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DOI:
10.1021/acs.est.9b03053

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Document Version
Peer reviewed version

Citation for published version (Harvard):
Alam, MS, Zeraati-Rezaei, S, Xu, H & Harrison, RM 2019, 'Characterization of gas and particulate phase organic emissions (C_9-C_{37}) from a diesel engine and the effect of abatement devices', *Environmental Science and Technology*, vol. 53, no. 19, pp. 11345-11352. https://doi.org/10.1021/acs.est.9b03053

Link to publication on Research at Birmingham portal

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Checked for eligibility: 06/11/19.

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Characterisation of Gas and Particulate Phase Organic Emissions (C_9-C_{37}) from a Diesel Engine and the Effect of Abatement Devices

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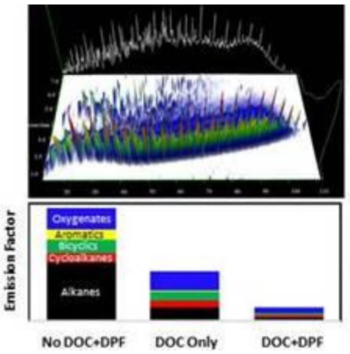
Emission Factor
Oxygenates
Aromatics
Bicyclics
Cycloalkanes
Alkanes
No DOC+DPF
DOC Only
DOC+DPF

ABSTRACT

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

INTRODUCTION

Diesel vehicles are an important source of atmospheric pollutants, particularly in urban environments[1]. Numerous studies have investigated diesel exhaust generated particulate matter (PM) due to the associated adverse health and environmental effects[2,3,4,5]. Diesel exhaust PM consists mainly of agglomerated solid carbonaceous material and ash, together with organic and sulphur containing compounds[6]. The organic fraction is mainly sourced from unburned/partially-oxidised fuel and lubricating oil while their contribution to emitted particles varies with engine design, operating conditions and fuel formulation, and can be between <10 to >90% by mass[6,7].

Traditional studies of organic species emitted in diesel engine exhaust have focused on volatile organic compounds (VOC) and primary organic aerosol (POA)[8,9,10,11]. More recently, the focus has been on the measurement of intermediate-volatility organic compounds (IVOC)[12,13,14,15,16] and semi-volatile organic compounds (SVOC)[17,18,19] which have effective saturation concentrations (C*) of 10^3-10^6 and 1-10^3 μg m^{-3}, respectively[20]. This typically corresponds to hydrocarbons in the range C_{12}-C_{22} and C_{15}-C_{35} for IVOC and SVOC in engine exhaust, respectively. SVOC include any compound with >1% of its mass in both the condensed and vapour phases, while IVOC are found almost exclusively in the vapour phase but have a high potential to generate lower volatility products after reaction[21]. Henceforth, in this study, S/IVOC will be taken to include both SVOC and IVOC. The emissions of S/IVOC can lead to the formation of ozone and secondary organic aerosol (SOA)[13,22,23,24]. A full understanding of the composition of POA from diesel emissions and its contribution to SOA formation still remain elusive, as many uncertainties exist relating to the semi-volatile component of the particles[18].

Emissions inventories such as the National Atmospheric Emissions Inventory (NAEI) in the UK (or NEI in the US) report many fuel based emissions factors (EF), including EFs of non-volatile particulate matter and volatile organic compounds <C_{12} in the vapour phase. EFs of S/IVOC from diesel vehicles, however are scarce and are usually reported only for individual species such as PAH or n-alkanes[25,26,27]. Recent literature has reported IVOC and SVOC emissions from diesel vehicles[11,14,15,28].

