

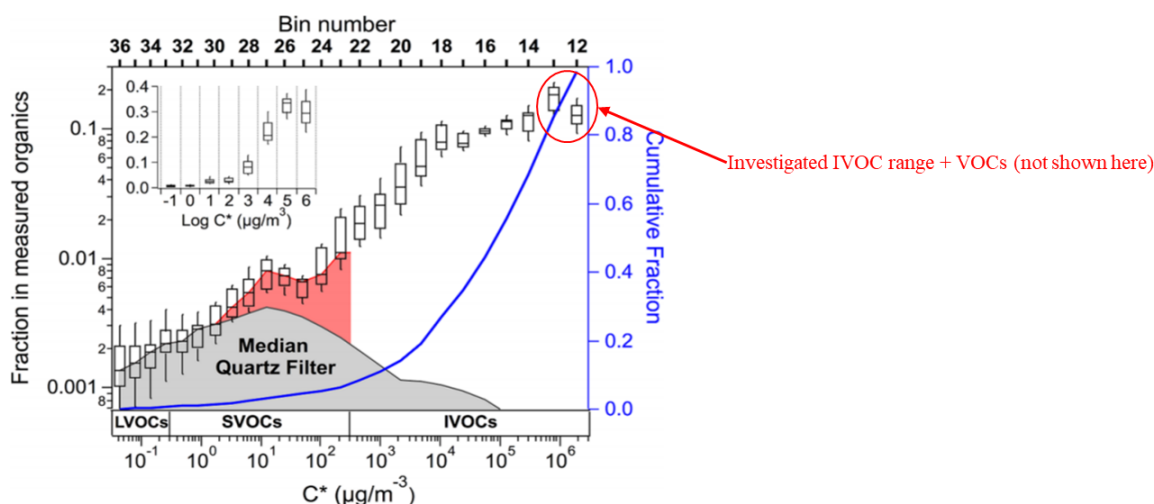
Response to Referees

The authors thank the referees for their comments. Please find our responses below:

1. Referee 1 Comments:

In Europe almost half of all new passenger cars are diesel vehicles. The large number of diesel vehicles means that their emissions are an important source of air pollution in urban environments. This study focuses on speciated VOCs, including 16 individual and 8 groups of compounds and effects of a home-retrofitted DOC on the mass emissions and chemical composition of these VOCs from an older diesel engine. VOCs contribute to less than half of the organics in diesel exhaust with these specific compounds contributing an even smaller fraction (e.g. classic paper Schauer et al. EST 1999 or more recent papers by Gentner PNAS 2013 or Zhao et al. EST 2015). The majority of organic emissions from diesel vehicles are IVOCs. This paper does not provide this important context.

IVOCs were investigated. The saturation concentration of the investigated compounds ranged from 10^5 to $10^8 \mu\text{g m}^{-3}$, capturing both VOCs ($C^* = > 10^6 \mu\text{g m}^{-3}$) and IVOCs ($C^* = 10^3 - 10^6 \mu\text{g m}^{-3}$). Based on the work shown in Zhao et al. 2015 (see below figure), we capture the most abundant volatility fraction of the IVOCs with online sampling (in contrast to Zhao et al. and Schauer et al.). We provide quantitative measurements of speciated VOCs and IVOCs, emission measurements, which supported by reviewer 2, are relatively rare. Contextualisation and discussion of the abundance of IVOCs in diesel exhaust emissions has been added into the manuscript, see page 3, line 30. The manuscript title has been changed to further highlight the study of IVOCs, reading ‘The Effect of Varying Engine Conditions on Unregulated VOC-IVOC Diesel Exhaust Emissions’.



The major weakness of the paper is that there is no substantive connection between the emissions data and air quality. Instead the paper focus on engine operations and emissions (an interesting topic but it seems outside the scope of ACP). Such a connection seems important for publishing in an atmospheric science journal. Therefore this study seems poorly suited to Atmospheric Chemistry and Physics.

The potential impacts of our findings on air quality has been discussed in section 3.5, within the limitations of the study. We cannot provide a substantive connection between the emissions data and air quality from one diesel engine, as one engine cannot be generalised to the entire vehicular fleet. Instead, we provide detailed information of how and why emissions change with varying engine conditions, specifically the effect of engine combustion efficiency and DOC HC removal efficiency on the exhaust gas composition. This information (with further work) could lead to improved refinement of air-quality models, predicting the impact of traffic emissions on air quality as a function engine temperature, which based on the result shown in this study, has a considerable effect on the composition

and abundance of the exhaust gas emissions. We have added further information on the possible atmospheric implications of our findings into the manuscript.

The paper makes numerous claims about the novelty and importance of the work. Many papers have examined VOC speciation of diesel exhaust and robust VOC speciation profile exist for diesel exhaust (the major problem with these profiles is the lack of IVOC data). The paper provides a very limited review of this literature and some readers may be confused on state of knowledge of diesel VOC emissions after reading the intro.

IVOCs have been investigated, see above comments. The point about a literature review of IVOC diesel profiling is addressed below.

The paper states multiple times that few studies have reported speciated emissions as a function of engine conditions. It is true that less is known about speciation as function of engine load and DOC then cycle based emissions (but much more work has been published than cited by this paper; a super quick search revealed multiple papers including Combust Flame, 118, 179, 1999; Atmos Env 42, 769, 2008, etc.). This paper, similar to the previously published work, clearly shows variations with engine loads and control technologies. The general trends (e.g. higher emissions at lower loads and changes in composition with loads) are consistent with the published literature. Similarly the results for the effectiveness of the DOC are similar to other studies (though at the low end of effectiveness presumably due to the retrofit nature of this application). More data are always good but the results are not especially novel from an emissions perspective. What are the implications of this new data from an atmospheric perspective (the focus of ACP)?

There is a considerable amount of papers which have investigated diesel exhaust emissions. Whilst every effort has been made to ensure we include at least the majority of these papers in the manuscript, there will be papers that we do not find, primarily because of the vast differences in titles and work aims. The papers cited above have now been included in the manuscript. See the below comments in response to the atmospheric implications of our work.

Air quality impacts depend on the integrated emissions (from many engines operated over a wide range of load conditions). The purpose of test cycles is to measure representative emissions that are relevant to atmosphere (emissions models like MOVES are moving to a more dynamic representation). Is there some problem with existing diesel VOC emissions profiles used by models and inventories that this paper is addressing? That was not clear (nothing jumps out to me), but I don't see an atmospheric question this paper is addressing. It seems more like engine / control technologies related questions. Maybe the paper belong in a different journal?

Air quality impacts do not just depend on integrated emissions using test cycles. Test cycles aim to represent on-road driving conditions. Whilst they cover a vast number of conditions in a single experiment, that all contribute to the emissions across the cycle, they cannot identify specific conditions that disproportionately contribute, nor can they isolate and completely characterise individual conditions. Our studies allow detailed characterisation of an instantaneous 'snapshot' and identify trends in these characteristics with changing engine conditions. The purpose of this work was not to repeat common exhaust measurements using driving cycles, but to ask the atmospherically relevant question, what engine factors are controlling the abundance and composition of VOCs and IVOCs in diesel exhaust emissions? This information could lead to the better constraint of atmospheric models and inventories. Using traffic flow models to identify vehicle use leading to engine conditions that are particularly polluting is not possible from averaged test-cycle derived emission factors. Furthermore, rather than using multiple test cycles to predict atmospheric emissions, we could use compositional trends based on one simple parameter (*i.e.* engine temperature) to estimate emissions in different driving conditions. The main results from this work show, (i) that engine temperature has a considerable effect on the composition and abundance of VOCs and IVOCs in the exhaust gas emissions, (ii) increasing combustion efficiency results in the increased formation of smaller, higher volatility *n*-alkanes in the

exhaust gas, which may be important in urban environments; *n*-alkanes are more efficient at producing SOA than their branched counterparts, and (iii) liquid fuel based estimates of SOA yields may be inconsistent with exhaust SOA yields, particularly at higher engine temperatures (*i.e.* high loads and speeds), due to the increased formation of smaller, more volatile *n*-alkanes at high engine combustion efficiencies (the contribution of *n*-alkanes increased by a factor of 1.6 in comparison to the contribution observed in cold-idle conditions (most similar to unburnt fuel). In addition to the above, IVOC measurements from diesel exhaust emissions are relatively rare, more measurements of these species are required (Gentner et al. 2017). We don't believe this manuscript is outside the remit of ACP, due to relevance of ACP literature to our work and the journal focus areas, laboratory measurements and chemical composition. We have also included further information on the possible atmospheric implications of our findings within the limitations of this study.

The study has used an advanced instrument (2D-GC-MS). However, the much of the analysis focuses on emissions of a commonly characterized subset of VOCs (*n*-alkanes and aromatics) that contribute a minor fraction of emissions. In addition, they are not the dominant source of SOA (e.g. dominated by IVOCs) or toxicity (carbonyls) from diesels. Not leveraging more the advanced 2D GC data seemed like a potentially missed opportunity.

We have investigated *n*-alkanes and branched aliphatics. The investigated compounds include, aliphatics (straight-chain and branched) and single-ring aromatics with two and three carbon substituents. These measurements were made using GC×GC-FID, not MS. Straight-chain and branched aliphatics constitute a considerable proportion of diesel exhaust emissions, primarily from unburnt fuel. Straight-chain and branched aliphatics have been found to constitute ~70% of the IVOC fractional composition at idle engine conditions (Cross et al. 2015). Contrary to the reviewer's assertions, we have investigated IVOC emissions, which we agree will contribute substantially to the SOA.

The engine is operated over extremely simple test cycles (e.g. constant speed and load or idle followed by constant load for a number of minutes). This is very unrepresentative of essentially all actual in-use scenarios and it is misleading to even refer to them as things like short journey. The real time data in engine literature shows that often emissions are dominated by hard transient events.

The reviewer is clearly missing the point of our study which was to gain a greater insight into the engine conditions controlling the composition and abundance of VOC-IVOCs in the exhaust emissions; experiments which cannot be performed using transient conditions due to averaging of emissions over entire driving cycles. However, we agree that use of the term 'short journey' could be misinterpreted. We have changed the term 'short journey' to 'cold loaded'.

It is helpful to understand results from laboratory studies by relating them to real-world measurements. In this study, agreement was found between engine tests and highway tunnel measurements for alkanes (C9-C13). Authors argue that "The emission factors in this study were comparable to on-road diesel vehicular emissions measured in Gentner et al. (2013), suggesting the results shown in this study are consistent with on-road diesel exhaust emissions." However, emission factors of hydrocarbons from diesel vehicles depend on many factors, such as vehicle type, driving condition, fuel type and aftertreatment devices. For example, Dallmann et al. (2012, EST) show that emission factors of pollutants for diesel vehicles span a wide range at the Caldecott tunnel where measurements in Gentner et al. (2013) were made. In the absence of further constraints, the comparison between measurements in this study and those in Gentner et al. (2013) might not lead to this claim of consistency in both measurements. If the author's claim is true, it means that other factors, including the fuel type, vehicle type and emission control device, are insignificant for diesel emissions. This is in contrast to results that both chassis dynamometer testing and field measurements that catalysed diesel particulate filters remove hydrocarbons very efficiently (Mayetal., 2014, AE; Dallmann et al., 2012 EST). Finally, this comparison is made with a 2010 fleet of on-road diesel trucks/vehicles. Shall we expect much lower emission factors from diesel vehicles from a present on-road fleet of diesel vehicles?

The Gentner et al. comparison has been removed from the manuscript.

Authors mention that a typical DOC is expected to remove 50 to 70% of the total hydrocarbon emissions. The DOC tested in this study likely has much lower removal efficiency for hydrocarbons, much lower than 46% for measured VOCs if considering the fall substantially lower or no removal efficiency for IVOCs by this DOC (e.g. their data suggest less efficient for removal of C12 branch aliphatics compared to other VOCs with lower carbon number. This indicates that the DOC has no effect on IVOCs, predominated by species with carbon number >12). It seems likely that the DOC tested in this study does not represent the performance of most DOCs and one must be careful trying to generalize. Manufacturers carefully consider thermal management and other operating conditions to ensure that a DOC operates effectively. It was not clear that installation of the DOC on this engine took those factors into account.

The results from the investigated DOC have not been generalised. We only discuss the hydrocarbon removal efficiency of the investigated DOC and whether the observed removal efficiency is in the expected range for a typical DOC. The life expectancy of a catalytic converter is ~ 50,000 miles. The average age of passenger cars in Europe is 10.7 years old (ACEA, 2017), with an average annual mileage of 13,000 km per annum (8078 miles). Thus, in Europe, the catalytic converter is likely to be changed at least once (on average) during the cars lifetime. The retrofitted nature of the DOC in this study, is therefore relevant to on-road vehicles and the age of the engine investigated (see page 5, line 24. Furthermore, the retrofitted DOC is the same as the VW catalyst that would be fitted to the engine if supplied for on-road use.

2. Referee 2 Comments:

General Comments:

This manuscript presents diesel exhaust measurements of from a light-duty diesel engine using an engine dynamometer. The study investigated the effects of engine load and use of diesel oxidative catalyst (DOC) on emissions of volatile and intermediate volatility organic compounds (VOCs/IVOCs) in diesel exhaust. The exhaust emissions were diluted in an atmospheric chamber and online sampling was conducted to measure speciated VOCs and grouped VOCs using a TD-GCxGC-FID system. The study results showed that VOC/IVOC emission rates and VOC profiles were greatly impacted by engine load and DOC efficiency. Intermediate volatility organic compounds (IVOCs) are quite difficult to sample and quantify accurately, and speciated IVOC emissions measurements are rare, particularly online measurements. Therefore, the publication of results from this work will be of significant benefit to the emissions research community to improve our understanding of IVOC emissions from a diesel engine and how they are impacted by engine conditions. However, there are several important issues raised below that must be addressed before this work is accepted for publication in ACP.

One major issue is that the rationale behind selection of the engine, fuel, experimental conditions was not articulated in the manuscript. Why was the particular engine with retrofitted DOC selected, and why was the goal to mimic Euro 4 emissions standard? I would imagine this engine/technology must be outdated compared to current and near future European light-duty vehicle fleet adhering to Euro 5 and 6 standards. Therefore, are these emission rate results at all relevant to the current European vehicle fleet?

The rationale behind the selection of the engine, emission control devices and experimental design have been added into the manuscript, see section '2.2 engine and exhaust sampling system' and newly added, '2.3 experimental design'. The auto-equivalent version of the engine has been used in several VW polo and Jetta models in the early 2000's and was chosen as an example of light-duty diesel engine. The aftertreatment was selected to meet Euro 4 emission control regulations required for such models. The retrofitted DOC is the same as the VW catalyst that would be fitted to the engine if supplied for on-road use. Euro 4 emission control regulations were first implemented for all new vehicles from

approximately January 2006, with Euro 5 emission control regulations starting post January 2011. Approximately 20% of the current EU diesel fleet are Euro 4 compliant (ACEA, 2017). Whilst vehicles conforming to Euro 5 and Euro 6 emission control regulations are increasing, the emission rates shown in this work are still relevant to the current EU diesel fleet.

Why were the specific experimental conditions chosen: specific engine loads, dilution ratios, speeds, multiple fuel batches? Based on the experiments listed on Table 1, the research strategy behind these measurements is very difficult to tease out. For example, in Section 3.1 the effects of engine load were discussed. However, because the DOC was also included, the results reflected the coupled effects of engine load and DOC that were interdependent. This is not ideal for a mechanistic study such as this work. Was it intended to study the effects of both simultaneously or was this an unintended consequence of the experimental design? Either way, no explanation was given. The rationale behind the experimental design and study conditions needs to be clearly described in order for the reader to interpret the results.

The rationale behind the experimental design has now been included in the manuscript. The rationale behind the engine loads, speeds, dilution ratios and fuel batches are also discussed below in the specific comments. The experiments discussed in this work formed a part of a wider project, ‘combustion particles in the atmosphere, (Com-Part)’. This project focused on the systematic characterisation of the chemical and physical transformations of primary and secondary particles emitted from a light-duty diesel engine, under a range of atmospheric dilution and oxidation conditions. Measurements of the direct exhaust gas emissions were essential to investigate the chemical and physical transformations of the particles (discussed in a separate publication), but were not the focus of the project and hence why the experimental rationale (without explanation) can be difficult to tease out. It was intentional to study the combined effect of different engine conditions (*i.e.* load and driving scenarios) and the DOC on the exhaust composition, as these engine conditions are most representative of on-road diesel vehicles. In addition, as observed in the manuscript, the exhaust gas composition was observed to change due to the combined effect of engine combustion and DOC HC removal, rather than when just one effect (*i.e.* engine combustion efficiency) was present (see section 3.4 driving scenarios for further information and the specific comments below); highlighting the importance of studying the combined effect of the DOC and specific engine conditions on the exhaust gas composition.

The second major issue is that a large portion of the discussion in the supplementary information is extremely important and should be provided in the main text. I believe some discussion points brought up in the SI are actually more scientifically relevant and impactful than some of the extended discussion about engine load and DOC effects in the main text that have been previously studied by others.

The experimental reproducibility and discussion of the fuel batches have been removed from the SI and added into the main text of the manuscript, see sections 2.5 liquid fuel analysis, 3.1 experimental reproducibility and 3.1.1. ULSD fuel: Batch A and B.

Experimental reproducibility is vital experimental information; this information (e.g. measurement replicates, test replicates) needs to be clearly detailed in the main text in order for the reader to assess the data quality and statistical power of the results. In Table 1, which experiments were meant to be replicate tests, and are the numbers in parentheses the measurement replicates or something else? Also, the origins of the error bars and emission rate standard deviation values need to be explained in the main text. If they are from the calibration propagation of error uncertainty calculations in SI Section 3.1, then how were measurement and test replicates included in the errors?

The replicate experiments are now clearly highlighted in Table 1 (see specific comments below). The numbers in the parentheses in Table 1 are for reference, to aid experimental discussion in the main text. An additional table has also been added into the SI, showing the number of exhaust measurements in each experiment, sampling times and exhaust injection times, see SI, Table S2. A brief explanation of

the uncertainty in measured emission rates has been provided in the main text (see 3.1 experimental reproducibility) – the detailed discussion on the calculation of the uncertainties has been reserved for the SI; we do not believe this information should be in the main text. The emission rates from sample replicates have been averaged and are not included in the propagation of error. The majority of experiments had two replicate measurements (see SI Table S2) of the exhaust gas due to the long GC×GC-FID sampling time; an insufficient number of replicates to calculate a RSD required for propagation. The averaging of emission rates has now been included in the manuscript, along with a description in each figure of what the error bars represent.

