary organic aerosol (POA) from direct
346 vehicular emissions in the absence of a catalysed DPF. Gentner et al.³⁶ suggest that it is unlikely that
347 alkenes, aromatics and oxygenates contribute to POA and although this may be true for vehicles fitted
348 with DOC+DPF, the results of this study show that in the absence of a catalysed DPF, oxygenated
349 compounds comprise a significant amount of the overall emitted composition. May et al.¹¹ reported
350 DPF-equipped diesel vehicles with gravimetric PM mass emissions over two orders of magnitude
351 lower than vehicles with no DPF and attributed the mass reduction to EC, which reduced from

352 approximately 200 mg/kg-fuel to less than 1 mg/kg-fuel. Although particulate OC was not
353 specifically targeted in their study, reductions of approximately 70% were observed in OC between
354 vehicles manufactured pre-1994 and in 1994-2003. Zhao et al.¹⁴ reported total-IVOC emissions from
355 on- and off-road diesel vehicles and showed that the magnitude of total-IVOC emissions was
356 substantially lower for vehicles with exhaust after-treatment devices but there was little variation in
357 the composition. This is in broad agreement with the results from this study apart from after DPF for
358 HS/HL conditions where we see a shift from LMW to HMW compound emissions (see Figure 2).

359

360 **Gas and Particulate Phase Partitioning**

361 Figure S5 illustrates the gas-particle phase distribution of the total characterised organic compounds
362 identified in this study. All compound classes exhibited the same characteristics in all speed/load
363 (with/without abatement devices) conditions investigated. Compounds $\geq C_{21}$ were >90% in the
364 particulate phase and species $\leq C_{16}$ were >90% in the vapour phase. Observations of organic
365 compounds between C_{17} – C_{20} showed varying ratios between the gas and particulate phases, apart
366 from monocyclic alkanes where compounds $\leq C_{18}$ were exclusively in the gas phase and $\geq C_{19}$ were in
367 the particulate phase. Up to 15% of C_{13} and C_{14} monocyclic aromatic compounds were also present
368 in the particulate phase. A slight increase in the vapour phase EF was observed for HS/HL between
369 C_{22} – C_{29} peaking at C_{26} , see Figure S4; in agreement with a previous report¹⁸. Tetralins and bicyclic
370 aromatics were only observed in the vapour phase and were below the detection limit of the
371 instrument in the particulate samples. Oxygenated compounds were only measured in the particulate
372 phase and not observed in the vapour phase, most probably due to their lower volatilities. The species
373 identified in the gas phase for all speeds/loads studied are very similar to the diesel fuel composition
374 suggesting unburned fuel emissions. However, when looking at the HS/HL particulate phase
375 emissions, the larger relative contribution of oxygenated compounds to the total concentration
376 indicates products of oxidation which partition into the particulate phase (see Figure 2, HS/HL).

377

378 The total gas and particulate phase EF for the three steady state conditions are shown in Table 1. The
379 EF ratios of total gas to total particulate phase identified for HS/HL, LS/LL and HS/LL are 1.5, 2 and
380 1 (before DOC); and 1.6, 6 and 7 (after DOC+DPF), respectively. This suggests that there is very
381 active partitioning between the gas and particulate phases within the DOC+DPF abatement devices,
382 and that the DOC+DPF are relatively ineffective in reducing gas phase emissions of hydrocarbons in
383 the molecular weight range studied. The average decreases in the total gas phase emissions are 42-
384 59%, and 44-89% for particulate phase emissions. Zhao et al.¹⁴ reported IVOC composition and EF
385 from on- and off-road diesel vehicles, evaluating the effects of driving cycles and exhaust abatement
386 devices. Little variation in IVOC composition was observed over different cycle tests but the
387 magnitude of the emissions varied significantly for vehicles with or without abatement devices (a
388 factor of 7 to 28 lower with DPF equipped vehicles, depending on driving cycle). In this study the EF
389 are reduced by a factor of 2-4 with DOC+DPF under the steady-state testing conditions.

390
391 This study observed a decrease in EF values from 305 mg kg⁻¹ to 85 mg kg⁻¹ for HS/LL to HS/HL,
392 respectively for experiments performed without emission control devices, which is consistent with
393 differences in combustion efficiency at different loads and with previous studies^{14,15,24}. Our results
394 also indicate that speed affects the EF (see Table 1), as the EF for LS/LL are a factor of 2 smaller
395 than HS/LL for engine runs without abatement devices, and 1.2 times smaller in the presence of
396 DOC+DPF.

397
398 The measured partitioning is likely to represent that in the engine exhaust system, and will not reflect
399 that in the atmosphere where the conditions are cooler and more dilute, and the matrix of other
400 absorbent/adsorbent particles is different. Some changes in partitioning may have occurred during
401 sampling, but these are expected to be small due to the very short residence times in the sampling
402 system (ca. 0.5s).