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

The majority of studies have investigated diesel emissions using a dynamometer rig, averaging emissions over a particular vehicle driving cycle (e.g. NEDC, WLTP, FTP-75, etc.) and thus attempting to simulate real world driving conditions[10,37]. Although the use of an engine or chassis dynamometer permits tight control of engine and abatement device parameters, these studies offer limited information with regard to combustion processes and specific engine conditions that play a crucial role in the emissions of S/IVOC, particularly when averaging data over an entire cycle. A limited number of studies have therefore investigated S/IVOC emissions under steady-state engine conditions (constant engine torque, speed, etc.) with and without emission control technologies[15,16,17]. The fraction of vehicles with diesel oxidation catalysts (DOC) and diesel particulate filters (DPF) is relatively smaller in developing countries[38], and so it is important to comprehensively characterise the composition of S/IVOC emissions from diesel engines both with and without abatement devices. The global on-road light duty diesel fleet includes older vehicles with no exhaust aftertreatment, vehicles of intermediate age with a DOC, and in countries where the fuel quality is adequate, vehicles with both a DOC and DPF. This study therefore includes measurements of all such configurations.

In this study we use thermal desorption coupled to comprehensive two dimensional gas chromatography time-of-flight mass spectrometry (TD-GC×GC-ToFMS) to characterise and quantify the composition of S/IVOC, both in the gas and particulate phases, from a light duty diesel engine under different steady-state operating conditions with and without exhaust aftertreatment systems. We investigate compositional changes and emission factors with varying engine speed/load, with and without DOC and DPF. Detailed chemical speciation based on structure and functionality is reported using an established mapping and quantification technique for isomer sets of S/IVOC[19]. The results aim to shed light ultimately on the atmospheric fate of emitted S/IVOC and to better understand the sources of emission which include unburned and partially burned fuel and lubricant, as well as products of pyrolysis of fuel/lubricant or products of catalysis.

EXPERIMENTAL

Sampling

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

A pilot+main fuel injection strategy was used for all of the engine operating conditions. Exhaust gas recirculation (EGR) and fuel injection pressure were fixed at approximately 55% and 500 bar, respectively, for 1.4 bar BMEP and 1000 RPM, 33% and 600 bar for 1.4 bar BMEP and 1800 RPM, 17% and 1000 bar for 5.9 bar BMEP and 1800 RPM. Sampling was started after ensuring that the engine was fully warmed-up and thermally stable. Standard European, EN590 specifications, ultra-low sulphur diesel (ULSD, $S < 10$ ppm) and 5W-30 part synthetic engine lubricating oil were used for the experiments. Comprehensive details regarding the engine test rig is described in a companion paper[39]. For S/IVOC characterisation, engine exhaust was diluted (1:50) using a modified TSI 3302A diluter described in detail elsewhere[18]. Briefly, the undiluted hot exhaust sample was delivered via a heated line maintained at 191°C (minimising sampling wall losses) and mixed with cleaned (moisture free) compressed air, at ambient temperature, by utilising a high flow rate moisture trap and two HEPA filters. The diluted sample was divided into two streams. Stream 1 was fixed to a flow rate of 9 L/min and was used to collect samples on 47mm quartz fibre filters (Whatman, Maidstone, UK). Stream 2 demonstrated a fixed flow rate of 2 L/min and was utilised to collect gas phase constituents using stainless steel thermal adsorption tubes packed with 1cm quartz wool, 300mg Carbograph 2TD 40/60 (Markes International) downstream of a polypropylene backed PTFE 47 mm filter (Whatman, Maidstone, UK) to remove any particulates. The temperatures at the sampling points were 25 ±5°C. A schematic representation of the experimental setup is presented in Figure S1. The sample collected via stream 1 (onto the quartz fibre filters) was classed as particulate, while samples collected via stream 2 (on the adsorption tubes) were classed as gas phase. The deposit collected on the PTFE filter upstream of the adsorption tube was also analysed for particulates and compared to the results obtained from the quartz filters. The results obtained between the two types of filters in these experiments were in good agreement and within ±10% across the entire carbon range (C_9-C_{37}), apart from C_{13} compounds where quartz filters exhibited up to 14% larger concentrations than PTFE filters.