The discussion in the SI indicated that dilution ratio had a substantial impact on IVOC emissions between two similar experiments. Given the wide range of dilution ratios used in this study, this issue warrants further discussion in the main text, particularly how this issue may have influenced the results. Furthermore, a discussion of the observed differences in emission rates for the two different fuel batches and linking them to fuel composition by 2DGC-TOF fuel analyses was very interesting and should be included in the main text.

This information has been included in the main text of the manuscript, see above comments and specific comments below.

The third major issue is that in Section 3.4 the comparison between these engine dynamometer emission rates with California tunnel measurements is misleading and not scientifically relevant. While I understand the desire to link these results to real world measurements, I don't see the scientific merit or rationale for making this particular comparison. This study used an engine, aftertreatment technology, and fuel that are not at all relevant for these CA on-road measurements. What I believe would be of much greater scientific benefit to the mobile source emissions research community is a thorough literature comparison of speciated IVOC measurements that are so rarely measured for at least light-duty diesel engines and vehicles from engine and chassis dynamometer studies. Are these measurements consistent with other light-duty (and perhaps also medium/heavy duty) diesel vehicles and how do they compare with Euro5 and Euro6 compliant engines/vehicles/fuels? If the IVOC data is lacking for modern vehicles with newer emission standard, how are the emissions expected to change from Euro 4 to Euro 5 and 6. Finally, how will the engine operation and other effects on VOC/IVOC emissions impact SOA formation from vehicle exhaust?

The Gentner comparison has been removed from the manuscript. A literature comparison was initially included but was later removed due to the lack of comparable studies. The vast majority of studies have reported emission rates in units of VOC mass emitted per distance travelled, units which are not comparable with this work. Furthermore, the large variation in the types of compounds speciated and their volatility, different engine types and emission control devices, made literature comparison extremely difficult. Whilst we agree that a literature comparison is extremely useful, there are too many important differences in the few studies we can compare with. We have instead, discussed the futility of the comparison of emission rates. It is worth noting, that (to our knowledge) there are no on-road light-duty diesel engine studies which report emissions rates with units comparable to this work. Furthermore, the lack of a distance measurement, means we are also unable to compare measured emission rates with set regulations. We agree that the comparison of IVOC emissions between Euro 4/5 and 6 would be a very useful piece of information. However, we cannot speculate as to how the speciated profile would change as there is insufficient data at present. These studies are still in their infancy. The nomenclature 'speciated' is unfortunately rather vague. This has led to it being used in different ways and to describe different fractions of IVOCs in the literature. The inter-group variability of 'speciated emissions' is large, meaning it is impossible at the minute to attempt the kind of analysis requested.

3. Referee 2 Specific Comments and Author Responses:

Section 1. Introduction: there are some repetitive statements (Page 2, Lines 17-20; Page 3, Lines 34-36; Page 4, Lines 1-2, 5-7). The introduction could be made more concise by removing the repetitive text.

Repetitive text removed.

Page 4, Lines 10-12. The introduction referenced research that has previously studied the effects of DOC and engine operating parameters on vehicle exhaust composition, e.g. Chin et al. 2012. Other studies have also investigated these effects on diesel vehicles/engines (e.g. Ballesteros et al. (2014), Zhu et al. (2013)). Can this statement be further clarified so that it is more accurate?

The above studies have been added into the manuscript and the text further clarified.

Page 4, Line 28. Please provide hygrometer vendor information.

Information added to manuscript.

Section 2.2. Section title is misleading. This section not only describes the engine but also exhaust sampling system. Please provide more detailed information on the engine specifications and about DOC usage status (mileage or rapid thermal aging hours) as this can significantly impact the emissions. Provide rationale behind the selection of the specific engine, aftertreatment and why Euro 4 emission control was approximated. Please provide a schematic of the dynamometer and sampling system (this may be included in the SI). Please describe all engine operating conditions including driving scenarios and include rationale behind the experimental design.

Section title has been changed to 'Engine and exhaust sampling system'.

The DOC was newly-bought (0 mileage hours). Page 5, line 21, now reads; 'The engine was mounted on an eddy current dynamometer rig (CM12, Armfield Ltd, Hampshire, UK) and the exhaust connected to a new (0 mileage hours) retrofitted DOC.'

The rationale behind the selection of the engine has been added into the manuscript, see page 5, lines 24 - 26. The engine does conform to Euro 4 emission control regulations; the use of 'approximated' has been removed. A schematic of the dynamometer and sampling system has been added to the SI. A more detailed description of the engine operating conditions and rationale behind the experimental design, has been added in to a new section, '2.3 experimental design', starting on page 6, line 10).

Page 5, Line 12-13. Was the MAC filled before exhaust was introduced? How were the dilution ratios decided upon and why did they vary from experiment to experiment? How long was the diluted exhaust allowed to equilibrate before sampling took place and were there any apparent losses in IVOCs over time?

The MAC was filled with clean air prior to the introduction of the exhaust emissions. Exhaust dilution ratios were varied to represent a range of ambient conditions from near to downwind of an emission source, capturing the chemical and physical transformations of semi-volatiles in the exhaust emissions with varying dilutions. The above has been added into the manuscript, see page 6, lines 21 -24.

The GC×GC-FID started sampling during chamber cleaning and sampled for 26 minutes per analysis. The sampling start time was on average 13 minutes after injection. No apparent losses of the IVOCs were observed during sampling. The average RSD of the investigated compounds from replicate exhaust measurements, over the longest measurement period (~ 2 hours), was 6.4%. This information has been added into the manuscript, see page 8, lines 18 – 24.

Page 5, Line 18. Please explain why two batches of diesel fuel were used. Please include any fuel composition or fuel property analyses that were conducted. What was the sulfur content of the two batches? Do both batches of the diesel fuel meet Euro 4 or Euro 5 specifications? Please discuss differences in fuel composition here. What is meant by "standard"?

The two batches of fuel were of same specification and obtained from the same local fueling station. A second batch of fuel was required due to a considerable increase in the number of planned experiments. The fuel used was 'standard' European ULSD and is Euro 5 compliant, conforming to EN590 specifications. The sulphur content was < 10 ppm. Readers have been referred to the 2009 EC directive for further information on the fuel specifications. 'Standard' refers to standard European specifications. The above has been added to the manuscript, see page 6, lines 3 – 9.

Page 5, Line 25. What temp was the line heated to?

The line was heated to ~ 70 °C. Page 7, line 15 now reads, 'The stainless steel tubing was heated to ~ 70 °C to reduce condensational losses of VOCs.'

Page 6, Line 17. How often was the calibration checked by a standard? Were MDLs determined? If so, explain how and provide MDL values for all compounds. This can be provided in the SI.

Calibrations were performed weekly using the NPL gas standard, or more frequently during instrument maintenance periods. The MDLs for the investigated compounds using this instrument, can be found in the SI of Dunmore et al. (2015). The above has been added into the manuscript, see page 8, lines 7 – 9.

Page 7, Line 1-4. The engine operating conditions should be described in detail in the experimental as well as justification for why these specific conditions were chosen.

This has been added in the manuscript under section '2.3 Experimental design', see above comment.

Page 7, Line 9. Not enough evidence has been provided to identify the grouped VOCs "branched aliphatics", particularly because these were not GC/MS measurements. These would be better labelled as unspciated or unresolved organics. The grouped VOCs should also not be called speciated VOCs because they are not individually speciated. Therefore, sum of SpVOC is a misleading term and should also be changed to minimize confusion. Also, please discuss why this narrow range of VOCs was studied? Was it intentional to focus on IVOCs or was this due to sampling/instrumental limitations?

Branched aliphatics can be identified using GC×GC in combination with commercially available standards. Two different stationary phases were used, separating compounds by two physical properties, boiling point (see Figure 1, x-axis, increasing from left-to-right) and polarity (y-axis, increasing from bottom-to-top). This separation creates a characteristic space where compounds are grouped by similar physical properties, providing the 'aromatic' and 'aliphatic' bandings observed with this technique (*e.g.* Hamilton and Lewis (2003),(Dunmore et al., 2015); bandings added to Figure 1 for clarity). Straight-chain aliphatics have lower boiling points than their branched counterparts with the equivalent number of carbon atoms. For example, *n*-nonane has a lower boiling point than 2-methyloctane (C₉ branched aliphatic). Thus, branched aliphatics elute to the righthand side of the equivalent carbon number straight-chain aliphatic in the chromatogram (see Figure 1). The use of external standards to identify the straight-chain aliphatics, in-turn allows the identification of the branched aliphatics based on their boiling point (*i.e.* chromatographic location) (*c.f.* Dunmore et al. 2015)

Whilst the branched aliphatics have not been individually speciated, 'unspciated' or 'unresolved organics' do not accurately describe these groupings. The branched aliphatics have identified functionality and have been speciated by the number of carbon atoms within each group, retaining some level of speciation; unlike the unidentified complex mixture (UCM) often observed with the use of one-dimensional GC. Subsequently, the term SpVOC has not been removed from the manuscript.

Diesel exhaust emissions consist mainly of aliphatic and aromatic species with a carbon range of ~ C₅ to C₂₂. The measured compounds include aliphatics and single-ring aromatics with a carbon range of C₆ to C₁₃. This narrow carbon range is the result of instrument temperature constraints. The boiling points of compounds above ~ C₁₅ are too high to be removed from the column at the maximum operating temperatures of the modulator, resulting in these species not being detected. IVOCs were intentionally

studied, with the aim of characterising the largest volatility range possible within instrument limitations. This has been added into the manuscript, starting page 18, line 9.

Page 7, Line 11. How often were the retention time windows confirmed? Were any internal standards used?

The shift in retention time that this comment relates to, occurred as a result of instrument maintenance, between the first and second set of experiments. As mentioned above, calibrations and thus retention times were confirmed weekly using the NPL gas standard, or more frequently during instrument maintenance periods.

Internal standards ideally need to be of similar chemical speciation to the sample. The composition of the exhaust emissions was largely unknown and thus it is likely the use of internal standard may add additional mass to compounds already present in the exhaust gas, resulting in sample contamination (*i.e.* unable to distinguish sample and standard concentrations).

Page 7, Line 23-24. Both reproducibility and dilution effects are important enough to merit detailed discussion in the main text. Please see general comments above.

The discussion reproducibility and dilution effects have been added into the main text, see section '3.1 experimental reproducibility'.

Page 7, Line 29-30. While similar sets of conditions have been compared in the discussion, emission factors are all presented for every experiment, allowing the reader to freely compare between experiments without fully understanding the impacts of differing dilution ratios unless they read the SI in detail. This is why a full discussion of the effects of dilution ratios is needed in the main text.

See above comment.

Section 3.1 Why were these loads chosen? Please state clearly whether these experiments (and for each subsection in the Results section and in all figure captions) are from tests with or without DOC? This section title is also misleading because the combined effects of engine load and DOC were studied simultaneously.

The engine loads investigated ranged from 0 (no load) to 53% (maximum engine load which could be safely applied by the dynamometer in the experimental setup). Within this range, 0, 30, 40 and 53% load were investigated. The experiments shown in this work form only a subset of total number of experiments performed, as a part of the wider project, combustion particles in the atmosphere. The GC×GC-FID was not in operation during every experiment. The above has been added into section 2.3 experimental design, starting page 6, line 10.

There appears to be too much emphasis on the DOC. Only one experiment was performed without a DOC to investigate the hydrocarbon removal efficiency of the catalyst and this is clearly shown in Table 1. A separate sub-heading has also been used (3.3. DOC removal efficiency) to separate these results from the other text. The other results sections 'engine load' and 'driving scenarios' show the combined effect of the investigated parameters with the DOC; conditions most representative of on-road vehicles. We do not believe these section titles are misleading. However, to avoid confusion, we have clarified the text in section 2.3 Experimental design (page 7, line 2), stating; 'All experiments except experiment 3 (see Table 1) were performed with the DOC.'

Page 8, Line 7. Is this statement suggesting that engine load is the most important factor that controls VOC emission rates, whereas other factors, e.g. aftertreatment and fuel, are less important? If not, please clarify. Also, please state clearly that the assumption was made that engine load is linearly related to engine combustion efficiency or provide ancillary measurements to confirm combustion efficiencies for each experiment.

We don't mean to suggest that engine load is the 'most important factor' that controls VOC emission rates. Rather, that a pattern is observed in the literature (and in this work) between increasing engine load and decreasing VOC emission rates. This same pattern is observed with the use of different fuel compositions and emission control devices, when all conditions except engine load are kept consistent in each study. The statement has been shortened to avoid confusion, reading (page 11, 20 -23), 'This trend of decreasing VOC emission rates with increasing engine load has been observed in a number of previous studies for light-duty and medium-duty diesel vehicles and can be explained by considering the engine operation.'

This linearity comment relates to page 11, lines 15 – 18 in the original manuscript (to avoid confusion; driving scenarios discussion), Linearity is not assumed in the engine load section. The relationship between engine load (and thus engine temperature) is relatively linear with engine combustion efficiency. Engine temperature increases with increasing engine load. The engine requires more power to achieve higher loads, which is achieved by increasing the amount of fuel injected into the combustion chamber. The increase in fuel, increases fuel combustion, generating more power and increasing temperature (combustion generates heat) (*e.g.* Kumar, 2009). This increase in temperature, in-turn increases engine combustion efficiency, as fuel components are more readily combusted at higher temperatures (Haywood (1988)). The relationship between engine temperature and combustion efficiency can be observed in Mikalsen and Roskilly (2008); shown as percentage in-cylinder heat transfer losses *vs.* engine efficiency, although as heat transfer losses are minimised, temperature increases and therefore supports the above. It is worth noting however, at high engine loads and relatively low speeds (not used in the driving scenario experiments), engine temperature and combustion efficiency eventually plateau due to a too lean air/fuel ratio, resulting in incomplete combustion (see Haywood (1988) for further information). At a constant speed, the air flow into the combustion chamber remains constant, but the amount of fuel injected continues to increase with increasing engine load. This results in insufficient oxygen content to burn all the fuel (*i.e.* incomplete combustion) and thus temperature and engine combustion efficiency plateaus. A more concise version of the above has been added into the manuscript, see page 15, line 32.

Page 8, Line 18, 20. Should the reference be Chin et al. (2012)?

Yes. The reference year has been changed.

Page 9, Lines 16-22. This text contradicts what is shown in Figure 2a, 2b and previous discussion on Page 8.

There are two factors influencing VOC emissions here, the DOC hydrocarbon removal efficiency and engine combustion efficiency. From 0 to 40% engine load, the compositional profiles display the effect of both increasing DOC hydrocarbon removal efficiency and engine combustion efficiency. The DOC hydrocarbon removal efficiency is near maximum at 40% engine load and thus cannot account for the considerable compositional shift observed at 53% engine load (see Figure 2B). This considerable increase in the percentage contribution of the C₇ to C₁₃ *n*-alkanes to the \sum SpVOC emissions at 53% engine load, has been attributed to engine combustion. We suggest that this high engine combustion efficiency results in an increase in the abundance of the *n*-alkanes to the \sum SpVOC emissions. This increase in the percentage contribution of the *n*-alkanes is not observed from 0 to 40 % engine load (appearing contradictory) and is likely the result of the DOC masking the effect of engine combustion efficiency on the exhaust composition. We later show this in the driving scenario experiments, where the effect of engine combustion efficiency on the VOC emissions can be observed without the DOC interference (DOC hydrocarbon removal efficiency is negligible in all driving scenario experiments). In the driving scenario experiments, we observe that as the internal combustion efficiency increases the contribution of the *n*-alkanes to the \sum SpVOC emissions also increases.

Page 13, lines 19 and 20 have been removed to avoid confusion and the text further clarified from lines 26 to 30.

Page 10, Lines 16-17. Did Alam et al. use the same type of DOC or was it different from what was used in this study? It may also be interesting to compare the results of Liu et al. (2010) with this work.

Alam et al. used a similar DOC (mixed platinum and rhodium). This has been added into the manuscript.

The results of Liu et al. (2010) and (2008) are very interesting, although we did not feel that this work was directly applicable in the DOC removal efficiency section.

Page 10, Lines 26-30. Please show how the conditions of these three scenarios change in a diagram in the experimental section or SI.

The cold-start experiment includes only one applied engine load and speed which can be observed in Table 1. A diagram for the engine sequences ('short journey' and 'warm following load') however, have been added to SI, Figure S2.

Page 11, Line 17-18. Relative abundances discussed here?

The relative abundance discussion starts at line 16 in the original manuscript.

Page 11, Line 18-22. It is not clear why the effect of the DOC are brought up here. It does not logically fit with the rest of the discussion in this paragraph.

See above comment to page 9, lines 16-22. The comments here refer to the additional information uncovered, the result of being able to observe the effect of only combustion efficiency on the exhaust emissions. The text has been further clarified to make this text easier to follow/understand. See page 16, lines 3-7.

Section 3.4. Please see general comments on this section. It would be extremely useful to conduct a literature comparison to assess whether the emission factors from this study are consistent with similar studies. The comparison with Gentner et al. (2013) is misleading and should not be included.

The Gentner et al. comparison has been removed from the manuscript. A literature comparison could not be performed. We have instead discussed the futility of the comparison of emission rates (see general comments above). See starting page 16, line 33.

Page 12. Line 32-33. Aldehydes are not at all mentioned here and represent arguably the most important air toxic/hazardous VOCs emitted from modern diesel vehicles.

Aldehydes are not mentioned in the manuscript as these compounds were not measured. We have not discussed other toxic/carcinogenic species that we have measured in manuscript and thus the addition of aldehydes, whilst we agree are important, does not fit within the discussion. Also, aldehyde measurements from diesel exhaust are fairly common.

Page 13. Lines 3-7. Please discuss differences between Euro 5 and Euro 6 emission standards in relation to the approximated Euro 4 emission standards simulated here and how modern vehicles and their aftertreatment technologies are specifically changing. How are these changes expected to impact VOC emissions? Emission control technologies targeting other pollutants may still have significant effects on VOC emissions. This is where the literature comparison of emission factors from this study with emission studies with Euro 5 and Euro 6 vehicles would provide insight (see general comments).

See general comments above.