403

404 **Comparison of Emission Factors with Other Studies**

405 In order to conduct a comparison, the emission factors for n-alkanes have been converted from $\mu\text{g}/\text{kg}$
406 fuel to $\mu\text{g}/\text{km}$ travelled using a vehicle fuel consumption of $0.06 \text{ kg.fuel}/\text{km}$ and assuming that the
407 engine runs for 33% of time at low load and the remainder at high load. The estimated emission
408 factors appear in Table S3, and can be compared with particle phase data for n-alkanes of $\text{C}_{19}\text{-C}_{26}$
409 reported by Charron et al.⁴⁸ for Euro 3 (E3) and Euro 4 (E4) diesel passenger cars with a DOC and
410 Euro 4 with a DOC and DPF. The two vehicles with DOC only tested by Charron et al.⁴⁸ showed
411 markedly different concentrations both peaking a C_{21} with emission factors (EF) of 31.5 (E3) and
412 5.84 (E4) $\mu\text{g}/\text{km}$ for the C_{21} n-alkane. This compares with EFs of 29.2 (before DOC) and 4.0 $\mu\text{g}/\text{km}$
413 (after DOC and DPF) in our data (Table S3), suggesting high comparability. Peak abundances in our
414 data (Table 4) are at C_{22} (before DOC) and C_{23} (after DOC), the small differences from Charron et
415 al.⁴⁶ probably explicable in terms of engine oil composition. The vehicle fitted with a DPF sampled
416 by Charron et al.⁴⁸ peaked at C_{20} with an EF of 2.8 $\mu\text{g}/\text{km}$ with concentrations of all compounds well
417 below those in our data (Table S3) indicating a more efficient emissions control system. Our EF data
418 may also be compared with EF values inferred for mixed vehicle fleets from atmospheric
419 concentration data, as reported by Xu et al.⁴⁹ who measured concentrations on Marylebone Road,
420 London and reviewed data from a Chinese road tunnel⁵⁰ and the Grenoble Ring Road, France⁴⁸. All
421 field-derived EF data show peak abundance at $\text{C}_{21}\text{-C}_{23}$ and broadly similar concentrations across all
422 field studies, comparable with our lab-derived data for a light duty diesel (Table S3). The on-road
423 vehicle fleet contains light duty gasoline and heavy duty diesel vehicles in addition to light duty
424 diesels and it appears the emissions from the heavy duty diesels counteract the beneficial effects of
425 gasoline vehicles for high molecular weight n-alkane emissions. The close comparison with some
426 published studies may be fortuitous due to the limited operating conditions and single engine used in
427 our study. This emphasises the need for studies of further engines or vehicles over full operating
428 cycles.

429

430 **DATA ACCESSIBILITY**

431 Data supporting this publication are openly available from the UBIRA eData repository at
432 <https://doi.org/10.25500/edata.bham.00000328>

433

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436 FASTER project (ERC-2012-AdG, Proposal No. 320821). They also thank Christopher Stark for
437 assistance with the chromatography/mass spectrometry and Zhirong Liang and Yasser Al Qahtani
438 who assisted in the engine operation experiments.

439

440 **SUPPORTING INFORMATION**

441 Supporting Information provides further details of analytical protocols, experimental conditions for
442 the engine, measured emission factors and the efficiency of abatement devices.

443

444 **CONFLICT OF INTERESTS**

445 The authors declare no competing financial interest.

446

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641 **TABLE LEGENDS**

642 **Table 1.** Emission factors of total identified compounds (as OC mass) in the gas and particulate
643 phases for three studied conditions.

644

645 **FIGURE LEGENDS**

646 **Figure 1.** Gas phase emission factors from the 2.2 L light-duty diesel engine under high speed /
647 high load (top), low speed / low load (middle) and high speed / low load (bottom).
648 Different coloured bars represent different compound classes identified in the engine
649 exhaust emissions. Black: n-+i-alkanes, red: monocyclic alkanes, green: bicyclic
650 alkanes, purple: monocyclic aromatics, blue: tetralins, orange: bicyclic aromatics. The
651 lighter shades of each colour represent emission factors with DOC and DOC+DPF
652 emission control devices.

653 **Figure 2.** Particulate phase emission factors from the 2.2 L light-duty diesel engine under high
654 speed / high load (top), low speed / low load (middle) and high speed / low load
655 (bottom). Different coloured bars represent different compound classes identified in
656 the engine exhaust emissions. Black: n-+i-alkanes, red: monocyclic alkanes, green:
657 bicyclic alkanes, orange: monocyclic aromatics, blue: oxygenated compounds. The
658 lighter shades of each colour represent emission factors with DOC and DOC+DPF
659 emission control devices.