Quantitative and Qualitative Analysis

Sample deposits were extracted from the filter after addition of deuterated standards by using dichloromethane (DCM), ultrasonicated and concentrated to 50 µL under a gentle flow of nitrogen for subsequent analysis using a 2-dimensional gas chromatograph (GC, 7890A, Agilent Technologies, Wilmington, DE, USA) equipped with a Zoex ZX2 cryogenic modulator (Houston, TX, USA). Samples collected on adsorption tubes were desorbed using thermal desorption (Unity 2, Markes International, Llantrisant, UK) and subsequently analysed using the GC×GC which was interfaced with a BenchTOF-Select, time-of-flight mass spectrometer (ToF-MS, Markes International, Llantrisant, UK) with a scan speed of 50 Hz and a mass range of 30 to 600 m/z. Electron impact ionisation energies were tuned between 10 and 70 eV, the former retaining the molecular ion and the latter causing extensive fragmentation and allowing comparison with standard library spectra[34]. All data produced were processed using GC Image v2.6 (Zoex Corporation, Houston, US). Individual compounds were identified on the basis of retention times (in two dimensions) and mass spectra, and were aggregated into compound groups according to their location in the 2D chromatogram. Quantification was on the basis of ion current after calibration with appropriate standards. Further details are provided in the Supplementary Information. In depth details regarding sample preparation, instrumental parameters, identification and quantification methodologies are presented in detail elsewhere[18.19].

RESULTS AND DISCUSSION

Over 500 compounds were identified and quantified, and aggregated into eight groups in the vapour phase and six groups in the particulate phase. On average 83% and 72% of the total ion current was accounted for in the gas and particulate phase sample chromatograms, respectively; in agreement with our previous work[19]. The EFs calculated in this study for the three steady state conditions with and without after-treatment devices are shown in Table S2, for the gas and particulate phases of all measured groups of compounds in the range C_9–C_{37}. The calculation method for the reported EFs in this study is described in S3 and further details are available in a companion paper[39]. Briefly, the EFs are emission concentrations normalised to the actual (measured) engine fuel consumption (kg.fuel) at each engine operating condition.

Gas Phase Emission Factors – Speeds and Loads

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

EF of compounds from the diesel engine in the gas phase before the diesel oxidation catalyst (DOC) and after the diesel particulate filter (DPF) at different speeds and loads. The most abundant compound class was the n- and i-alkanes accounting for 37-60% and 46-68% of the total identified organic compounds between C_{11}-C_{18} before DOC and after DOC+DPF, respectively. The majority of C_{19} compounds (90%) were n- and i-alkanes and C_{20}-C_{26} compounds were exclusively n-alkanes, although present in relatively low concentrations. This is because the majority of compounds in this volatility range would be expected to be in the particulate phase. The largest total EF of $C_{11} – C_{26}$ gas phase compounds were in the order of HS/LL > LS/LL > HS/HL (for both before DOC and after DOC+DPF). This general trend was only observed for the n- and i-alkanes and monocyclic alkanes (the two most abundant compound classes). For all other compound classes the largest EF were observed in the order LS/LL > HS/LL > HS/HL. Some bicyclic alkanes (C_{11} and C_{15}) were significantly larger in LS/LL conditions, factors of 1.8–10.2 larger than other conditions before DOC and after DOC+DPF. Bicyclic alkanes have been shown to be both thermally stable and endothermic fuel components for advanced jet fuels which may give rise to the larger EF for bicyclic alkanes for LS/LL[40]. The presence of bicyclic alkanes in diesel fuel can reduce smoke emissions without sacrifices in brake specific energy consumption[41]. The longer ignition-delay of some bicyclic alkanes makes it possible to complete fuel injection early in the combustion stage and thus decreases the quantity of fuel directly injected into the hot flame zone which leads to reduced smoke emissions[41].