Page 13. Lines 7-8. Please see general comments about this comparison.

Text removed.

Page 13. Lines 11-13. Please see earlier comment on the veracity of this statement.

We do not believe this comment requires modification. Several compositional changes observed in the exhaust gas with different engine conditions agreed with the results of previous studies. The earlier comment ('Page 8, Line 7') has been changed.

Table 1. Please clearly indicate which tests were replicate tests and which tests had replicate measurements. Figure 1. What are the compounds below B and above G? What is the peak above #8? Why does benzene elute after toluene – are those labels correct? Have any attempts been made to quantify the lighter compounds and to assess total unspciated organics?

Replicate experiments have been highlighted using superscript letters, see Table 1. The compounds below B are likely single-ring aromatics with four carbon substitutions, based on the elution patterns in Dunmore et al. (2015). The compounds above G are possibly single-ring aromatics with five carbon substitutions, although this cannot be determined without commercially available standards. The labels for benzene and toluene are incorrect. Benzene elutes before toluene; the manuscript has been corrected. No attempts have been made to assess to quantify the light compounds.

Figure 2. What do error bars represent? Are these tests with or without DOC? Toluene and benzene colors are difficult to distinguish.

The error bars represent the uncertainty in the measured VOC emission rates based on; (i) the standard deviation in the replicate measurements of the calibration standard and the reported uncertainty in the standard VOC mixing ratios, (ii) standard deviation of the replicate measurements of the liquid standards used for the calculation of the RRF (where applicable), and (iii) a 5% standard deviation in the chamber volume. The uncertainty in the measured emissions are discussed in the SI, Section 1.1. A description of the error bars has now been included in all applicable Figures.

These tests are performed with a DOC. See section 3.1 comments above.

The benzene colour has been changed.

Figure 4. Evidence was not provided to speciate into aliphatic and aromatic components.

See above comments, 'Page 7, Line 9'.

Figure 5. See general comments on this comparison.

Figure removed. See section 3.4 comments above.

Supplementary Information Page 4, Lines 13-14. Why was toluene used and not an n-alkane?

Toluene, in comparison to the *n*-alkanes, was much more resolved and easier to distinguish in the chromatogram. The reference compound (*i.e.* toluene) does not need to be structurally similar to the analyte (*i.e.* *n*-alkane), to calculate the analyte concentration. The response of a FID is proportional to the number of carbon atoms in a compound. The structure of the compound has a very small effect (within detector variation) on the detector response. The resolution of the reference compound is much more important, as poor resolution will increase the measured area of the reference compound, in-turn inaccurately increasing the concentration of the analyte. A more concise version of the above has been added into the SI, see page 4, line 14.

References

ACEA Report: Vehicles in use Europe 2017. (URL: http://www.acea.be/uploads/statistic_documents/ACEA_Report_Vehicles_in_use-Europe_2017.pdf)

Dunmore, R. E., Hopkins, J. R., Lidster, R. T., Lee, J. D., Evans, M. J., Rickard, A. R., Lewis, A. C., and Hamilton, J. F.: Diesel-related hydrocarbons can dominate gas phase reactive carbon in megacities, *Atmos. Chem. Phys.*, 15, 9983-9996, 10.5194/acp-15-9983-2015, 2015.

Gentner, D. R., Jathar, S. H., Gordon, T. D., Bahreini, R., Day, D. A., El Haddad, I., Hayes, P. L., Pieber, S. M., Platt, S. M., de Gouw, J., Goldstein, A. H., Harley, R. A., Jimenez, J. L., Prévôt, A. S. H., and Robinson, A. L.: Review of Urban Secondary Organic Aerosol Formation from Gasoline and Diesel Motor Vehicle Emissions, *Environmental science & technology*, 51, 1074-1093, 10.1021/acs.est.6b04509, 2017

Hamilton, J. F., and Lewis, A. C.: Monoaromatic complexity in urban air and gasoline assessed using comprehensive GC and fast GC-TOF/MS, *Atmospheric Environment*, 37, 589-602, [https://doi.org/10.1016/S1352-2310\(02\)00930-5](https://doi.org/10.1016/S1352-2310(02)00930-5), 2003.

Heywood J. B., *Internal combustion engine fundamentals* (London: McGraw-Hill Inc. 1988). ISBN 0-07-100499-8.

Mikalsen, R and Roskilly, A., The fuel efficiency and exhaust gas emissions of a low heat rejection free-piston diesel engine, *SAGE*, 233, 4, DOI: 10.1243/09576509JPE653, 2008.

The Effect of Varying Engine Conditions on Unregulated VOC-IVOC Diesel Exhaust Emissions

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Abstract

An extensive set of measurements were performed to investigate the effect of different engine conditions (*i.e.* load, speed, temperature, 'driving scenarios') and emission control devices (with/without diesel oxidative catalyst, DOC) on the composition and abundance of unregulated exhaust gas emissions from a light-duty diesel engine. Exhaust emissions were introduced into an atmospheric chamber and measured using thermal desorption comprehensive two-dimensional gas chromatography coupled to a flame ionisation detector (TD-GC×GC-FID). In total, 16 individual and 8 groups of ~~volatile organic~~ compounds (~~VOCs~~) were measured in the exhaust gas, ranging from volatile to intermediate volatility. The total speciated VOC-IVOC ($\sum\text{SpVOC}$) emission rates varied significantly with different engine conditions, ranging from 70 to 9268 milligrams of VOC mass per kilogram of fuel burnt (mg kg^{-1}). $\sum\text{SpVOC}$ emission rates generally decreased with increasing engine load and temperature, and to a lesser degree, engine speed. The exhaust gas composition changed as a result of two main influencing factors, the DOC hydrocarbon (HC) removal efficiency and engine combustion efficiency. Increased DOC HC removal efficiency and engine combustion efficiency resulted in a greater percentage contribution of the C₇ to C₁₂ branched aliphatics and C₇ to C₁₂ *n*-alkanes, respectively, to the $\sum\text{SpVOC}$ emission rate. At low engine temperatures (< 150°C), the contribution of *n*-alkanes in the exhaust gas increased with increasing combustion efficiency and may be important in urban environments, as *n*-alkanes are more efficient at producing SOA than their branched counterparts. At very high engine temperatures, the *n*-alkane contribution increased by a factor of 1.6 times greater than observed in the cold-start experiment (most similar to unburnt fuel) and may suggest liquid fuel based estimates of secondary organic aerosol (SOA) yields may be inconsistent with exhaust SOA yields, particularly at high engine temperatures (*i.e.* high engine speeds and loads). The investigated DOC removed 46 ± 10 % of the $\sum\text{SpVOC}$ emissions, with removal efficiencies of 83 ± 3 % for the single-ring aromatics and 39 ± 12 % for the aliphatics (branched and straight-chain). The DOC aliphatic removal efficiency generally

decreased with increasing carbon chain length. ~~The emission factors of *n*-nonane to *n*-tridecane were compared with on-road diesel emissions from a highway tunnel in Oakland California. Comparable emission factors were from experiments with relatively high engine loads and speeds, engine conditions which are consistent with the driving conditions of the on-road diesel vehicles. Emission factors from low engine loads and speeds (e.g. cold start) showed no agreement with the on-road diesel emissions as expected, with the emission factors observed to be 2 to 8 times greater.~~ To our knowledge, this is the first study which has explicitly discussed the effect of the DOC HC removal efficiency and combustion efficiency on the exhaust gas composition. With further work, compositional differences in exhaust gas emissions as a function of engine temperature, could be implemented into air-quality models, resulting in improved refinement and better understanding of diesel exhaust emissions on local air quality.

10 **1. Introduction**

Urban air pollution is detrimental to human health, adversely effecting air quality and resulting in increased morbidity and mortality rates (Han and Naeher, 2006; Cohen et al., 2005; Prüss-Üstün and Corvalán, 2006). The World Health Organisation attributed 1.34 million premature deaths to urban air pollution in 2008 (WHO, 2006; Krzyzanowski and Cohen, 2008). Of these deaths, 1.09 million could have been prevented if the air quality guidelines had been met (WHO, 2006; Krzyzanowski and Cohen, 2008). Over half of the world's population now live in urban areas (Prüss-Üstün and Corvalán, 2006; UnitedNations, 2014). By 2050, this populous is expected to grow to 6.34 billion people, with an estimated 66% of the world's population living in urban environments (Prüss-Üstün and Corvalán, 2006; UnitedNations, 2014). Road transport emissions are a dominant source of urban air pollution (DEFA, 1993; Colvile et al., 2001; HEI, 2010) with common road-traffic pollutants including gaseous hydrocarbons (including volatile organic compounds, VOCs), nitrogen oxides (sum of NO + NO₂), carbon oxides (CO and CO₂) and particulate matter (PM), with secondary reaction processes resulting in the formation of ozone and secondary aerosol (WHO, 2006; HEI, 2010). Exposure to road-traffic air pollutants, both primary and secondary, are of a major health concern (UnitedNations, 2014; WHO, 2006; HEI, 2010). Secondary aerosol formation from diesel and gasoline powered motor vehicles has received considerable attention in recent years (Gentner et al., 2017). ~~There~~ Motor vehicles emit thousands of gaseous hydrocarbons of differing chemical composition and volatility. These compounds undergo atmospheric oxidation, resulting in lower volatility species which can partition into the particulate phase forming secondary organic aerosol (SOA) (Hallquist et al., 2009). A considerable proportion of urban organic aerosol is from secondary sources (de Gouw et al., 2005; Takegawa et al., 2006; Volkamer et al., 2006; Kondo et al., 2007; Matsui et al., 2009). However currently, there is considerable debate as to whether diesel or gasoline powered motor vehicles are more important for secondary organic aerosol (SOA) formation SOA and which precursors are the most efficient at forming SOA (Gentner et al., 2017). In Europe, almost half of all new passenger cars are diesel (49.5%), with petrol (45.8%), electric hybrids (2.1%), electric (1.5%) and alternative fuels (1.2%) accounting for the remaining fraction (ACEA, 2016). Diesel exhaust emissions vary considerably with vehicle type, age, operation conditions, fuel, lubricant oil and emission control devices, among other factors (HEI, 2010). Emission

regulations of nitrogen oxides, carbon monoxide, PM and total hydrocarbon mass has resulted in the reduction of exhaust emissions (HEI, 2010). However, this ‘blanket approach’ for the reduction of total hydrocarbon mass, has in-part, resulted in few studies investigating the detailed chemical composition of exhaust emissions with varying engine conditions (Yamada et al., 2011). Another contributing factor, is the difficulty in exhaust gas measurement (Yamada et al., 2011; Rashid et al., 2013).

5 On-road measurements of exhaust gas are difficult, due to the continually evolving chemical composition, requiring techniques capable of providing detailed chemical speciation in real-time, or near-real-time. Furthermore, the abundance of gaseous compounds in exhaust emissions often involves lengthy quantification processes. The detailed chemical characterisation of exhaust gas with varying engine conditions however, can considerably aid emission inventories and provide a greater understanding of exhaust emissions on local air quality. In addition, this information could serve to influence the design of
10 emission control devices, reducing the emission rates of potentially harmful unregulated exhaust gas components.

On-road measurements of unregulated exhaust gas emissions are often performed in tunnels, on roadsides, or motorways (*e.g.* (Gentner et al., 2013; Liu et al., 2015; Ježek et al., 2015; Zavala et al., 2006; Jiang et al., 2005; Kristensson et al., 2004; Fraser et al., 1998; Miguel et al., 1998)). These measurements provide a compositional overview of the exhaust emissions from the
15 on-road vehicular fleet, consisting of a vast range of vehicle types (*e.g.* light-duty, heavy-duty), emission control devices (*e.g.* with/without exhaust gas recirculation) and fuel composition (*e.g.* ultra-low sulfur diesel (ULSD), super unleaded petrol, premium unleaded petrol, biofuel, among others). These measurements however, do not allow the effect of different engine conditions or emission control devices on the exhaust gas composition to be investigated. Dynamometer engines or chassis dynamometers can afford compositional insight into exhaust emissions with varying engine conditions, providing a high degree
20 of control and reproducibility (Tadano et al., 2014; Louis et al., 2016). Several studies have used ~~chassis~~ dynamometers to investigate the changes in unregulated exhaust gas composition with the use of different transient driving cycles, for petrol engines (Pang et al., 2014; Baldauf et al., 2005), diesel (Yamada et al., 2011; Cross et al., 2015; Schauer et al., 1999), or both (Alves et al., 2015; Chirico et al., 2014; Alkurdi et al., 2013; Caplain et al., 2006; Schmitz et al., 2000; Louis et al., 2016).
Driving cycles (often performed with a chassis dynamometers)~~dynamometer~~ are designed to simulate real-world driving
25 conditions, allowing the exhaust emissions from individual vehicles to be investigated. However, these driving cycles offer limited information on the effect of combustion or specific engine conditions (*e.g.* engine load, speed) on unregulated exhaust emissions, due to the averaging of emissions over entire driving cycles and lack of steady-state engine conditions (Cross et al., 2015); compositional information which is easily obtained with the use of a single-engine dynamometer rig (~~*e.g.*~~ (Chin et al., 2012; Cross et al., 2015)). ~~Recently, Cross et al.~~ Recent studies have focused on the measurement of al (2015) investigated
30 intermediate-VOCs in VOC diesel exhaust emissions, primarily due to advances in instrumentation to allow the detection of these species using a dynamometer rig. IVOCs have an effective saturation concentration (C^*) of 10^3 to 10^6 $\mu\text{g m}^{-3}$ and reside almost exclusively in the gas-phase at atmospheric conditions (Donahue et al., 2006). IVOCs comprise a considerable fraction of diesel exhaust emissions, with studies attributing ~ 20 to 60% of the non-methane organic gases to IVOCs (Schauer et al., 1999; Siegl et al., 1999; Zhao et al., 2015; Gordon et al., 2014). IVOC diesel exhaust emissions are relatively poorly

characterised, yet are contribute significantly to SOA formation (Gentner et al., 2017). Recently, Cross et. al (2015) investigated IVOC diesel exhaust emissions using a dynamometer rig. It was found that IVOC diesel exhaust emissions were highly dependent on engine power. At low engine loads, the exhaust gas composition was dominated by saturated hydrocarbons, likely the result of unburnt fuel. At high engine loads however, the exhaust gas composition changed, including newly formed unsaturated hydrocarbons and oxidised compounds from incomplete combustion (Cross et al., 2015). Furthermore, Chin et. al. (2012) found the composition of VOC and IVOC diesel exhaust emissions (generated under steady-state engine conditions) depended on engine load, fuel type (ULSD and biodiesel) and emission control devices. (Chin et al., 2012).

~~Unregulated gaseous exhaust emissions contain compounds which are carcinogenic, toxic, or serve as precursors to secondary pollutants, such as ozone and SOA formation. Few studies have investigated the effect of different engine conditions on the composition of gaseous exhaust emissions, and thus the impact of uncontrolled exhaust emissions on urban air quality is not fully known. Detailed compositional information is required to further understand the effects of unregulated traffic emissions on air quality (Dunmore et al., 2015; Gentner et al., 2017) and how these emissions change with different engine conditions.~~

This study investigates the compositional changes of unregulated exhaust emissions with varying engine conditions (*i.e.* engine load, speed and ‘different driving scenarios’) and emission control devices (with/without DOC) using a dynamometer rig. ~~Previous studies have investigated the effect of different engine conditions on exhaust gas composition using dynamotor rig, via detailed chemical speciation of individual compounds (*i.e.* compound identification) ranging from volatile to intermediate volatility (Chin et al., 2012), or via bulk composition properties (*i.e.* compound class) of IVOCs (Cross et al., 2015).~~ In contrast to previous ~~studies, work~~, this ~~workstudy~~ combines both detailed chemical speciation and groupings of VOC – IVOCs ($C^* 10^5$ to $10^8 \mu\text{g m}^{-3}$) species based on their structure and functionality, ~~of VOCs to IVOCs ($C^* 10^2$ to $10^6 \mu\text{g m}^{-3}$)~~, providing a more detailed compositional overview of the effect of different engine conditions on exhaust gas emissions. In addition, to our knowledge, this is the first study which attempts to decouple the effect of the diesel oxidation catalyst (DOC) and combustion efficiency on the exhaust gas composition. The emissions from a light-duty 1.9L Volkswagen diesel engine were investigated. Exhaust emissions from different engine conditions were introduced into an atmospheric chamber which was used as a ‘holding-cell’ for sampling, allowing lower time resolution techniques to be used. In total, 16 individual ~~VOCs~~ and 8 groups of compounds were measured in the exhaust gas using comprehensive two-dimensional gas chromatography coupled to a flame ionisation detector (GC×GC-FID). The effect of different engine conditions and emission control devices on the composition and abundance of the speciated ~~VOC-IVOCs~~ ~~VOCs~~ is discussed. Finally, the possible atmospheric implications of these results are ~~compared with on road diesel emissions and the possible impacts on urban air quality are~~ discussed.