660

661

662

663 **Table 1.** Emission factors of total identified compounds (as OC mass) in the gas and particulate
 664 phases for three studied conditions.

TOTAL OC (mg/kg-fuel)	HS / HL			LS / LL			HS / LL		
	Gas	Particulate	Total	Gas	Particulate	Total	Gas	Particulate	Total
None	51.2	33.9	85.1	97.9	49.5	147	154	151	305
DOC							101	33.7	135
DOC+DPF	25.9	16.3	42.2	55.3	9.31	64.6	68.2	9.84	78.1
% Decrease (DOC)							34 %	78%	56%
% Decrease (DOC+DPF)	49%	52%	50%	44%	81%	56%	56 %	93%	74%

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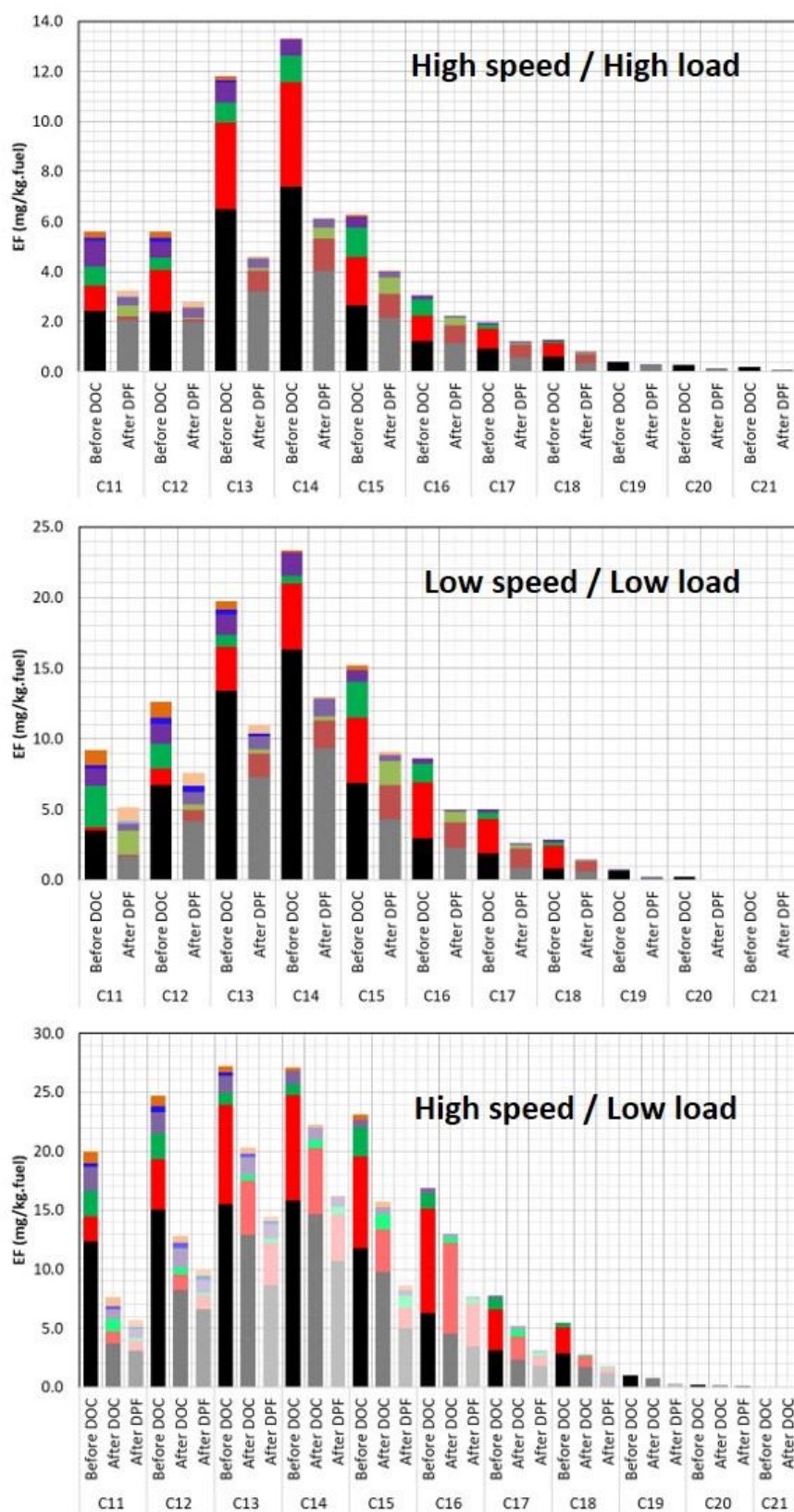


Figure 1. Gas phase emission factors from the 2.2 L light-duty diesel engine under high speed / high load (top), low speed / low load (middle) and high speed / low load (bottom). Different coloured bars represent different compound classes identified in the engine exhaust emissions. Black: n+i-alkanes, red: monocyclic alkanes, green: bicyclic alkanes, purple: monocyclic aromatics, blue: tetralins, orange: bicyclic aromatics. The lighter shades of each colour represent emission factors with DOC and DOC+DPF emission control devices.