As previously reported the gas phase emissions are remarkably similar to diesel fuel while the particulate phase emissions resemble that of the composition of lubricating oil[18.19]. In this study the S/IVOC gas phase composition between different speeds/loads does not differ much, in contrast to previous studies of IVOC emissions by Cross et al.[15] who reported IVOC EF and chemical compositional changes over a wider range of engine conditions, using a medium duty diesel engine. At low loads, IVOC emissions were dominated by saturated hydrocarbon species similar to unburned fuel, but at higher loads the IVOC emissions became increasingly characterised by unsaturated hydrocarbons and oxygenated species, possibly formed from incomplete combustion processes[15]. In this study a larger relative proportion of classes of compounds other than alkanes contributed to the overall EF for LS/LL in comparison to the HS/HL and HS/LL conditions. The largest gas phase EF were present in low load conditions (LS/LL and HS/LL), but did not seem to vary greatly with speed. This may suggest that the contribution of unburned fuel is larger for low load conditions, and improved combustion efficiency is observed for the fuel for higher loads. In a diesel engine, for a given speed, the equivalence ratio, defined as the ratio of the actual fuel/air ratio to the stoichiometric fuel/air ratio, normally increases with load. CO, total hydrocarbon (THC) and organic gas phase compounds would expect to typically increase with equivalence ratio; however, other factors such as the in-cylinder gas turbulence and temperature, fuel injection timing and pressure calibration and/or number of injection events can also play vital roles and differ depending on a particular engine.

Effect of Abatement Devices on Gas Phase Constituents

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

HS/LL (both after DOC+DPF) in this study where a more uniform decrease in EF as a function of carbon number is observed for acyclic alkanes. The average decreases in the total organic EF for HS/HL, LS/LL and HS/LL are 50%, 56% and 74% using the DOC+DPF, respectively. DOCs have been reported as typically reducing emissions of PM by 20-40% or more and gaseous emissions by 50-70%[42]. Figure S3 also shows the percentage decrease of organic vapour phase compounds for HS/LL conditions after the DOC and after the DPF. The EFs of gas phase C_{11}-C_{18} compounds were reduced on average by 40% after the DOC and a further 34% after the DPF. The HMW gas phase species (C_{18}-C_{26}) showed a modest 20% average decrease after the DOC and a further 53% after the DPF. These results appear to reflect oxidation of vapour on the catalytic surfaces of the DPF.

Particulate Phase Emission Factors – Speeds and Loads

The six groups with their relative contributions to the total identified organic compounds for all the conducted experiments included; normal (n-) and branched (i-) alkanes (37 – 68%), monocyclic alkanes (5 – 19%), bicyclic alkanes (3 – 10%), monocyclic aromatics (3 – 12%), oxygenated compounds, including alkyl-3(2H)furanones, aldehydes and ketones (13 – 37%) and PAH (<1%). Figure 2 shows the EF of compounds emitted in the particulate phase before the DOC and after the DOC+DPF at the three studied steady state conditions. As for the gas phase, the most abundant compound class was the n- and i-alkanes accounting for 63-65% (before DOC) and 37-68% (after DOC+DPF) of the total identified organic compounds between C_9-C_{37}. The lower average abundance of acyclic alkanes after the DOC+DPF must reflect the efficiency of the DOC+DPF in the removal of these compounds. The majority (>83%) of particulate phase compounds $\geq C_{28}$ were n- and i-alkanes and all measureable compounds $\geq C_{33}$ were exclusively n-alkanes. LMW particulate species with C_9-C_{13} were exclusively oxygenated compounds, present in modest concentrations relative to the aliphatic alkanes for HS/HL (before DOC and after DOC+DPF) and HS/LL (after DOC+DPF), see Figure 2. Some of the most abundant identified oxygenated compounds are presented in Supplementary Information S4. In our previously published work, bimodal peaks were observed for the particulate phase for HS/HL steady state conditions and 2D-chromatography of the particulate phase indicated the presence of two unresolved complex mixtures[18]. The LMW UCM was attributed to a diesel fuel component while the HMW UCM indicated emissions from the lubricating oil. Previously published measurements using the same techniques have shown that the composition of the same diesel fuel used for this study did not contain oxygenated compounds[19]. Thus, the origin of the oxygenated compounds in this study is not from unburned fuel or lubricating oil, but more likely from combustion products. Wagner and Wyszyński[43] showed how hydrocarbons from unburned fuel are oxidised to aldehydes and ketones during in-cylinder mixing and in the exhaust manifold. The formation of these oxygenated compounds, however, is dependent upon numerous engine parameters, including speed and load, mixture composition, compression ratio, air-fuel ratio and heat losses to the wall/in the exhaust. The larger EF of these oxygenated compounds for HS/HL and HS/LL suggest that the engine parameters are such that they favour their formation in comparison to LS/LL, which is a factor of 3-6 smaller (for before DOC). There is much debate whether diesel fuel composition has a significant effect on the oxygenated hydrocarbon emissions. Some studies suggest low density and low aromatic content diesel fuel produces minimal aldehyde emissions[44], and others show no notable difference[45]. In this study we observe a notable difference in the emissions of oxygenated compounds with varying speed and load, but do not test the effect of different fuel formulation.