2. Experimental

2.1 Chamber ~~setu~~experiments

Experiments were performed in the Manchester Aerosol Chamber (MAC) located within the University of Manchester, UK. The MAC consists of an 18 m³ fluorinated ethylene propylene (FEP) Teflon bag with the following dimensions; 3m (L) × 3m (W) × 2m (H). The chamber is supported by three rectangular aluminium frames, two of which are free moving, allowing the chamber to expand and collapse as sample air flow is introduced or extracted. Irradiation is achieved through a series of wall mounted halogen lamps (Solux 12V, 50W, 4700K, New York, USA) and two filtered 6 kW Xenon Arc lamps (XBO600W/HSLA OFR, Osram, Germany) located within the chamber enclosure. Purified air is used within the chamber and is humidified prior to introduction. A suite of instruments was used to measure chamber temperature (series of cross-calibrated thermocouples), relative humidity ([Dewmaster chilled mirror dewpoint hygrometer, Edgetech Instruments, USA](#)), CO₂ (model 6262, Li-Cor Biosciences, USA), NO_x (model 42i, Thermo Scientific, MA, USA), O₃, (model 49C, Thermo Scientific, MA, USA) and ~~VOC-IVOCs~~VOCs (comprehensive two-dimensional gas chromatography flame ionisation detection, see below for further details). Particle number, mass and diameter were measured using a differential mobility particle sizer (DMPS (Williams et al., 2007)) consisting of a differential mobility analyser (DMA (Winklmayr et al., 1991)) and a condensation particle counter (CPC, model 3010, TSI Inc., USA). Further technical information regarding the chamber design can be found in Alfarrá et al. (2012). ~~A series of experiments were performed during July and August 2014, and September to November 2015. The experimental dates and engine operating parameters can be found in Table 1.~~

2.2 Engine and exhaust sampling system ~~2.2 Diesel engine~~

The emissions from a light-duty Volkswagen (VW) 1.9L diesel engine was investigated. ~~A schematic of the dynamometer and exhaust sampling system is shown in SI Figure S1. The engine had 4 cylinders with a capacity of 1896 cm³ and a compression ratio of 19.5 : 1. The engine was mounted on an eddy current dynamometer rig (CM12, Armfield Ltd, Hampshire, UK) and the exhaust connected to a new (0 mileage hours) retrofitted DOC. DOC. The DOC was purchased from a local garage (Oldham Tyre and Exhaust, Oldham, UK) and consisted of a mix of platinum and rhodium. No diesel particulate filter (DPF) was used, conforming to approximating Euro 4 emission control regulations. The auto-equivalent version of this engine has been used in several VW polo and Jetta models in the early 2000's and was chosen as an example of light-duty diesel engine. The aftertreatment was selected to meet Euro 4 emission control regulations required for such models.~~ Engine running parameters (*i.e.* rpm, load, and throttle) were controlled using a dedicated software package (Armfield Ltd, Hampshire, UK) ~~on a separate PC.~~ The engine temperature was measured *via* an in-built thermocouple located inside the engine exhaust pipe, next to the engine. ~~The DOC temperature has been inferred from the measured exhaust temperature. The DOC temperature will be lower than the measured exhaust temperature, due to the DOC being located further down the exhaust pipe.~~ A 2-meter-long, 2-inch bore, stainless steel tube with a computer controlled pneumatic valve, was used to allow the engine emissions to be introduced into the MAC or diverted to waste. The timed control of the pneumatic valve allowed a proportion of the exhaust emissions to

be introduced into the chamber, controlling dilution. The final exhaust dilution ratios were calculated from the measured CO₂ concentration prior to, and after the introduction of the exhaust emissions. Further information regarding the exhaust dilution calculations can be found in Whitehead et al. (2017, in preparation). The engine was fuelled with standard European (EN590 specifications, Euro 5 compliant) ULSD obtained from a local fueling station. Two batches of fuel were obtained, the first in June 2014 (batch A) and the second in November 2014 (batch B). A second batch of fuel was required due to a considerable increase in the number of planned experiments. The fuel batches were of the same specification and obtained from the same local fueling station. Batch A was used in experiments 1 to 9 and batch B in experiments 10 to 16 (see Table 1 and section 3.1.1). The sulphur content was < 10 ppm. Further information regarding the standard European ULSD fuel specifications can be found in 2009 EC directive (EU, 2009).

2.3 Experimental design

A series of experiments were performed in July to August 2014, November 2014, and September to October 2015, as a part of the project, COMbustion PARTicles in the atmosphere (Com-Part). Experiments were designed to systematically characterise the chemical and physical transformations of primary and secondary particles emitted from a light-duty diesel engine under a range of atmospheric dilution and oxidation conditions. The work characterised the transformation of gaseous and particulate phase emissions across a range of steady-state engine conditions. The results shown here, focus on the effect of different engine conditions on the composition and abundance of VOC-IVOCs in the raw exhaust emissions, which formed a subset of the total number of experiments performed. The experimental descriptions and engine operating parameters discussed here, can be found in Table 1. A range of engine conditions were studied, including: (i) engine speed, ranging from 1150 rpm (idle) to 3000 rpm (maximum engine output), (ii) engine load, ranging from 0 % (no load) to 53 % (the maximum load which could be safely applied to by the dynamometer in the experimental setup), (iii) emission control devices (with and without the DOC) and, (iv) ‘driving scenarios’ (see below for further details). The MAC was filled with clean air prior to the introduction of the exhaust emissions. Exhaust dilution ratios were varied to represent a range of ambient conditions from near to downwind of an emission source, capturing the chemical and physical transformations of semi-volatiles in the exhaust emissions with varying ambient dilutions.

The majority of experiments focused on steady-state engine conditions, where selected engine running parameters were applied to the engine and the engine temperature allowed to stabilise, prior to the introduction of the exhaust emissions into the MAC. Steady-state engine conditions are (defined here, as a constant engine temperature within ±10% of the steady-state average,) were achieved prior to the introduction of the exhaust emissions into the MAC, unless otherwise stated. Steady-state engine conditions were not performed for the ‘driving scenario’ (exp. 8 and 9, see Table 1) and achieved for the cold-start experiments (exp. 6, 7 and 14, Table 1), with the cold-start experiments requiring exhaust injection emissions injected into the MAC after ~ 1 to 2 minutes within one minute of engine start-up (i.e. cold-engine). A sequence of engine conditions was performed for the driving scenario experiments, with the injection of the exhaust emissions into the MAC after the completion of the

sequence, but prior to achieving steady-state engine conditions. These experiments were performed to gain a greater insight into engine conditions controlling VOC-IVOC emission rates. The sequence of engine conditions used in the driving scenario experiments, 'cold loaded' (exp. 8, Table 1) and 'warm idle following load' (exp. 9, Table 1) are shown in Table 1, and SI Figure S2. All experiments except experiment 3 (see Table 1) were performed with the DOC. This allowed the combined effect of the DOC and different engine conditions on the exhaust emissions to be observed; engine conditions most representative of on-road diesel vehicles. The engine was fuelled with a standard low sulphur diesel obtained from a local fueling station. Two batches of fuel were used. Batch A was used in experiments 1 to 9 and batch B in experiments 10 to 16 (see Table 1 and supplementary information, SI).

2.43 TD-GC×GC-FID

VOC-IVOC exhaust emissions were measured using thermal desorption comprehensive two-dimensional gas chromatography with a flame ionisation detector (TD-GC×GC-FID) operating at 200 Hz. A TT24-7 thermal desorption unit (Markes International, Llantrisant, UK) with an air server attachment was used for sample collection. The inlet of the TD unit was connected to MAC using ~ 2.5 meters of heated 1/4" stainless steel tubing. The stainless steel tubing was heated to ~ 70 °C to reduce condensational losses of VOCs. An in-line unheated particulate filter prevented sampled particles from entering the TD unit. The in-line filter was replaced prior to each experiment, minimising particulate loadings. A clean air diaphragm pump (model PM25602-86, KNF Neuberger, Oxfordshire, UK) was used to extract an overflow of sample air from the MAC, a proportion of which was sampled into the TD unit. Two sequential glass traps cooled to -20 °C in an ethylene glycol bath were used to remove water vapour from the sampled air. No significant VOC losses have been found using this method of water vapour removal (Lidster, 2012). Air samples were trapped onto Tenax sorbent tubes (Markes International, Llantrisant, UK) held at -10°C during sampling (26 minute sampling duration) and heated to 230°C upon desorption.

An Agilent 7890 GC (Agilent Technologies, Wilmington, USA) with a modified modulation valve, consisting of a 6-port, 2-way diaphragm valve (Valco Instruments, Texas, USA) and 50 µL sample loop (Thames Resteck, UK) was used (see Lidster et al. (2011) for further information). Cryogenic cooling (liquid CO₂, BOC, UK) was used to re-focus the sample on the head of the primary column upon desorption. Compound separation was achieved using a primary 25 meter 5% phenyl polysilphenylene-siloxane column (BPX5, SGE, Ringwood, Australia) with a 0.15 mm internal diameter and 0.4 µm film thickness, and a secondary 7-meter polyethylene glycol column (BP20 SGE, Ringwood, Australia) with a 0.25 mm internal diameter and 0.25 µm film thickness. Helium (CP grade, BOC, UK) was used as the carrier gas. Primary and secondary column pressures were controlled using an electronic pneumatic control (Agilent 7890 EPC) and were set at 50 and 23 psi, respectively. The modulator was heated to 120°C with a 5 second cycle time, comprising of 0.3 second injection and a 4.7 second sample introduction. The oven temperature program consisted of a two-stage ramp; holding at 70°C for 1 minute, increasing to 160°C at 16 minutes (6°C min⁻¹), then 200°C at 20 minutes (10°C min⁻¹) with an additional 2-minute hold, giving a total runtime of

22 minutes. The FID heater was set to 300°C with a hydrogen flow of 30 ml min⁻¹ (CP grade, BOC, UK) and an air flow of 300 ml min⁻¹ (BTCA 178 grade, BOC UK).

5 A National Physical Laboratory (NPL30, Teddington, UK) gas standard (see SI) was used to monitor instrument variability over the course of the experiments. VOC-IVOC concentrations were determined using either the NPL gas standard or the relative response factors (RRF) of liquid standards (see SI for further information). Calibrations were performed weekly using the NPL gas standard, or more frequently during instrument maintenance periods. The instrument detection limits for the investigated compounds can be found in the SI of Dunmore et al. (2015). Where possible, compoundsVOCs were integrated using GC Image software (Zoex Corporation, Houston, USA). The abundance of VOC-IVOCsVOCs in the diesel exhaust emissions and the fast method runtime, resulted in some peaks having poor resolution. The automated peak integration in the GC Image software package was unable to distinguish closely eluting peaks, resulting in the use of one-dimensional chromatographic integration using Chemstation (Agilent, CA, USA). The minimum peak volume was set to 10 pixels for the automated peak integration in GC Image software. Only samples where no changes had been made to the chamber conditions were analysed. The exhaust emissions were blank subtracted using the chamber background measurement/s prior to the introduction of the exhaust emissions. In two experiments (exp. 1 and 6, see Table 1), the chamber background measurements were deemed unsuitable for the use of blank subtraction due to changing chamber conditions (*e.g.* cleaning cycle had not completed before blank sampling had started). Instead, the most recent chamber background measurement to that experiment was used. The GC×GC-FID started sampling during chamber cleaning and sampled for 26 minutes per analysis. The sampling start time was on average 13 minutes after exhaust injection (see SI Table S2). A minimum of two replicate measurements of the exhaust emissions was performed for the majority of experiments. The emission rates shown are averages of the replicate measurements. No apparent losses of the VOC-IVOCs were observed during sampling. The relative standard deviation from replicate measurements, of the investigated compounds over ~2 hours of sampling (longest sampling time period investigated), ranged between 1.9 to 14.2%, with an average of 6.4% (exp. 6, see Table 1 and SI Table S2).

2.5 Liquid fuel analysis

25 The two batches of ULSD fuel (see section 2.2 and 3.1.1) were analysed using comprehensive two-dimensional gas chromatography (model 6890N, Agilent Technologies, UK) coupled to a time-of-flight mass spectrometer (Pegasus 4D, Leco, MI, USA) (GC×GC-TOFMS). Compound separation was achieved using a primary 15 meter 5% phenyl polysilphenylene-siloxane (BPX5, SGE, Ringwood, Australia), column with a 0.25 mm film thickness and 0.25 mm internal diameter, and a secondary 2 meter 50% phenyl polysilphenylene-siloxane (BPX50, SGE, Ringwood, Australia) column with a 0.25 mm film
30 thickness and 0.25 mm internal diameter. Samples were introduced into the GC×GC-TOFMS using a Gerstel multipurpose sampler (MPS 2, Gerstel, USA) with dedicated controller (model C506, Gerstel, USA). A 1 µL injection volume was used with a split ratio of 100:1. The transfer line was set to 270°C. Cryo-jet modulation cooling was used to achieve comprehensive two-dimensional separation. Helium (CP grade, BOC, UK) was used as the carrier gas with a constant flow rate of 1.5 ml min⁻¹

1. The oven starting temperature was set to 65°C with a 0.2 minute hold, followed by a temperature ramp of 4°C min⁻¹ to 240°C, with a further 10 minute hold. The modulator and secondary oven temperature was set to 15°C and 20°C above the oven temperature, respectively. The TOFMS acquisition rate was set to 50 spectra per second, with a scan range of mass-to-charge (*m/z*) 35 to 500. The data was analysed using Leco ChromaTOF software version 4.51.6 (Leco, MI, USA). Compounds were identified using the National Institute of Standard and Technology (NIST) standard reference database (version 11).

3. Results and discussion

A series of experiments were performed ~~as a part of which investigated the project, COMbustion PARTicles in the atmosphere (Com-Part), investigating the effect of VOC emission rates from a light duty VW diesel engine operated under~~ different engine conditions (*i.e.* speed, load, 'driving scenarios'), exhaust dilution ratios and ~~with/without~~ emission control devices (with and without the τ -DOC) on the composition and abundance of VOC-IVOCs in the exhaust emissions from a light duty VW diesel engine.~~)-~~ The experimental dates, descriptions and engine operating parameters are shown in Table 1. This study focuses on steady-state engine conditions, allowing the direct comparison of engine speed and load on VOC-IVOC emission rates, which would otherwise not be captured with the use of transient driving cycles. A variety of engine loads and speeds were investigated, ranging from 0 (no load) to 53% load (maximum load which could be safely applied by the dynamometer in the experimental setup) and a speed of 1150 (idling) to 3000 rpm (maximum engine output). Further details regarding the experimental design can be found in section 2.3. A proportion of the exhaust emissions from each experiment (see Table 1) were introduced into the MAC. The MAC was used as a holding-cell, allowing multiple instruments and instruments requiring longer sampling times than near-real time to be used.

VOC-IVOC emissions were measured using TD-GC×GC-FID. In total, 16 individual ~~VOCs~~ and 8 groups of compounds were speciated. The individual ~~compounds~~VOCs included nine single-ring aromatics: benzene, toluene, ethyl benzene, meta- and para-xylene (grouped), ortho-xylene, styrene, 1,3,5-TMB, 1,2,4-TMB and 1,2,3-TMB, and 7 *n*-alkanes from *n*-heptane to *n*-tridecane. Grouped ~~compounds~~VOCs consisted of C₇ to C₁₃ branched aliphatics grouped by carbon number and single-ring aromatics with three carbon substitutions (*i.e.* those in addition to the trimethylbenzene isomers above). The emission rates of *n*-tridecane and the C₁₃ branched aliphatic grouping were not measured in some experiments due to a shift in the instrument retention time, resulting in these species not being observed. The saturation concentration (C*, μg m⁻³ (Donahue et al., 2006)) of the speciated ~~compounds~~VOCs ranged between 10⁵–10⁸ μg m⁻³, classifying these species as intermediate to volatile organic compounds (VOC-IVOCs). The most abundant volatility fraction of IVOCs from diesel exhaust emissions were measured, see Zhao et al. (2015) for further information. An annotated chromatogram displaying the speciated ~~compounds~~VOCs, is shown in Figure 1. The use of two different stationary phases in GC×GC allows compounds to be separated by two physical properties, such as boiling point and polarity, as shown here (see Figure 1). This two-dimensional separation, creates a characteristic space where compounds are grouped by similar physical properties (*e.g.* aromatic and aliphatic bandings (see Figure 1, *c.f.*

Hamilton and Lewis (2003), Dunmore et al. (2015),- aiding in the identification of unknowns. This characteristic space, in combination with the use of commercially available standards and the elution patterns observed in previous work using this instrument (Dunmore et al., 2015), allowed 8 compound VOC groupings to be identified. The identification of all the individual compounds VOCs (except styrene, see SI) were confirmed using commercially available standards. The emission rates of the individual and grouped compounds VOCs and their percentage contribution to the total speciated VOC-IVOC $\sum_{Sp} VOC$ emission rate (hereafter referred to as $\sum_{Sp} VOC$), in each experiment, are shown in the SI Tables S3S2 to S6S5. No corrections have been made for gas-phase absorption to PM in this work. Gas-phase absorption to PM is negligible due to the relatively high vapour pressures of the compounds speciated, low VOC-IVOC mixing ratios and small amount of aerosol mass present after exhaust dilution.

10 3.1 Experimental reproducibility

The reproducibility of the measured VOC-IVOC emission-emissions rates with different engine conditions and exhaust dilution ratios were investigated and are discussed below in the SI. The VOC-emission rates from two replicate cold-start experiments (1150 rpm, 0% load, exp. 6 and 7, see Table 1) and two replicate and-warm with load (WWL) experiments (2000 rpm, 30% load, exp. 15 and 16, see Table 1) are shown in Figure 2 and SI Figure S3, respectively. Both replicate experiments were performed with engine conditions using similar exhaust dilution ratios. The displayed very good reproducibility, with all VOC emission rates from the replicate cold-start and WWL experiments displayed excellent reproducibility, considering the vast number of variables in these experiments (e.g. combustion and DOC HC removal efficiency). All emission rates, except styrene in one experiment (<below limit of detection), were observed to be within the calculated uncertainty (see SI). The emission rates from two replicate warm high load experiments (2500 rpm, 40% load, exp. 1 and 2, see Table 1) with different exhaust dilution ratios is shown in SI Figure S4. The exhaust dilution ratios in these experiments were 166 and 313 in experiments 1 and 2 (see Table 1), respectively. The emission rates in these experiments are relatively comparable. Only one measurement of the exhaust emissions was made in each experiment. The majority of experiments had a minimum of two replicate measurements of the exhaust emissions (see SI Table S1), possibly accounting for slight differences observed in the measured VOC-IVOC emissions rates.

The emission rates from two replicate WWL experiments (2000 rpm, 30% load, exp. 4 and 5, see Table 1) error. The reproducibility of the VOC emission rates at the extremes of the investigated exhaust dilution ratios are shown in SI Figure S5. The exhaust dilution ratios were 1158 and 60 in experiments 4 and 5, respectively. The emission rates in these experiments however displayed some disagreement. The lack of an engine thermocouple was unresponsive temperature measurement during one of these experiments (exp. 4, see Table 1). Consequently, it is not known if may account for the differences observed (i.e. steady-state engine conditions were temperature may not have been achieved prior to the introduction of the exhaust emissions into the MAC and whether the engine temperature upon injection was comparable to replicate experiment, possibly accounting of the observed differences in the VOC-IVOC emission rates.) Nevertheless, no experiments

with such large differences in the exhaust dilution ratios have been directly compared in the following work and where engine conditions are compared, experiments with similar exhaust dilution ratios and engine temperatures have been used. These experiments highlight the importance of replicate measurements and the comparison of VOC-IVOC emission rates from experiments with similar engine temperatures. A propagation of errors was calculated to determine the uncertainty in the measured emission rates and is discussed in the SI. The uncertainty in the measured emission rates for the investigated compounds, ranged from 6 to 50 %, with an average of 22%.