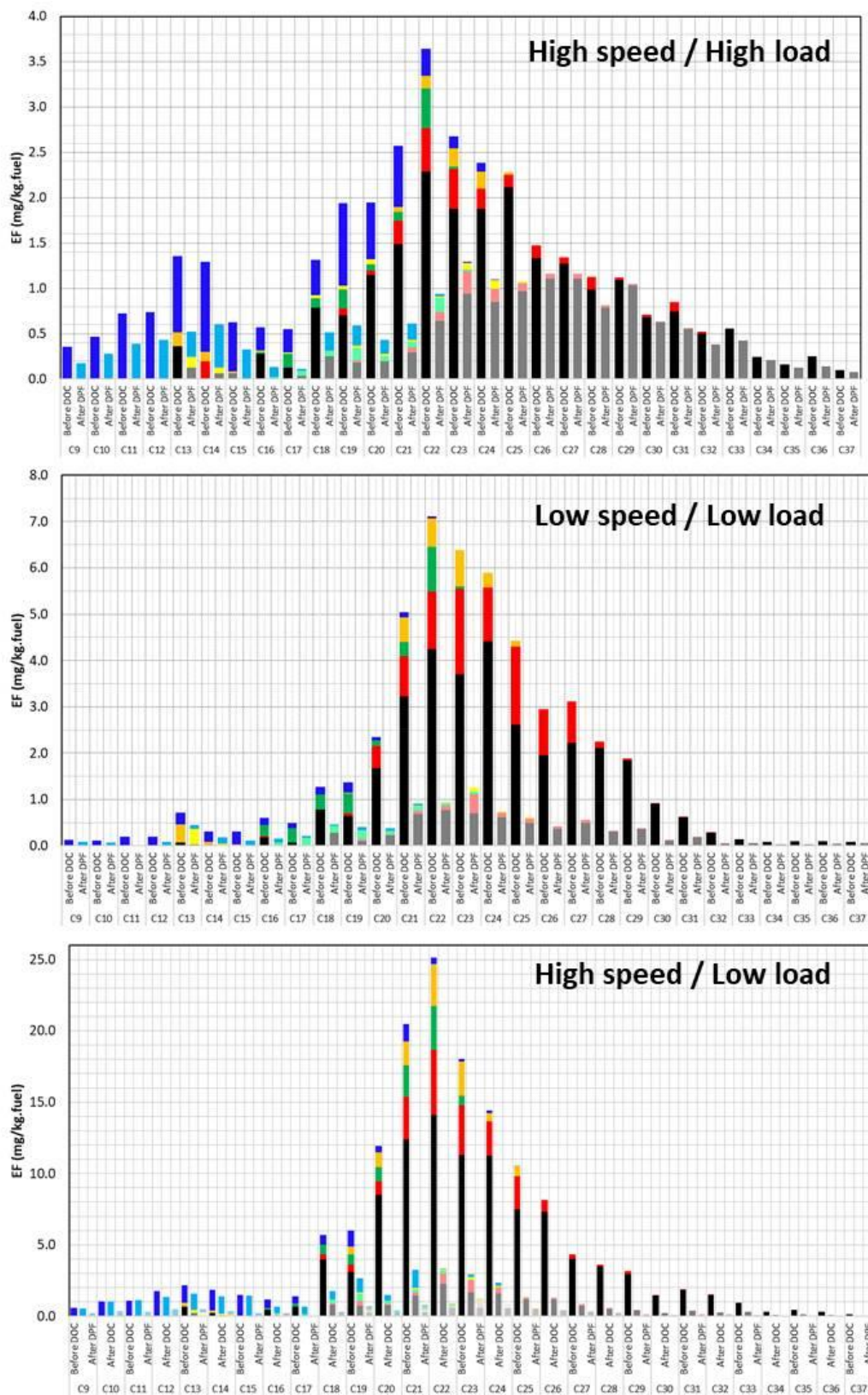


Figure 2. Particulate phase emission factors from the 2.2 L light-duty diesel engine under high speed / high load (top), low speed / low load (middle) and high speed / low load (bottom). Different coloured bars represent different compound classes identified in the engine exhaust emissions. Black: n-+i-alkanes, red: monocyclic alkanes, green: bicyclic alkanes, orange: monocyclic aromatics, blue: oxygenated compounds. The lighter shades of each colour represent emission factors with DOC and DOC+DPF emission control devices.