Effect of Abatement Devices on Particulate Phase Constituents

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

HS/LL may reflect the composition and concentration of organics, as total EF for HS/LL were a factor of 3.0 and 2.3 larger than HS/HL and LS/LL, respectively. The acyclic alkanes are the main constituent in the organic particulate fraction and so the overall efficiency of the DOC+DPF is dependent upon the removal of these species. For LS/LL the decrease in the total EFs of organic species C_9 – C_{18} (which are predominantly in the vapour phase, see Figure S4) was 54%, significantly lower than compounds C_{19}-C_{37} which was 75%. Although this observation is similar to HS/LL (albeit to a lesser extent, see C_9-C_{16} HS/LL, Figure S3), it is in contrast to HS/HL, where reductions in EFs of species after the DOC+DPF was lower (38%) for HMW compound C_{19} – C_{37}, see Figure S3. The reduced efficiency of the abatement devices for removing the particulate phase HMW aliphatic alkanes for HS/HL may reflect a shift in the volatility distribution or n-alkyl hydrocarbon thermocracking. At elevated temperatures (~250°C) during engine operation n-alkyl substituted naphthenic and naphthalene-aromatic compounds have been reported to undergo mild thermocracking, preferably at the tertiary carbon atom, leading to the production of HMW alkanes, even when the fuels/lubricants were originally deficient in those compounds[8,46]. The EF of LMW alkanes (C_9- C_{18}) for HS/HL are reduced by 56% and the overall EFs after the DOC+DPF are within 25% of LS/LL and HS/LL, indicating similar emissions for LMW alkanes for all steady state conditions. This suggests that the efficiency of the DOC+DPF for removing HMW alkanes is dependent upon driving conditions and is less effective for HS/HL conditions. However, it may also indicate a shift in volatility distribution of the acyclic alkane emissions. Cross et al.[15] did not observe significant differences in IVOC volatility profiles when investigating different loads, and this was attributed to the possibility of different types of IVOC being emitted at differing loads but with the same volatility distributions. In this study, for HS/HL we observe a possibility of a volatility shift for the acyclic alkanes, but in the presence of a DOC+DPF, which may most likely be the inefficiency of DOC+DPF removal of these compounds. Williams et al.[47] reported that the survival rate of fuel aliphatic components increases with molecular weight, when investigating the role of unburned fuel, which gives rise to the larger relative EFs after DOC+DPF. However, unburned fuel is expected to be a larger fraction of the emissions for lower exhaust gas temperatures and for conditions of low speed/load[17]; thus the HMW aliphatic alkanes (C_{19} – C_{37}) probably originate from unburned lubricating oil rather than fuel[18,32,35]. Alam et al.[18] reported <25% particulate phase concentration reductions of n-alkanes for HS/HL conditions in the presence of a DOC only, in agreement with the small reductions in EFs observed in this study for the same conditions. Huang et al.[17] reported large reductions in concentrations (>99%) in PM including PAH, NPAH, hopane and sterane emission rates, but also reported reductions of 83-99% during regeneration of the DPF in comparison to emissions without a DPF. During regeneration, exhaust temperatures increase burning off PM accumulated in the DPF, therefore it can possibly increase the emissions of PM and S/IVOC. We do not believe that the reduced reduction of HMW alkanes is due to active regeneration in this study, as exhaust back pressure was insufficient to trigger active regeneration.