3.1.1 ULSD fuel: Batch A and B

Two batches of ULSD fuel were used (see section 2.2). Both batches of fuel were of the same specification and obtained from the same local fueling station. One batch was purchased in June 2014 (batch A, used in experiments 1 to 9) and the second, in November 2014 (batch B, used in experiments 10 to 16). The emission rates from three replicate cold-start experiments, two using fuel batch A (exp. 6 and 7, see Table 1) and one using fuel batch B (exp. 14), are shown in Figure 3. From Figure 3, it can be observed that there is a considerable difference in the emission rates of the C₇ to C₁₂ branched aliphatics between replicate experiments 6 and 7, and experiment 14. The emission rates of the C₇ to C₁₂ branched aliphatics decreased by a factor of ~ 4 with the use of fuel batch B (exp. 14). The excellent agreement of the emission rates between replicate cold-start experiments 6 and 7, suggests the compositional differences observed in experiment 14, is the result of a slight difference in the fuel composition between batches A and B. GC×GC-TOFMS was used to further investigate any compositional differences between the fuel batches. An extensive analysis of the diesel fuel was not performed. The aim of this analysis was to investigate whether there were any apparent differences in the fuel composition that would prevent a direct comparison of the emission rates from fuel batches A and B. An extracted ion chromatogram for m/z 57 (dominant aliphatic fragment ion) from fuel batch A and B is shown in SI Figure S6 A and B, respectively. The chromatograms were normalised to the total peak area to allow direct comparison of peak intensity between the chromatograms. The highlighted region in SI Figure S6 displays straight-chain and branched aliphatics with a carbon number range of approximately C₇ to C₁₂ (determined from the NIST library). The peak intensities in the chromatograms from fuel batches A and B are largely comparable, except for the highlighted region, where a slightly lower peak intensity is observed in fuel batch B. As a result, the emission rates from fuel batches A and B have not have been directly compared. The reason for the observed compositional differences between fuel batches A and B is unclear, although suggests a possible change in the refining process between the purchase of both fuel batches used.

3.21 Engine load

The \sum SpVOC emissions were observed to decrease with increasing engine load, with \sum SpVOC emission rates of 1019±65, 365±24 and 70±4 mg kg⁻¹ at 30, 40 and 53% load, respectively (see SI Table S7S6). This trend of decreasing VOC emission rates with increasing engine load has been observed in a number of previous studies for light-duty and medium-duty diesel vehicles (Cross et al., 2015; Shirneshan, 2013; Chin et al., 2012; Yamada et al., 2011) and can be explained by considering, irrespective of the engine operation. At low engine temperatures (i.e. low engine loads use of different emission control devices

(with/without DOC, exhaust gas recirculation) and diesel fuel composition (low sulfur diesel (shown here) and idling conditions), the fuel flow is increased to provide easily combustible conditions within the engine cylinder. This additional ~~ultra-low sulfur diesel~~ fuel flow creates a rich air/fuel ratio, where there is insufficient oxygen to burn the fuel, resulting in incomplete combustion and higher VOC-IVOC emission rates from the unburnt fuel. As the engine temperature increases (e.g. with increasing engine load), the in-cylinder oxidation rate increases as the fuel components become more easily combustible at higher temperatures, increasing ~~ULSD~~, suggesting engine combustion efficiency and decreasing VOC-IVOC emission rates (Heywood, 1988). ~~largely controls emission rates.~~ The effect of different engine loads, at a constant speed, on the VOC-IVOC emission rates is shown in Figure ~~4A2A~~. The VOC-IVOC emission profiles are characteristic of typical diesel exhaust emissions with a DOC (c.f. (Chin et al., 2012; Bohac et al., 2006)), displaying a high abundance of C₈ to C₁₂ *n*-alkanes and C₈ to C₁₃ branched aliphatics, with a smaller contribution from single-ring aromatics. The carbon number distribution of the *n*-alkanes and branched aliphatics at 30% and 40% engine load are comparable. Branched aliphatics display an increase in abundance from C₇, reaching peak concentration at C₁₀, followed by a decrease to C₁₃, similar to that observed in Bohac et al. (2006). Straight-chain alkanes do not display the same increase and decrease in abundance, with the emission rates of *n*-nonane and *n*-dodecane greater than *n*-undecane, displaying no obvious trend. At 53% engine load, the VOC emission profile changes. The most abundant *n*-alkane and branched aliphatic grouping shifts to higher carbon numbers at higher loads, changing from *n*-nonane to *n*-undecane and from C₁₀ to C₁₂ branched aliphatics. The *n*-alkanes now display a sequential increase and decrease in their emission factors, as observed with the branched aliphatics. This compositional shift to higher carbon number species under higher engine loads, has also been observed in Chin et al. (20122015) for *n*-alkanes from an Isuzu 1.7L diesel engine fuelled with ULSD. Whilst no explanation was provided for this observation, Chin et al. (20122015) found the most abundant *n*-alkane shifted from *n*-nonane at idling conditions (800 rpm) with no load, to *n*-tridecane at 2500 rpm with maximum applied engine load (900 brake mean effective pressure, kPa).

The percentage contribution of the individual and grouped ~~VOCs~~ VOCs to the \sum SpVOC emission rate in each experiment, is shown in Figure ~~4B2B~~. The percentage composition from a cold-start experiment (exp. 14) has also been included on the left of Figure ~~4B2B~~, to provide a comparison between cold idle engine conditions (which has a compositional profile most similar to unburnt fuel) and different engine loads. The percentage contribution of the individual and grouped ~~VOCs~~ VOCs to the \sum SpVOC emissions changed considerably with different engine loads. All aromatics, except benzene, displayed a nonmonotonic behaviour with increasing engine load; their percentage contribution is high at cold idle and 40% load, with a smaller contribution at 30% and 53% load. This nonmonotonic behaviour has also been observed in Cross et al. (2015). Cross et al. (2015) investigated the load-dependant emissions from a 5.9L medium-duty diesel engine, fuelled with ULSD. It was found that the fractional contribution of oxidised species and aromatics (not explicitly mentioned but shown in the data) varied inconsistently with increasing engine load. The reason for this nonmonotonic behaviour is currently unclear. The percentage contribution of benzene generally decreased with increasing engine load. Interestingly, the percentage contribution of the *n*-alkanes continued to decrease from cold idle to 40% load, followed by a considerable increase

at 53% load. At 53% load, the *n*-alkanes represented 55% of the Σ SpVOC emissions, 1.6 times greater than observed in the cold-start experiment. Conversely, branched aliphatics displayed the opposite trend. The percentage contribution of the branched aliphatics continued to increase from cold idle to 40% load, followed by a considerable decrease at 53% load, to approximately the same percentage contribution observed in cold-start experiment.

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This change in the percentage contribution of the *n*-alkanes and branched aliphatics at 53% engine load, can be explained by considering the DOC HC removal efficiency and the internal combustion temperature. The DOC HC removal efficiency is strongly dependant on working temperature. Below 200°C the DOC HC removal efficiency is close to zero, rising sharply to near 100% HC removal efficiency at ~ 430°C (Korin et al., 1999; Roberts et al., 2014; Majewski and Khair, 2006; Russell and Epling, 2011). From cold idle to 40% engine load, the engine temperature increased from < 100°C at cold idle, to 445°C at 40% load. The DOC HC removal efficiency is thus increasing from near zero at cold idle, to near maximum at 40% load, ~~possibly explaining why a sequential increase and decrease in the percentage contribution of the branched aliphatics and *n*-alkanes, respectively, is observed.~~ At 53% load, the steady-state engine temperature reached 700°C. The DOC HC removal efficiency was near maximum at 40% load and it is therefore unlikely that the DOC would account for such a considerable shift in the percentage contribution of the *n*-alkanes and branched aliphatics at 53% load. This shift in the composition is most likely the result of the considerably higher engine temperature, resulting in the fragmentation of higher molecular weight *n*-alkanes as a result of increased internal combustion efficiency. Straight-chain alkanes are more easily fragmented during combustion than branched aliphatics (Fox and Whitesell, 2004), resulting in a higher percentage contribution of smaller (*i.e.* C₇ to C₁₂) *n*-alkanes. ~~In addition, the higher percentage contribution of the *n*-alkanes to the Σ SpVOC emissions at 53% engine-load, in comparison to cold idle. The compositional profiles from 0 to 40% engine load, display the combined effect of increasing, further supports the increased fragmentation of higher molecular weight *n* alkanes at high engine temperatures and thus, high engine combustion efficiency and DOC HC removal efficiency, possibly explaining why a higher percentage contribution of C₇ to C₁₂ *n*-alkanes is not observed with increasing engine load as a result of increasing engine combustion efficiency (*i.e.* DOC is likely masking the effect of increasing combustion efficiency on Σ SpVOC emissions).~~

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efficiencies.

3.3.2 DOC removal efficiency

The HC removal efficiency of the DOC was investigated by performing two repeat experiments (exp. 2 and 3, ~~see~~ Table 1), with and without the DOC. The additional backpressure created due to the in-line DOC, appeared to have no effect on engine operation, allowing a direct comparison between experiments 2 and 3. The engine speed and load was set to 2500 rpm and 40% load, respectively. The steady-state engine temperature in both experiments was 450°C, ~~ensuring~~ the DOC was near maximum HC removal efficiency (Korin et al., 1999; Roberts et al., 2014; Majewski and Khair, 2006; Russell and Epling, 2011). The HC removal efficiency was calculated using the equation shown in Roberts et. al. (2013). The removal efficiency of the DOC for the speciated ~~compounds~~ VOCs is shown in Table 2. The DOC removed 46 ± 10 % of the Σ SpVOC emissions,

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with 83 ± 3 % for the single-ring aromatics and 39 ± 12 % for the aliphatics (branched and straight-chain). A typical DOC is expected to remove 50 to 70% of the total HC emissions (Johnson, 2001; Alam et al., 2016). For the investigated compounds, the total DOC removal efficiency is at the lower limit of this expectation. The DOC removal efficiency for styrene, m/p- and o-xylene, ethylbenzene (C_2 aromatic substitution grouping) and benzene, was greater than 90%. In addition, the trimethylbenzenes (TMB) were not observed with the use of the DOC (~ 100 % removal efficiency). This high HC removal efficiency however, was not observed for all the single-ring aromatics. Toluene had a relatively poor removal efficiency in comparison, at 59 ± 9 %. Furthermore, the removal efficiency of the unspecified C_3 aromatic substitution grouping (*i.e.* less branched aromatic isomers of TMB) was determined to be 63 ± 22 %, suggesting the isomeric structure influences removal efficiency, possibly the result of reactivity and/or adsorption to the metal binding sites in the DOC (*c.f.* (Salge et al., 2005; Russell and Epling, 2011)).

Generally, the HC removal efficiency decreased with increasing carbon chain length. This was particularly evident with the branched aliphatics, with the removal efficiency decreasing from 72% to 14 % from C_7 to C_{12} , with a sharp decrease in the removal efficiency from C_{10} to C_{12} . Analogous to the branched aliphatics, the *n*-alkanes displayed the same rapid decrease in the HC removal efficiency between *n*-decane and *n*-dodecane, with the DOC observed to have no effect on the emission of *n*-dodecane. The removal of *n*-alkanes in the DOC have been found to decrease with increasing carbon chain length, a result of the greater number of adjacent sites in the DOC required to achieve absorption (Yao, 1980; Russell and Epling, 2011), supporting the results shown here. However, recently Alam et. al. (2016) investigated the HC removal efficiency of a similar specification DOC (*i.e.* mixed platinum and rhodium)DOC for C_{12} to C_{33} *n*-alkanes, among other species. It was found that the DOC HC removal efficiency did not continue to decrease with increasing carbon chain length, rather decreasing from C_{12} to C_{16} , followed by an increase (C_{17} to C_{23}) and further decrease (C_{24} to C_{32}). Few studies have investigated the HC removal efficiency of individual species and grouped counterparts, expressing DOC HC removal efficiency as total HC, with no reference to possible compositional and structural effects, which based on the results shown in this study and Alam et. al. (2016), require further study.

25 **3.4.3 Driving scenarios**

The VOC-IVOC emission rates from several driving ‘scenarios’ were investigated. The driving scenarios included either; (i) a single applied engine load and speed, and injection before a steady-state engine temperature had been achieved (similar to transient conditions) or, (ii) a sequence of different engine loads and speeds, during which and injection after a steady-state engine temperature ~~was had been~~ achieved. These experiments were performed to gain a greater insight into the factors controlling VOC-IVOC emission rates. VOC emissions in real world conditions. Three experiments were performed, cold-start (exp. 6), cold loaded short journey (exp. 8) and warm idle following load (WIFL, exp. 9). The sequence of engine conditions used in each of these experiments can be found in SI Figure S2. Cold loaded short journey included a cold engine start followed by the immediate application of 1500 rpm and 20% load, with a one minute hold before injection. WIFL included a cold engine

start, followed by the immediate application of 2000 rpm and 28-30% load with a 7-minute hold (during which a steady-state engine temperature was achieved), followed by one minute of idling speed (1150 rpm) and 0% load before injection. The $\sum\text{SpVOC}$ emission rates in each experiment was 9268 ± 699 , ~~2902~~~~2904~~ ± 199 and 1438 ± 96 mg kg⁻¹ in the cold-start, cold loaded short journey and WIFL, respectively. The application of 1500 rpm and 20% load for 1 minute (short-journey) resulted in a decrease in the $\sum\text{SpVOC}$ emissions by a factor of ~ 3 , in comparison to the cold-start engine conditions; highlighting the importance of engine combustion efficiency on VOC-IVOC emission rates. The VOC-IVOC emission rates and the exhaust composition ~~in~~ of the investigated driving ~~scenario experiments~~~~scenarios~~ can be observed in Figure ~~53~~.

The engine temperature in the cold-start and cold loaded short journey experiments was 85°C and 169°C, respectively. In the WIFL experiment, the engine temperature reached 290°C during steady-state, decreasing to 150°C upon injection. The $\sum\text{SpVOC}$ emission rates were lower in the WIFL experiment than observed in the cold loaded short journey experiment, where a higher engine temperature was measured upon injection. The HC removal efficiency of the DOC below 200°C is close to zero (Korin et al., 1999; Roberts et al., 2014; Majewski and Khair, 2006; Russell and Epling, 2011), suggesting the lower $\sum\text{SpVOC}$ emissions observed in the WIFL experiment, is the result of increased combustion efficiency from the higher engine speed and load applied before idling conditions. Engine ‘warm-up’ increases the temperature of the lubricant, coolant and engine components, reducing friction and increasing combustion efficiency, thus resulting in less unburnt fuel emissions in the exhaust gas (*c.f.* (Roberts et al., 2014)). This increased combustion efficiency in the WIFL experiment is also supported by the exhaust gas composition (see Figure ~~5B2B~~). Considerably higher engine temperatures resulted in a greater proportion of higher molecular weight *n*-alkanes in the exhaust gas, an observation which could not be explained by the DOC and was attributed to combustion ~~(see section 3.2)~~. The engine temperatures in all three experiments were below 200°C and consequently, the DOC had a minimal effect on HC removal in these experiments. Therefore, the observed compositional changes in exhaust gas is the result of increasing combustion efficiency, which is supported by the sequential increase in the abundance of the *n*-alkanes as the internal combustion efficiency increases. The relationship between internal combustion efficiency and engine temperature is relatively linear (e.g. (Mikalsen and Roskilly, 2009)), with the exception of high engine loads and relatively low speeds (not performed here), where the engine combustion efficiency and temperature eventually plateau due to a too lean air/fuel ratio, resulting in incomplete combustion (see Haywood (1988) for further information). These experiments also provide additional information on the effect of the DOC on the exhaust gas emissions. In the engine load experiments (see section 3.2), the combined effect of increasing combustion efficiency and DOC HC removal efficiency on the exhaust gas emissions were observed from 0 to 40 % engine load, making it difficult to separate the effects of both factors on the exhaust gas composition. However, this observation of increasing *n*-alkane abundance with increasing engine combustion efficiency ~~also~~ suggests that the increase in the abundance of the branched aliphatics at cold idle (exp. 14), 30% (exp. 12) and 40% load (exp. 13) (see section 3.2 and Figure 4B2B), respectively, is the result of the DOC fragmenting higher molecular weight branched aliphatics with increasing HC removal efficiency; indicating that the branched aliphatics are more easily fragmented in the DOC than *n*-alkanes, possibly the result of the fewer binding sites required in the DOC for adsorption.

The carbon number distribution of the branched aliphatics and *n*-alkanes in all three driving scenario experiments were comparable, dissimilar to the carbon number shift observed at high engine loads (*i.e.* 53% load). Furthermore, the nonmonotonic behaviour observed with the single-ring aromatics with increasing engine load was only observed with benzene.

5 The percentage contribution of the C₃ aromatic substitution grouping to the Σ SpVOC emissions, displayed no obvious change with increasing combustion efficiency (within the calculated uncertainty). However, the abundance of the C₂ aromatic substitution grouping and toluene generally decreased with increasing combustion efficiency, with the percentage contribution observed to plateau in the cold-start and cold loaded short journey experiment, followed by a decrease in the WIFL experiment.

3.5 Atmospheric implications~~3.4 Comparison with on-road diesel emissions~~

10 The measured Σ SpVOC emission rates in each experiment (ordered from highest to lowest) are shown in Figure 64, along with the corresponding engine load, speed and temperature. The Σ SpVOC emission rates varied significantly with different engine conditions, ranging from 70 to 9268 mg kg⁻¹. The aliphatics represented 56 to 97% of the Σ SpVOC emission rates, with the single-ring aromatics accounting for the remainder. The highest Σ SpVOC emissions were observed in a cold-start experiment (exp. 6), with no applied load and idling speed (1150 rpm). Conversely, the lowest Σ SpVOC emissions were
15 observed in the experiment with highest applied engine load and speed (exp. 11, 3000 rpm, 53% load). The Σ SpVOC emissions were observed to decrease with increasing engine load and temperature, and to a lesser degree, engine speed. This result is consistent with increased combustion efficiency and DOC HC removal efficiency with increasing temperature, similar to that observed in previous studies (*e.g.* (Cross et al., 2015; Chin et al., 2012)).
20 The direct comparison of emission rates is difficult due to the vast number of differences between studies (*e.g.* types of speciated VOCs, vehicle types, emission control devices *etc.*). Furthermore, the majority of studies have investigated diesel exhaust emissions using chassis dynamometers, averaging emissions over entire driving cycles and often reporting emission rates as VOC mass per distance travelled; emissions and units which are not directly comparable with the emission rates shown here.

The different types emission rates of the C₉ to C₁₃ *n*-alkanes in this study, were compared with emission factors of instruments used to measure on-road diesel exhaust emissions and the difficulties in from a highway tunnel in Oakland California (Caldecott tunnel). Gentner et al. (2013) measured gasoline and diesel exhaust tunnel emissions, and using a fuel composition based method, determined the measurement fraction of low volatility species, has in-part, resulted in considerable variation in the types emissions which were from diesel exhaust. The emission factors in their study represent a diesel fleet primarily consisting of 'speciated' compounds between studies, making the direct comparison of emission rates extremely difficult. For example,
25 Zhao et al. (2015) reported speciated and unspeciated IVOC emission rates from both medium-duty and heavy-duty diesel vehicles. In their study, speciated IVOCs included: straight and branched-chain alkanes, alkylcyclohexanes, unsubstituted and substituted polycyclic aromatic hydrocarbons and alkylbenzenes, with a volatility range of 10² to 10⁶ μ g m⁻³. Similarly, Cross et al. (2015) measured IVOC emission rates from a medium-duty diesel engine, driving at a steady speed of 80 km h⁻¹ on a
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4% incline through the tunnel. The emission rates reported in their study were based on compounds with a volatility range of $\sim 10^3$ to $10^7 \mu\text{g m}^{-3}$ and included cycloalkanes, bicycloalkanes, tricycloalkanes, straight and branched-chain aliphatics, and groupings of 'aromatics', 'oxidised' and 'remainder'. Moreover, Gordon et al. (2015) measured the of the C_9 to C_{13} *n*-alkanes in this study were converted to micrograms of carbon per litre of fuel burnt ($\mu\text{gC L}^{-1}$), based on the number of carbon atoms in each *n*-alkane and a liquid fuel density of 852 g L^{-1} . The emission rates of non-methane organic gases from medium-duty and heavy-duty diesel engines. In their study, speciated compounds included single-ring aromatics, straight and branched-chain aliphatics, cycloalkanes and non-aromatic carbonyls, with a volatility range of $\sim 10^6$ to $10^9 \mu\text{g m}^{-3}$. In this study, the factors of the C_9 to C_{13} *n*-alkanes which were within the reported error shown in Gentner et. al. (2013), can be observed in Figure 5. In total, 19 emission rates from a light-duty diesel engine were reported, based on the emissions of straight and branched-chain aliphatics and single-ring aromatics, with a volatility range of $\sim 10^5$ to $10^8 \mu\text{g m}^{-3}$. The investigated volatility range and chemical composition can have a considerable impact on the reported factors from 10 experiments, were comparable with the on road diesel emission rates (e.g. (Zhao et al., 2015)). Whilst the above studies have comparable units to factors. Interestingly, the emission rates shown in this work, factors in this study that were most comparable with the on road diesel emissions, were from experiments with relatively high engine speed and load, with an average speed of 2375 rpm and load of 35%. The on road diesel emissions will be representative of warm vehicles, ranging from slightly loaded (to account for driver and vehicle weight which is not included in this study) to loaded. The emission rates have not been compared due to the differences in vehicular type (medium-duty and heavy-duty vs. light-duty) and factors from experiments with low engine temperatures (i.e. cold start, short journey and WIFL) showed no agreement with the volatility and chemical composition of the speciated compounds. Further studies are required, providing on road diesel emissions as expected, with the emission rates of individually speciated compounds (where possible), factors observed to be 2 to facilitate direct comparison. 8 times greater.

Urban driving conditions are characterised by low engine speed, load and exhaust gas temperatures (c.f. (Franco et al., 2014; EEA, 2016)). Conversely, motorway or highway driving typically result in higher engine temperatures, due to increased engine speed and load. The results from this study show at low engine loads and speeds the emission rates of unregulated VOC-IVOCs per kilogram of fuel burnt, are considerably greater than emitted at higher engine speeds and loads. Furthermore, it was found that the exhaust gas composition varied depending primarily on combustion efficiency and DOC HC removal efficiency, both which are strongly dependent on working temperature (Korin et al., 1999; Roberts et al., 2014; Majewski and Khair, 2006; Russell and Epling, 2011). Diesel exhaust emissions contain thousands of compounds ranging from $\sim \text{C}_5$ to C_{22} , with contributions of up to C_{33} from lubricant oil (Alam et al., 2016; Gentner et al., 2017). Only a proportion of these emissions were speciated in this study. The measured compounds included aliphatics (branched and straight-chain) and single-ring aromatics with two and three carbon substituents, over a carbon range of C_6 to C_{13} . The narrow carbon range investigated is the result of instrument temperature constraints. The boiling points of compounds above $\sim \text{C}_{15}$ are too high to be removed from the column at the maximum operating temperature of the modulator, resulting in these species not being detected. Of the measured compounds, Of the measured VOCs, branched aliphatics generally dominated the exhaust gas composition. However,

at low engine temperatures ($< 150^{\circ}\text{C}$), the proportion of *n*-alkanes in the exhaust gas were observed to increase with increasing combustion efficiency and could be important in urban environments; straight-chain alkanes are more efficient at producing SOA than their branched counterparts (Presto et al., 2010; Tkacik et al., 2012; Lim and Ziemann, 2009). Previous studies have suggested liquid fuel based emission factors are consistent with unburnt fuel in diesel exhaust emissions. For example, Gentner et al. (2013) showed the majority of VOC and IVOC diesel exhaust emissions were within 70% uncertainty of liquid fuel based emission factors. This work shows as combustion efficiency increases, the contribution of smaller, more volatile *n*-alkanes in the exhaust gas also increases, the result of increased fragmentation of higher molecular *n*-alkanes. This may suggest liquid diesel fuel based estimates of SOA yields may be inconsistent with diesel exhaust SOA yields, particularly at high engine temperatures (*i.e.* high engine loads and speeds). In recent years, emission regulations have focused on reducing NO_x emissions from diesel vehicles with the introduction of emission control technologies, such as exhaust gas recirculation (EGR), lean-burnt NO_x traps and selective catalytic reduction (Yang et al., 2015). To our knowledge, there are no further emission control technologies planned for the reduction of total hydrocarbon mass or unregulated VOCs. The emission rates from only one diesel engine was investigated in this study. ~~However, the emission factors in this study were comparable to on road diesel vehicular emissions measured in Gentner et al. (2013), suggesting the results shown in this study are consistent with on-road diesel exhaust emissions. Furthermore,~~ several compositional changes in the exhaust gas were comparable with previous studies, suggesting compositional changes are relatively consistent between studies. The emission control devices used in this study were Euro 4 compliant. Euro 4 emission control regulations were first implemented for all new vehicles from approximately January 2006, with Euro 5 emission control regulations starting post January 2011. In the European Union (EU), ~ 27% of all on-road vehicles (both gasoline and petrol) were bought between 2006 to 2011 and thus conform to Euro 4 emission control regulations (ACEA, 2017). Of these vehicles, 75% are diesel (ACEA, 2017) and thus ~ 20% of the current EU diesel fleet are Euro 4 compliant. ~~with different vehicular types (*e.g.* medium duty, heavy duty) and engine conditions.~~ To our knowledge, this is the first study which has explicitly discussed the effect of the DOC HC removal efficiency and combustion efficiency on the exhaust gas composition. With further work, changes in exhaust gas composition as a function of engine temperature, could be implemented into atmospheric models, improving model refinement and providing a better understanding of diesel exhaust emissions on local air quality.

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4. References

- Share of Diesel in New Passenger Cars: <http://www.acea.be/statistics/tag/category/share-of-diesel-in-new-passenger-cars>, access: 04/04/2017, 2016.
- [ACEA: ACEA Report: Vehicles in use Europe 2017, 2017.](#)
- 5 Alam, M. S., Zeraati-Rezaei, S., Stark, C. P., Liang, Z., Xu, H., and Harrison, R. M.: The characterisation of diesel exhaust particles - composition, size distribution and partitioning, *Faraday discussions*, 189, 69-84, 10.1039/C5FD00185D, 2016.
- Alkurdi, F., Karabet, F., and Dimashki, M.: Characterization, concentrations and emission rates of polycyclic aromatic hydrocarbons in the exhaust emissions from in-service vehicles in Damascus, *Atmos Res*, 120–121, 68-77, <http://dx.doi.org/10.1016/j.atmosres.2012.08.003>, 2013.
- 10 Alves, C. A., Lopes, D. J., Calvo, A. I., Evtuyugina, M., Rocha, S., and Nunes, T.: Emissions from light-duty diesel and gasoline in-use vehicles measured on chassis dynamometer test cycles, *Aerosol Air Qual Res*, 15, 99-116, 2015.
- Baldauf, R. W., Gabele, P., Crews, W., Snow, R., and Cook, J. R.: Criteria and Air-Toxic Emissions from In-Use Automobiles in the National Low-Emission Vehicle Program, *Journal of the Air & Waste Management Association*, 55, 1263-1268, 10.1080/10473289.2005.10464722, 2005.
- 15 [Ballesteros, R., Guillén-Flores, J., and Martínez, J. D.: Carbonyl emission and toxicity profile of diesel blends with an animal-fat biodiesel and a tire pyrolysis liquid fuel. *Chemosphere*, 96, 155-166, <https://doi.org/10.1016/j.chemosphere.2013.10.017>, 2014.](#)
- Bohac, S. V., Han, M., Jacobs, T. J., López, A. J., Assanis, D. N., and Szymkowicz, P. G.: Speciated Hydrocarbon Emissions from an Automotive Diesel Engine and DOC Utilizing Conventional and PCI Combustion, 2006.
- 20 Caplain, I., Cazier, F., Nouali, H., Mercier, A., Déchaux, J.-C., Nollet, V., Joumard, R., André, J.-M., and Vidon, R.: Emissions of unregulated pollutants from European gasoline and diesel passenger cars, *Atmospheric Environment*, 40, 5954-5966, <http://dx.doi.org/10.1016/j.atmosenv.2005.12.049>, 2006.
- Chin, J.-Y., Batterman, S. A., Northrop, W. F., Bohac, S. V., and Assanis, D. N.: Gaseous and Particulate Emissions from Diesel Engines at Idle and under Load: Comparison of Biodiesel Blend and Ultralow Sulfur Diesel Fuels, *Energy & Fuels*, 26,
- 25 6737-6748, 10.1021/ef300421h, 2012.
- Chirico, R., Clairotte, M., Adam, T. W., Giechaskiel, B., Heringa, M. F., Elsasser, M., Martini, G., Manfredi, U., Streibel, T., Sklorz, M., Zimmermann, R., DeCarlo, P. F., Astorga, C., Baltensperger, U., and Prevot, A. S. H.: Emissions of organic aerosol mass, black carbon, particle number, and regulated and unregulated gases from scooters and light and heavy duty vehicles with different fuels, *Atmos. Chem. Phys. Discuss.*, 2014, 16591-16639, 10.5194/acpd-14-16591-2014, 2014.
- 30 Cohen, A. J., Ross Anderson, H., Ostro, B., Pandey, K. D., Krzyzanowski, M., Künzli, N., Gutschmidt, K., Pope, A., Romieu, I., Samet, J. M., and Smith, K.: The Global Burden of Disease Due to Outdoor Air Pollution, *Journal of Toxicology and Environmental Health, Part A*, 68, 1301-1307, 10.1080/15287390590936166, 2005.

- Colville, R., Hutchinson, E., Mindell, J., and Warren, R.: The transport sector as a source of air pollution, *Atmospheric environment*, 35, 1537-1565, 2001.
- Cross, E. S., Sappok, A. G., Wong, V. W., and Kroll, J. H.: Load-Dependent Emission Factors and Chemical Characteristics of IVOCs from a Medium-Duty Diesel Engine, *Environmental science & technology*, 49, 13483-13491, 10.1021/acs.est.5b03954, 2015.
- de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *Journal of Geophysical Research: Atmospheres*, 110, n/a-n/a, 10.1029/2004JD005623, 2005.
- DEFA: Diesel Vehicle Emissions and Urban Air Quality - Second QUARG report, 1993.
- Donahue, N., Robinson, A., Stanier, C., and Pandis, S.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, *Environmental science & technology*, 40, 2635-2643, 2006.
- Dunmore, R. E., Hopkins, J. R., Lidster, R. T., Lee, J. D., Evans, M. J., Rickard, A. R., Lewis, A. C., and Hamilton, J. F.: Diesel-related hydrocarbons can dominate gas phase reactive carbon in megacities, *Atmos. Chem. Phys.*, 15, 9983-9996, 10.5194/acp-15-9983-2015, 2015.
- EEA: Explaining road transport emissions, 22, 2016.
- [EU: Official Journal of the European Union: Directive 2009/30/EC, L 140/88, 2009.](#)
- Fox, M., and Whitesell, J.: *Organic Chemistry*, Third ed., Jones and Bartlett, London, 1140 pp., 2004.
- Franco, V., Sánchez, F. P., German, J., and Mock, P.: Real-world exhaust emissions from modern diesel cars, 8, 2014.
- Fraser, M. P., Cass, G. R., and Simoneit, B. R. T.: Gas-Phase and Particle-Phase Organic Compounds Emitted from Motor Vehicle Traffic in a Los Angeles Roadway Tunnel, *Environmental science & technology*, 32, 2051-2060, 10.1021/es970916e, 1998.
- Gentner, D. R., Worton, D. R., Isaacman, G., Davis, L. C., Dallmann, T. R., Wood, E. C., Herndon, S. C., Goldstein, A. H., and Harley, R. A.: Chemical Composition of Gas-Phase Organic Carbon Emissions from Motor Vehicles and Implications for Ozone Production, *Environmental science & technology*, 47, 11837-11848, 10.1021/es401470e, 2013.
- Gentner, D. R., Jathar, S. H., Gordon, T. D., Bahreini, R., Day, D. A., El Haddad, I., Hayes, P. L., Pieber, S. M., Platt, S. M., de Gouw, J., Goldstein, A. H., Harley, R. A., Jimenez, J. L., Prévôt, A. S. H., and Robinson, A. L.: Review of Urban Secondary Organic Aerosol Formation from Gasoline and Diesel Motor Vehicle Emissions, *Environmental science & technology*, 51, 1074-1093, 10.1021/acs.est.6b04509, 2017.
- [Gordon, T. D., Presto, A. A., Nguyen, N. T., Robertson, W. H., Na, K., Sahay, K. N., Zhang, M., Maddox, C., Rieger, P., Chattopadhyay, S., Maldonado, H., Maricq, M. M., and Robinson, A. L.: Secondary organic aerosol production from diesel vehicle exhaust: impact of aftertreatment, fuel chemistry and driving cycle, *Atmos. Chem. Phys.*, 14, 4643-4659, 10.5194/acp-14-4643-2014, 2014.](#)

- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and J., W.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos Chem Phys*, 9, 5155-5236, 2009.
- Han, X., and Naeher, L. P.: A review of traffic-related air pollution exposure assessment studies in the developing world, *Environment International*, 32, 106-120, <http://dx.doi.org/10.1016/j.envint.2005.05.020>, 2006.
- HEI: Traffic-Related Air Pollution: A Critical Review of the Literature on Emissions, Exposure, and Health Effects, 2010.
- Heywood, J. B.: Internal combustion engine fundamentals, McGraw-hill New York, 1988.
- Ježek, I., Katrašnik, T., Westerdahl, D., and Močnik, G.: Black carbon, particle number concentration and nitrogen oxide emission factors of random in-use vehicles measured with the on-road chasing method, *Atmos. Chem. Phys.*, 15, 11011-11026, 10.5194/acp-15-11011-2015, 2015.
- Jiang, M., Marr, L. C., Dunlea, E. J., Herndon, S. C., Jayne, J. T., Kolb, C. E., Knighton, W. B., Rogers, T. M., Zavala, M., Molina, L. T., and Molina, M. J.: Vehicle fleet emissions of black carbon, polycyclic aromatic hydrocarbons, and other pollutants measured by a mobile laboratory in Mexico City, *Atmos. Chem. Phys.*, 5, 3377-3387, 10.5194/acp-5-3377-2005, 2005.
- Johnson, T. V.: Diesel Emission Control in Review, 2001.
- Kondo, Y., Miyazaki, Y., Takegawa, N., Miyakawa, T., Weber, R. J., Jimenez, J. L., Zhang, Q., and Worsnop, D. R.: Oxygenated and water-soluble organic aerosols in Tokyo, *Journal of Geophysical Research: Atmospheres*, 112, n/a-n/a, 10.1029/2006JD007056, 2007.
- Korin, E., Reshef, R., Tshernichovesky, D., and Sher, E.: Reducing cold-start emission from internal combustion engines by means of a catalytic converter embedded in a phase-change material, *Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering*, 213, 575-583, doi:10.1243/0954407991527116, 1999.
- Kristensson, A., Johansson, C., Westerholm, R., Swietlicki, E., Gidhagen, L., Wideqvist, U., and Vesely, V.: Real-world traffic emission factors of gases and particles measured in a road tunnel in Stockholm, Sweden, *Atmospheric Environment*, 38, 657-673, <http://dx.doi.org/10.1016/j.atmosenv.2003.10.030>, 2004.
- Krzyzanowski, M., and Cohen, A.: Update of WHO air quality guidelines, *Air Quality, Atmosphere & Health*, 1, 7-13, 10.1007/s11869-008-0008-9, 2008.
- Lidster, R. T.: Development of comprehensive two-dimensional gas chromatography for the analysis of volatile organic compounds in the atmosphere, University of York, 2012.
- Lim, Y. B., and Ziemann, P. J.: Effects of Molecular Structure on Aerosol Yields from OH Radical-Initiated Reactions of Linear, Branched, and Cyclic Alkanes in the Presence of NO_x, *Environmental science & technology*, 43, 2328-2334, 10.1021/es803389s, 2009.