The overall reduction in EF of monocyclic alkanes and aromatics for LS/LL, HS/LL and HS/LL are between 60-94% using DOC+DPF. Although the overall decrease in EF for oxygenated compounds is 59%, 61% and 82% for LS/LL, HS/HL and HS/LL, respectively, with DOC+DPF, there is an inefficiency of the removal of this compound class by the DOC. An average of 15% reduction in EF was observed for oxygenated compounds C_9-C_{26}, after the DOC, compared to >81% reduction for other compound classes. This increased to 82% removal after the DPF for HS/LL. Thus 40% of the total particulate organic composition, between C_9-C_{26}, after the DOC are oxygenated compounds. This indicates a contribution of oxygenated compounds to primary organic aerosol (POA) from direct vehicular emissions in the absence of a catalysed DPF. Gentner et al.[36] suggest that it is unlikely that alkenes, aromatics and oxygenates contribute to POA and although this may be true for vehicles fitted with DOC+DPF, the results of this study show that in the absence of a catalysed DPF, oxygenated compounds comprise a significant amount of the overall emitted composition. May et al.[11] reported DPF-equipped diesel vehicles with gravimetric PM mass emissions over two orders of magnitude lower than vehicles with no DPF and attributed the mass reduction to EC, which reduced from approximately 200 mg/kg-fuel to less than 1 mg/kg-fuel. Although particulate OC was not specifically targeted in their study, reductions of approximately 70% were observed in OC between vehicles manufactured pre-1994 and in 1994-2003. Zhao et al.[14] reported total-IVOC emissions from on- and off-road diesel vehicles and showed that the magnitude of total-IVOC emissions was substantially lower for vehicles with exhaust after-treatment devices but there was little variation in the composition. This is in broad agreement with the results from this study apart from after DPF for HS/HL conditions where we see a shift from LMW to HMW compound emissions (see Figure 2).

Gas and Particulate Phase Partitioning

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

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

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

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

Comparison of Emission Factors with Other Studies

In order to conduct a comparison, the emission factors for n-alkanes have been converted from µg/kg fuel to µg/km travelled using a vehicle fuel consumption of 0.06 kg.fuel/km and assuming that the engine runs for 33% of time at low load and the remainder at high load. The estimated emission factors appear in Table S3, and can be compared with particle phase data for n-alkanes of C_{19}-C_{26} reported by Charron et al.[48] for Euro 3 (E3) and Euro 4 (E4) diesel passenger cars with a DOC and Euro 4 with a DOC and DPF. The two vehicles with DOC only tested by Charron et al.[48] showed markedly different concentrations both peaking a C_{21} with emission factors (EF) of 31.5 (E3) and 5.84 (E4) µg/km for the C_{21} n-alkane. This compares with EFs of 29.2 (before DOC) and 4.0 µg/km (after DOC and DPF) in our data (Table S3), suggesting high comparability. Peak abundances in our data (Table 4) are at C_{22} (before DOC) and C_{23} (after DOC), the small differences from Charron et al.[46] probably explicable in terms of engine oil composition. The vehicle fitted with a DPF sampled by Charron et al.[48] peaked at C_{20} with an EF of 2.8 µg/km with concentrations of all compounds well below those in our data (Table S3) indicating a more efficient emissions control system. Our EF data may also be compared with EF values inferred for mixed vehicle fleets from atmospheric concentration data, as reported by Xu et al.[49] who measured concentrations on Marylebone Road, London and reviewed data from a Chinese road tunnel[50] and the Grenoble Ring Road, France[48]. All field-derived EF data show peak abundance at C_{21}-C_{23} and broadly similar concentrations across all field studies, comparable with our lab-derived data for a light duty diesel (Table S3). The on-road vehicle fleet contains light duty gasoline and heavy duty diesel vehicles in addition to light duty diesels and it appears the emissions from the heavy duty diesels counteract the beneficial effects of gasoline vehicles for high molecular weight n-alkane emissions. The close comparison with some published studies may be fortuitous due to the limited operating conditions and single engine used in our study. This emphasises the need for studies of further engines or vehicles over full operating cycles.

DATA ACCESSIBILITY

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

ACKNOWLEDGEMENTS

The authors express gratitude to the European Research Council for funding this work as part of the FASTER project (ERC-2012-AdG, Proposal No. 320821). They also thank Christopher Stark for assistance with the chromatography/mass spectrometry and Zhirong Liang and Yasser Al Qahtani who assisted in the engine operation experiments.