- Liu, Y., Gao, Y., Yu, N., Zhang, C., Wang, S., Ma, L., Zhao, J., and Lohmann, R.: Particulate matter, gaseous and particulate polycyclic aromatic hydrocarbons (PAHs) in an urban traffic tunnel of China: Emission from on-road vehicles and gas-particle partitioning, *Chemosphere*, 134, 52-59, <http://dx.doi.org/10.1016/j.chemosphere.2015.03.065>, 2015.
- Louis, C., Liu, Y., Tassel, P., Perret, P., Chaumond, A., and André, M.: PAH, BTEX, carbonyl compound, black-carbon, NO₂ and ultrafine particle dynamometer bench emissions for Euro 4 and Euro 5 diesel and gasoline passenger cars, *Atmospheric Environment*, 141, 80-95, <http://dx.doi.org/10.1016/j.atmosenv.2016.06.055>, 2016.
- Machado Corrêa, S., and Arbilla, G.: Carbonyl emissions in diesel and biodiesel exhaust, *Atmospheric Environment*, 42, 769-775, <https://doi.org/10.1016/j.atmosenv.2007.09.073>, 2008.
- Majewski, W. A., and Khair, M. K.: Diesel emissions and their control, SAE Technical Paper, 2006.
- 10 Matsui, H., Koike, M., Takegawa, N., Kondo, Y., Griffin, R. J., Miyazaki, Y., Yokouchi, Y., and Ohara, T.: Secondary organic aerosol formation in urban air: Temporal variations and possible contributions from unidentified hydrocarbons, *Journal of Geophysical Research: Atmospheres*, 114, n/a-n/a, 10.1029/2008JD010164, 2009.
- Miguel, A. H., Kirchstetter, T. W., Harley, R. A., and Hering, S. V.: On-Road Emissions of Particulate Polycyclic Aromatic Hydrocarbons and Black Carbon from Gasoline and Diesel Vehicles, *Environmental science & technology*, 32, 450-455, 10.1021/es970566w, 1998.
- 15 Nelson, P. F., Tibbett, A. R., and Day, S. J.: Effects of vehicle type and fuel quality on real world toxic emissions from diesel vehicles, *Atmospheric Environment*, 42, 5291-5303, <https://doi.org/10.1016/j.atmosenv.2008.02.049>, 2008.
- Pang, Y., Fuentes, M., and Rieger, P.: Trends in the emissions of Volatile Organic Compounds (VOCs) from light-duty gasoline vehicles tested on chassis dynamometers in Southern California, *Atmospheric Environment*, 83, 127-135, 20 <http://dx.doi.org/10.1016/j.atmosenv.2013.11.002>, 2014.
- Presto, A. A., Miracolo, M. A., Donahue, N. M., and Robinson, A. L.: Secondary Organic Aerosol Formation from High-NO_x Photo-Oxidation of Low Volatility Precursors: n-Alkanes, *Environmental science & technology*, 44, 2029-2034, 10.1021/es903712r, 2010.
- Prüss-Üstün, A., and Corvalán, C.: Preventing disease through healthy environments, Geneva: World Health Organization, 25 2006.
- Rashid, G., Hekmat, R., Nejat, L. A., Payam, J., and Farzad, J.: Comparative analysis of exhaust gases from MF285 and U650 tractors under field conditions, *Agricultural Engineering International: CIGR Journal*, 15, 101-107, 2013.
- Roberts, A., Brooks, R., and Shipway, P.: Internal combustion engine cold-start efficiency: A review of the problem, causes and potential solutions, *Energy Conversion and Management*, 82, 327-350, 30 <http://dx.doi.org/10.1016/j.enconman.2014.03.002>, 2014.
- Russell, A., and Epling, W. S.: Diesel Oxidation Catalysts, *Catalysis Reviews*, 53, 337-423, 10.1080/01614940.2011.596429, 2011.
- Salge, J., Deluga, G., and Schmidt, L.: Catalytic partial oxidation of ethanol over noble metal catalysts, *Journal of Catalysis*, 235, 69-78, 2005.

- Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of Emissions from Air Pollution Sources. 2. C1 through C30 Organic Compounds from Medium Duty Diesel Trucks, *Environmental science & technology*, 33, 1578-1587, 10.1021/es980081n, 1999.
- Schmitz, T., Hassel, D., and Weber, F.-J.: Determination of VOC-components in the exhaust of gasoline and diesel passenger cars, *Atmospheric Environment*, 34, 4639-4647, [http://dx.doi.org/10.1016/S1352-2310\(00\)00303-4](http://dx.doi.org/10.1016/S1352-2310(00)00303-4), 2000.
- 5 [Schulz, H., Bandeira De Melo, G., and Ousmanov, F.: Volatile organic compounds and particulates as components of diesel engine exhaust gas, *Combustion and Flame*, 118, 179-190, \[https://doi.org/10.1016/S0010-2180\\(98\\)00146-1\]\(https://doi.org/10.1016/S0010-2180\(98\)00146-1\), 1999.](#)
- Shirmeshan, A.: HC, CO, CO₂ and NO_x Emission Evaluation of a Diesel Engine Fueled with Waste Frying Oil Methyl Ester, *Procedia - Social and Behavioral Sciences*, 75, 292-297, <http://dx.doi.org/10.1016/j.sbspro.2013.04.033>, 2013.
- 10 [Siegl, W. O., Hammerle, R. H., Herrmann, H. M., Wenclawiak, B. W., and Luers-Jongen, B.: Organic emissions profile for a light-duty diesel vehicle, *Atmospheric Environment*, 33, 797-805, \[https://doi.org/10.1016/S1352-2310\\(98\\)00209-X\]\(https://doi.org/10.1016/S1352-2310\(98\)00209-X\), 1999.](#)
- [Staelin, J., Keller, C., Stahel, W., Schläpfer, K., and Wunderli, S.: Emission factors from road traffic from a tunnel study \(Gubrist tunnel, Switzerland\). Part III: Results of organic compounds, SO₂ and speciation of organic exhaust emission, *Atmospheric Environment*, 32, 999-1009, \[https://doi.org/10.1016/S1352-2310\\(97\\)00339-7\]\(https://doi.org/10.1016/S1352-2310\(97\)00339-7\), 1998.](#)
- 15 Tadano, Y. S., Borillo, G. C., Godoi, A. F. L., Cichon, A., Silva, T. O. B., Valebona, F. B., Errera, M. R., Penteadó Neto, R. A., Rempel, D., Martin, L., Yamamoto, C. I., and Godoi, R. H. M.: Gaseous emissions from a heavy-duty engine equipped with SCR aftertreatment system and fuelled with diesel and biodiesel: Assessment of pollutant dispersion and health risk, *Science of The Total Environment*, 500–501, 64-71, <http://dx.doi.org/10.1016/j.scitotenv.2014.08.100>, 2014.
- Takegawa, N., Miyakawa, T., Kondo, Y., Blake, D. R., Kanaya, Y., Koike, M., Fukuda, M., Komazaki, Y., Miyazaki, Y.,
- 20 Shimono, A., and Takeuchi, T.: Evolution of submicron organic aerosol in polluted air exported from Tokyo, *Geophysical Research Letters*, 33, n/a-n/a, 10.1029/2006GL025815, 2006.
- Tkacik, D. S., Presto, A. A., Donahue, N. M., and Robinson, A. L.: Secondary Organic Aerosol Formation from Intermediate-Volatility Organic Compounds: Cyclic, Linear, and Branched Alkanes, *Environmental science & technology*, 46, 8773-8781, 10.1021/es301112c, 2012.
- 25 United Nations: World Urbanization Prospects: The 2014 Revision, Highlights. Department of Economic and Social Affairs, Population Division, United Nations, 2014.
- Volkamer, R., Jimenez, J. L., San Martini, F., Dzepina, K., Zhang, Q., Salcedo, D., Molina, L. T., Worsnop, D. R., and Molina, M. J.: Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, *Geophysical Research Letters*, 33, n/a-n/a, 10.1029/2006GL026899, 2006.
- 30 [Westerholm, R. N., Almen, J., Li, H., Rannug, J. U., Egebaeck, K. E., and Graegg, K.: Chemical and biological characterization of particulate-, semivolatile-, and gas-phase-associated compounds in diluted heavy-duty diesel exhausts: a comparison of three different semivolatile-phase samplers, *Environmental science & technology*, 25, 332-338, 10.1021/es00014a018, 1991.](#)
- WHO: World Health Organization Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide: global update 2005: summary of risk assessment, 2006.

- Williams, P. I., McFiggans, G., and Gallagher, M. W.: Latitudinal aerosol size distribution variation in the Eastern Atlantic Ocean measured aboard the FS-Polarstern, *Atmos. Chem. Phys.*, 7, 2563-2573, 10.5194/acp-7-2563-2007, 2007.
- Winklmayr, W., Reischl, G. P., Lindner, A. O., and Berner, A.: A new electromobility spectrometer for the measurement of aerosol size distributions in the size range from 1 to 1000 nm, *Journal of Aerosol Science*, 22, 289-296, 5 [http://dx.doi.org/10.1016/S0021-8502\(05\)80007-2](http://dx.doi.org/10.1016/S0021-8502(05)80007-2), 1991.
- Yamada, H., Misawa, K., Suzuki, D., Tanaka, K., Matsumoto, J., Fujii, M., and Tanaka, K.: Detailed analysis of diesel vehicle exhaust emissions: Nitrogen oxides, hydrocarbons and particulate size distributions, *Proceedings of the Combustion Institute*, 33, 2895-2902, <http://dx.doi.org/10.1016/j.proci.2010.07.001>, 2011.
- Yang, L., Franco, V., Mock, P., Kolke, R., Zhang, S., Wu, Y., and German, J.: Experimental Assessment of NO_x Emissions 10 from 73 Euro 6 Diesel Passenger Cars, *Environmental science & technology*, 49, 14409-14415, 10.1021/acs.est.5b04242, 2015.
- Yao, Y.-F. Y.: Oxidation of Alkanes over Noble Metal Catalysts, *Industrial & Engineering Chemistry Product Research and Development*, 19, 293-298, 10.1021/i360075a003, 1980.
- Zavala, M., Herndon, S. C., Slott, R. S., Dunlea, E. J., Marr, L. C., Shorter, J. H., Zahniser, M., Knighton, W. B., Rogers, T. 15 M., Kolb, C. E., Molina, L. T., and Molina, M. J.: Characterization of on-road vehicle emissions in the Mexico City Metropolitan Area using a mobile laboratory in chase and fleet average measurement modes during the MCMA-2003 field campaign, *Atmos. Chem. Phys.*, 6, 5129-5142, 10.5194/acp-6-5129-2006, 2006.
- Zhao, Y., Nguyen, N. T., Presto, A. A., Hennigan, C. J., May, A. A., and Robinson, A. L.: Intermediate Volatility Organic 20 Organic Aerosol Production. *Environmental science & technology*, 49, 11516-11526, 10.1021/acs.est.5b02841, 2015.
- Zhu, L., Cheung, C. S., Zhang, W. G., Fang, J. H., and Huang, Z.: Effects of ethanol-biodiesel blends and diesel oxidation catalyst (DOC) on particulate and unregulated emissions, *Fuel*, 113, 690-696, <https://doi.org/10.1016/j.fuel.2013.06.028>, 2013.

Table 1 – Experimental dates, descriptions and engine operating parameters.

Experiment	Experiment Date	Experiment Description	Engine Conditions							Exhaust emission†			
			RPM	Throttle (%)	Load (%)	Torque (Nm)	DOC	Engine Temp (°C)	Fuel Burnt (g)	Exhaust dilution ratio	NO ($\frac{g}{kg}^{-1}(ppbv)$)	NO ₂ ($\frac{g}{kg}^{-1}(ppbv)$)	Particle mass ($\frac{mg}{kg}^{-1}\frac{g}{g}$ m^{-3})‡
1	30.07.14	Warm high load ^a	2500	57	40	75	Yes	460	6.13	166	27.67546	3.2571	302493
2	31.07.14	Warm high load ^b	2500	57	40	75	Yes	450	2.45	313	23.42569	1.9134	23532
3	01.08.14	Warm high load, NDOC	2500	57	40	75	No	450	2.45	325	21.72460	2.5185	19827
4	05.08.14	Warm with load ^b	2000	40	30	50	Yes	**	0.41	1158	26.1497	0.56	2205
5	08.08.14	Warm with load ^b	2000	40	30	50	Yes	300	8.27	60	20.77950	3.1776	268423
6	06.08.14	Cold Start ^c	1150	0	0	1.5	Yes	85	0.59	389	7.2196	15.0269	115938
7	07.08.14	Cold Start ^c	1150	0	0	2	Yes	83	0.59	564***	7.9212	14.6256	91530
8	06.08.14 (2)	Cold loaded ^c Short Journey	1500	30	20	32	Yes	169	1.19	312	17.3940	9.8349	1218
9	06.08.14 (3)	Warm idle following load ^a	1180	0	0	0.3	Yes	150	1.18	775	13.1700	0.933	16844
10	13.11.14 (1)	Warm with load ^b	2000	40	30	50	Yes	300	0.41	840	31.5579	2.024	3518
11	13.11.14 (2)	High RPM, 53% load	3000	75	53	112	Yes	700	3.28	353	21.73201	1.9181	2146291
12	14.11.14 (1)	High RPM, 30% load	3000	48	30	50	Yes	345	1.74	198	39.23070	5.3268	60058
13	14.11.14 (2)	High RPM, 40% load	3000	57	40	70	Yes	445	2.39	191	44.64805	8.6602	65587
14	25.11.14	Cold Start ^c	1150	0	0	2	Yes	**	0.59	564***	6.3166	10.6183	115938
15	01.10.15	Warm with load ^b	2000	40	28	50	Yes	292	1.57	331	12.8930	0.526	29826
16	29.09.15	Warm with load ^b	2000	40	28	50	Yes	293	1.57	337	12.2876	0.524	24121

Superscript letters a, b and c highlight replicate experiments using the same engine conditions. Fuel batch A used in experiments 1 to 9 and fuel batch B, used in experiments 10 to 16, see section 2.2 and 3.1.1 for further information. NDOC = no diesel oxidative catalyst. * = Sequence of engine conditions performed, see section 2.3 and SI Figure S2, 7 minutes of 2000 rpm and 28-30% load, followed by idling speed (1150 rpm) and 0% load prior to injection. ** No engine temperature measurement (engine thermocouple non-responsive). *** Estimated exhaust dilution ratio based on pneumatic valve introduction time. † Expressed as emission factors (i.e. mass of emission per kg of fuel burnt). ‡ Not corrected for exhaust dilution. § Wall loss corrected.

Table 2 – Calculated diesel oxidative catalyst hydrocarbon removal efficiency for the speciated VOCs. Determined from measured emissions rates of the speciated VOCs in two replicate experiments with (exp. 2) and without (exp. 3) a diesel oxidative catalyst.

	Emission without catalytic converter (mg kg ⁻¹)	Emission with catalytic converter (mg kg ⁻¹)	Removal efficiency (%)
Individual Compounds			
Benzene	19.50±1.75	1.88±0.17	90.4±9.0
Toluene	3.89±0.37	1.58±0.15	59.3±9.4
Ethyl benzene	1.56±0.36	0.05±0.01	97.1±22.8
m/p-xylene	2.98±0.62	0.13±0.03	95.7±20.9
o-xylene	2.17±0.55	0.22±0.06	89.7±25.3
Styrene	2.74±0.69	0.01±0.004	99.5±25.3
1,3,5-TMB	2.26±0.36	0	100*
1,2,4-TMB	2.45±0.21	0	100*
1,2,3-TMB	1.92±0.20	0	100*
Heptane	2.37±0.14	0.53±0.03	77.4±5.7
Octane	4.96±0.57	0	100*
Nonane	11.72±1.08	2.44±0.22	79.2±9.2
Decane	33.83±3.11	7.30±0.67	78.4±9.2
Undecane	49.76±4.57	32.34±2.97	35.0±9.2
Dodecane	137.65±12.64	156.60±14.38	0**
Groupings			
Branched aliphatics			
C ₇	4.41±1.00	1.25±0.28	71.6±22.6
C ₈	18.77±4.76	3.68±0.93	80.4±25.4
C ₉	46.78±10.70	6.65±1.52	85.8±22.9
C ₁₀	76.81±18.78	17.33±4.24	77.4±24.4
C ₁₁	71.95±16.43	31.97±7.30	55.6±22.8
C ₁₂	86.36±20.80	74.41±17.92	13.8±24.1
Aromatic substitutions			
C ₃	14.18±3.13	5.20±1.15	63.3±22.1
Total groupings			
Aliphatics	545.37±37.22	334.50±24.74	38.66±11.7
Aromatics	53.65±3.81	9.07±1.17	83.09±2.6
Total speciated	599.02±37.41	343.58±24.77	45.64±9.7

* Compound not observed (< instrument LOD). **No observed decrease in concentration. TMB = trimethyl benzene.