SUPPORTING INFORMATION

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

CONFLICT OF INTERESTS

The authors declare no competing financial interest.

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TABLE LEGENDS

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

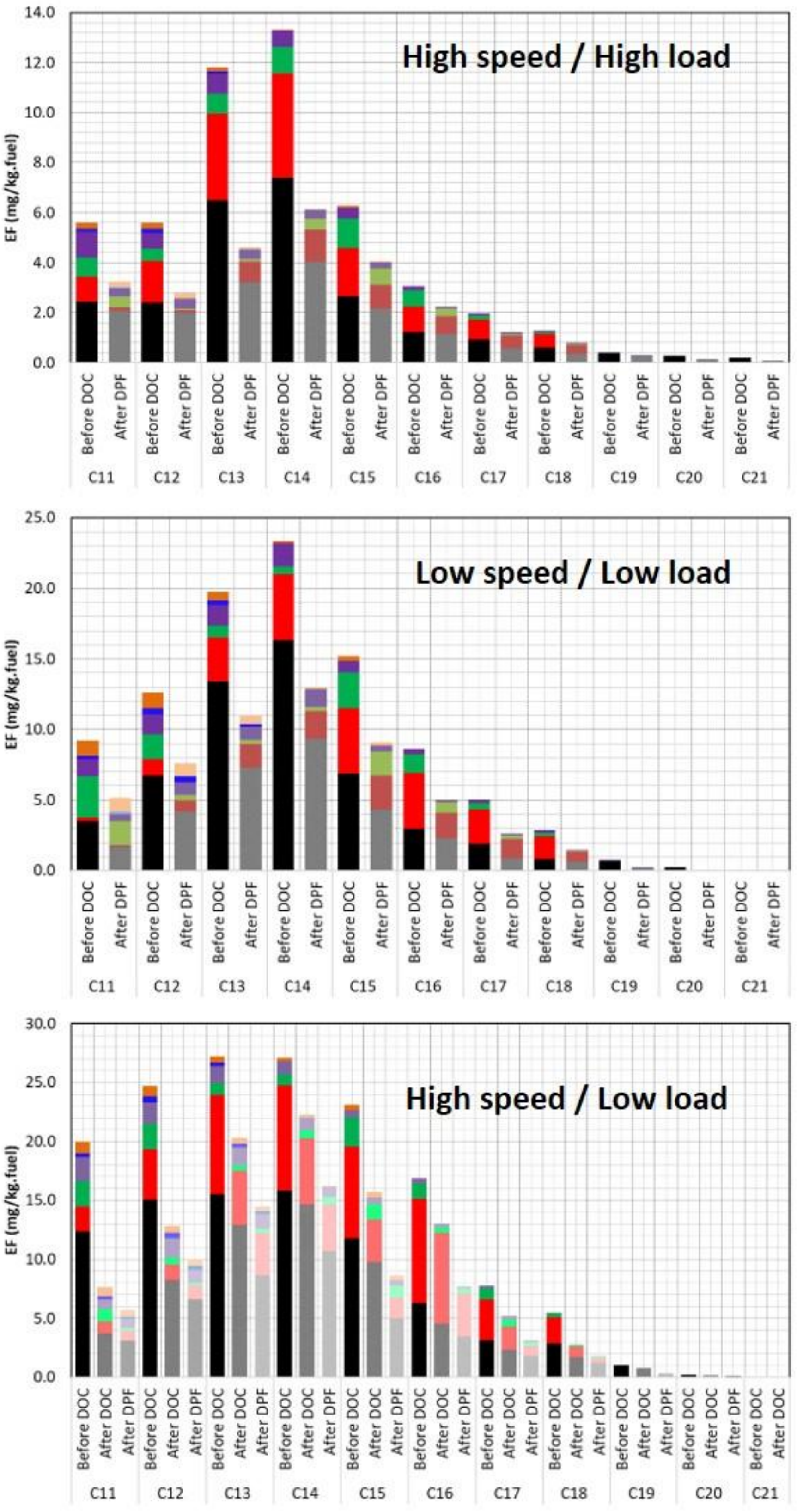
FIGURE LEGENDS

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.

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

	HS / HL			**LS /LL**			**HS / LL**		
TOTAL OC (mg/kg-fuel)	**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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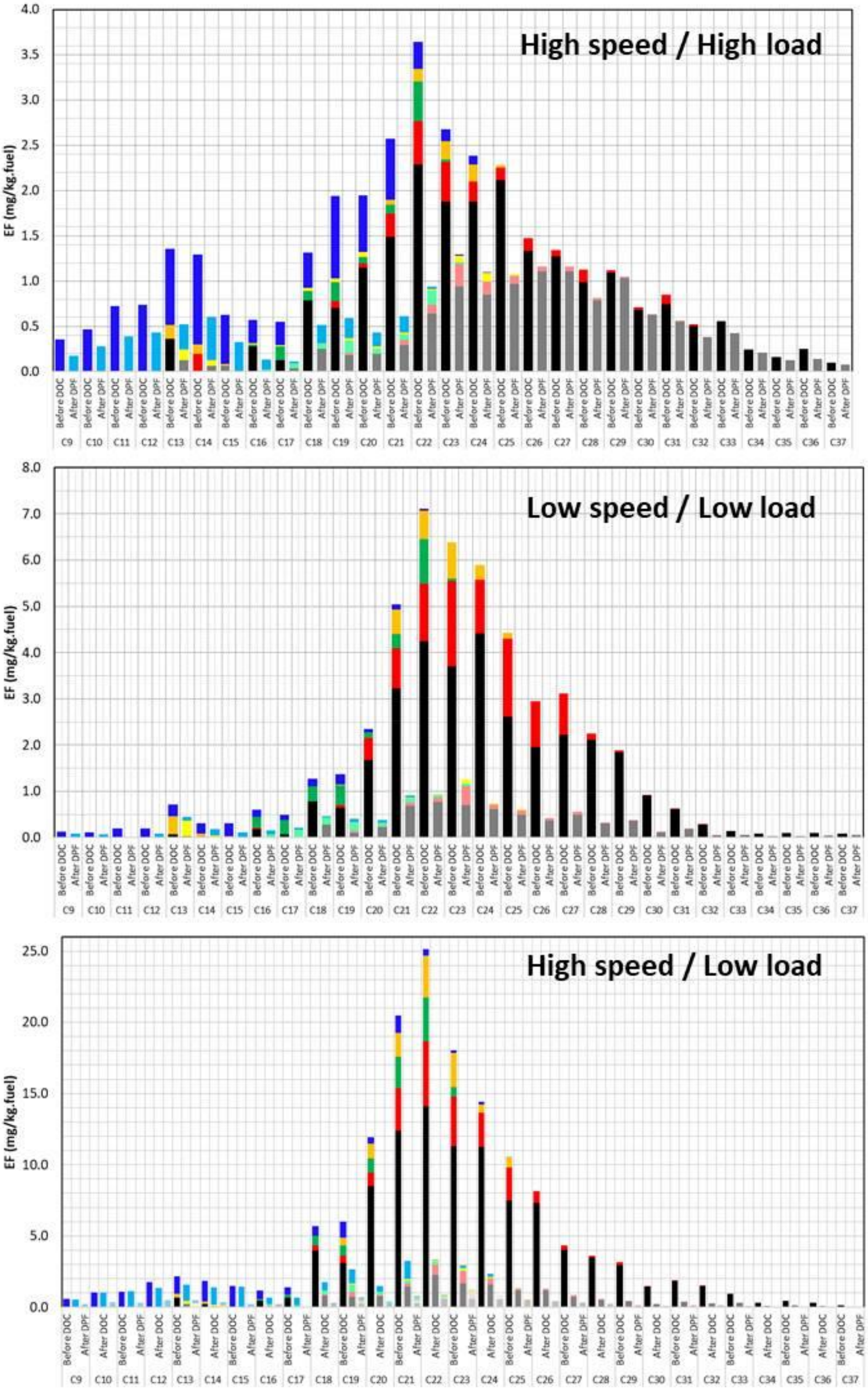

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