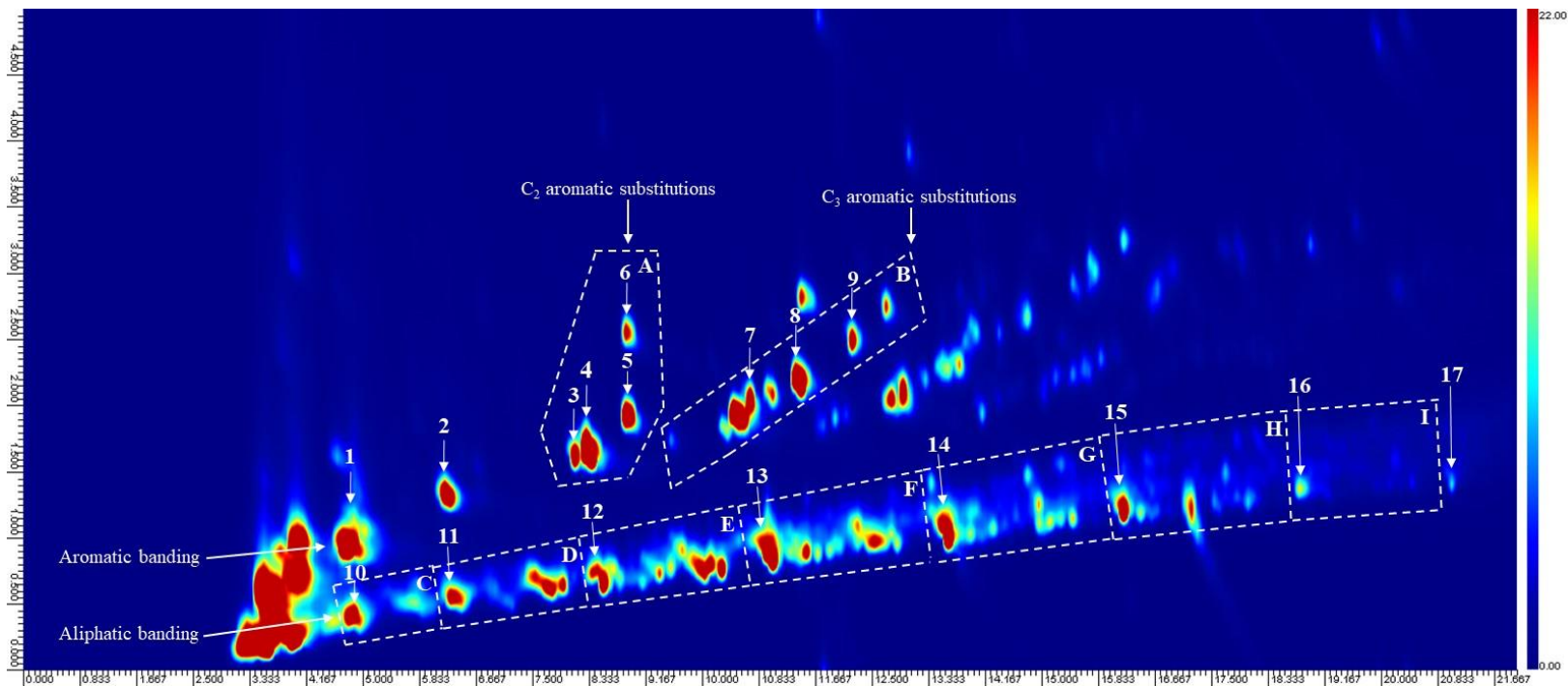


Figure 1 – An annotated chromatogram displaying the speciated VOC-IVOCs. Chromatogram axis, x = first dimension separation (boiling point, increasing from left-to-right), y = second dimension separation (polarity, increasing from bottom-to-top). Colour scale represents peak intensity, increasing from blue to red. Letters refer to compound groupings; A = single-ring aromatics with two carbon substitutions, B = single-ring aromatics with three carbon substitutions, C to I = C₇ to C₁₃ aliphatics grouped by carbon number (*i.e.* C = C₇ aliphatics, D = C₈ aliphatics *etc.*). Numbers refer to individual compounds; 1 = benzene, 2 = toluene, 3 = ethyl benzene, 4 = meta/para-xylene (co-elution), 5 = ortho-xylene, 6 = styrene, 7 = 1,3,5-trimethyl benzene, 8 = 1,2,4-trimethyl benzene, 9 = 1,2,3-trimethyl benzene, 10 = heptane, 11 = octane, 12 = nonane, 13 = decane, 14 = undecane, 15 = dodecane, 16 = tridecane, 17 = tetradecane (not quantified). Aromatic and aliphatic bandings often observed with this technique are shown (*c.f.* Hamilton and Lewis (2003) and Dunmore et al. (2015)). The start and end of each aliphatic grouping is marked by the lower and higher carbon number *n*-alkane (*i.e.* nonane marks the start of the C₉ aliphatic grouping, decane marks the end of this group).

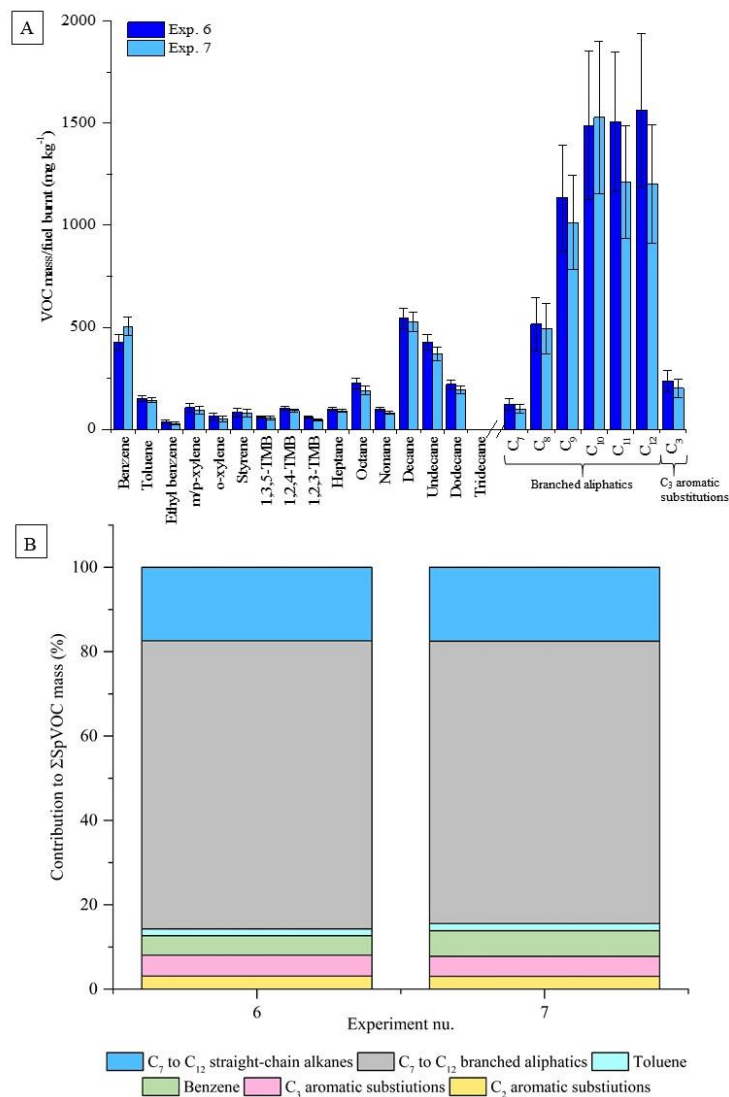


Figure 2 – Comparison of measured VOC-IVOC emission rates in replicate cold-start experiments (exp. 6 and 7) (A). Comparison of the percentage contribution of the individual and grouped compounds to the Σ SpVOC emission rates in exp. 6 and 7 (B). The emission rates of tridecane and the C₁₃ branched aliphatic grouping has not been included in (B) to allow direct comparison between other experiments where these species were not measured. Error bars represent the calculated uncertainty in the measured emission rates, see the SI section 1.1 for further information.

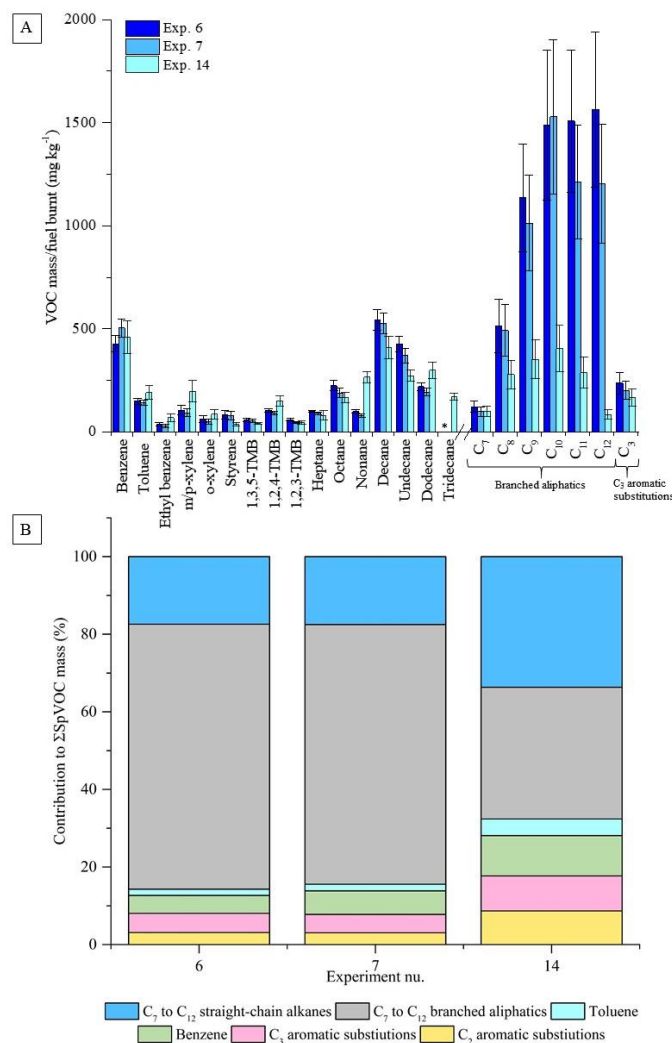
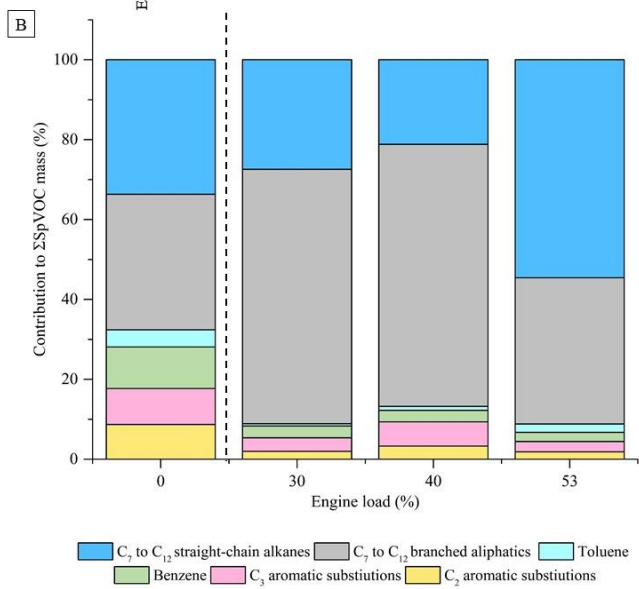
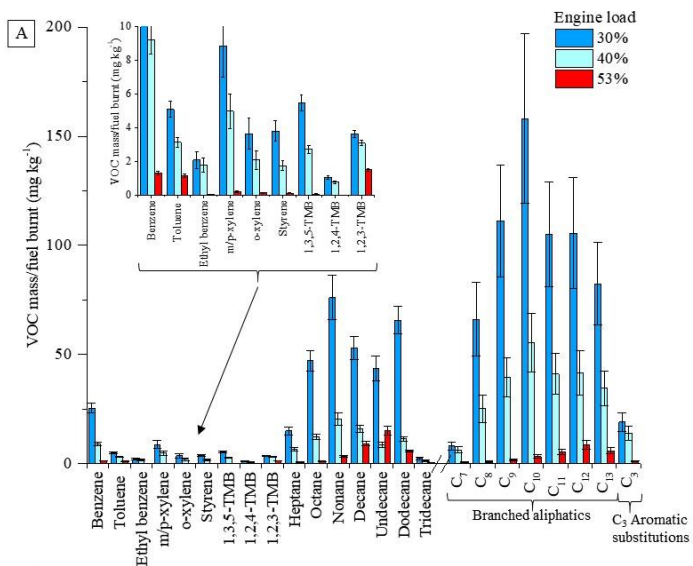


Figure 3 – Comparison of measured VOC-IVOC emissions rates in replicate cold-start experiments 6 and 7 (fuel batch A) with cold-start experiment 14 (fuel batch B) (A). Comparison of the percentage contribution of the individual and grouped compounds to the Σ SpVOC emission rates in experiments 6, 7, 14 (B). The emission rates of tridecane and the C₁₃ branched aliphatic grouping has not been included in (B) to allow direct comparison between other experiments where these species were not measured. Error bars represent the calculated uncertainty in the measured emission rates, see the SI section 1.1 for further information.



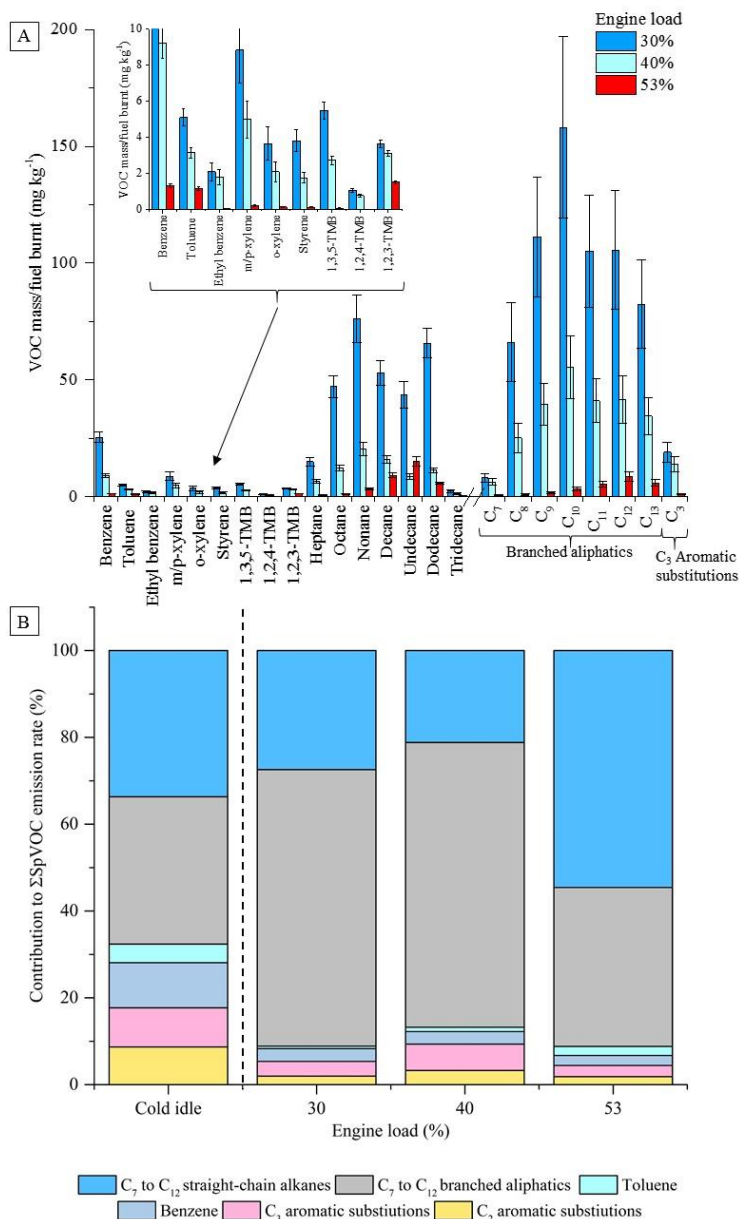
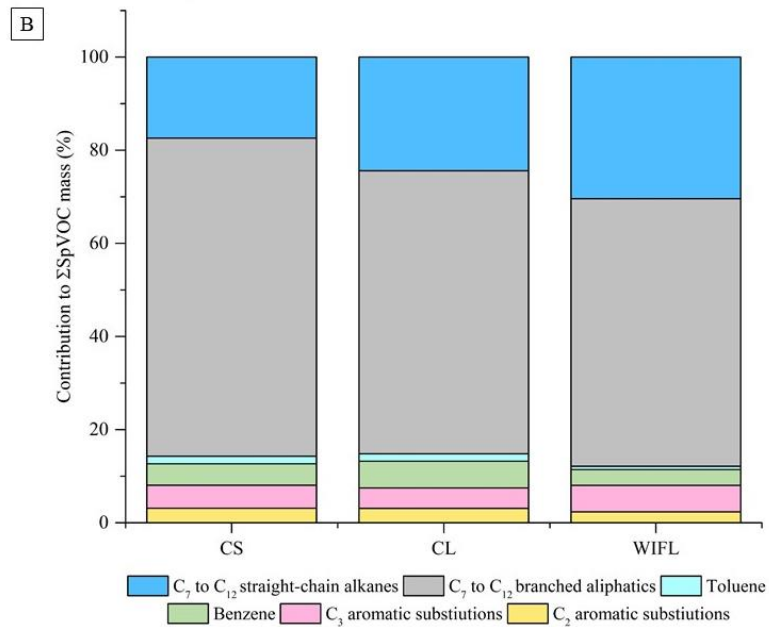
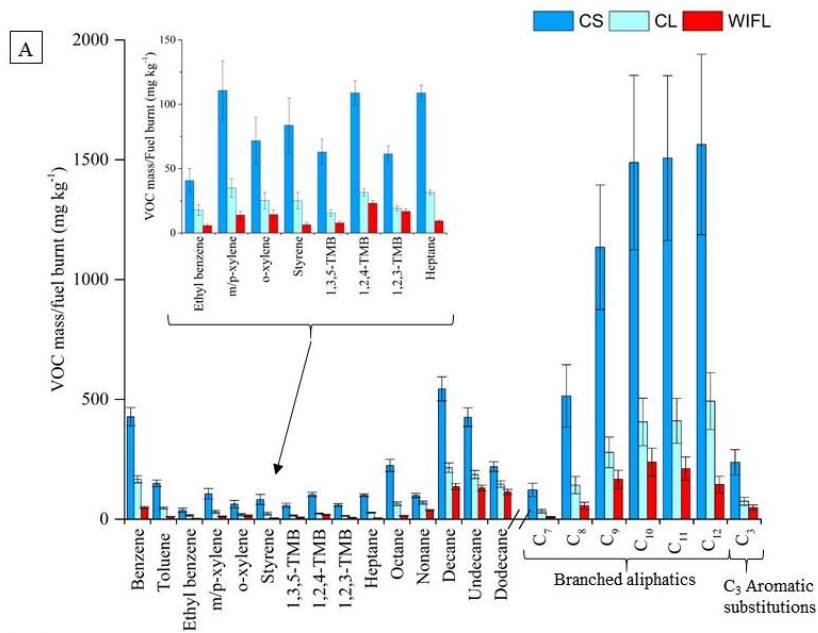


Figure 42 – Effect of different engine loads on measured VOC-IVOC emission rates (A) and the percentage contribution of the individual and grouped compoundsVOCs to the Σ SpVOC_{total-speciated-VOC} emission rate at 0 (exp. 14), 30 (exp. 12), 40 (exp. 13) and 53% (exp. 11) engine load (B). (Σ SpVOC) (B). The emission rates of tridecane and the C₁₃ branched aliphatic grouping have not been included in (B) to allow direct comparison between other experiments where these species were not measured. For comparison, the percentage contribution of the individual and grouped compoundsVOCs to the Σ SpVOC emission rate in a cold idle experiment (exp. 14) has been included on the left of (B), see text for further details. Error bars represent the calculated uncertainty in the measured emission rates, see the SI section 1.1 for further information.



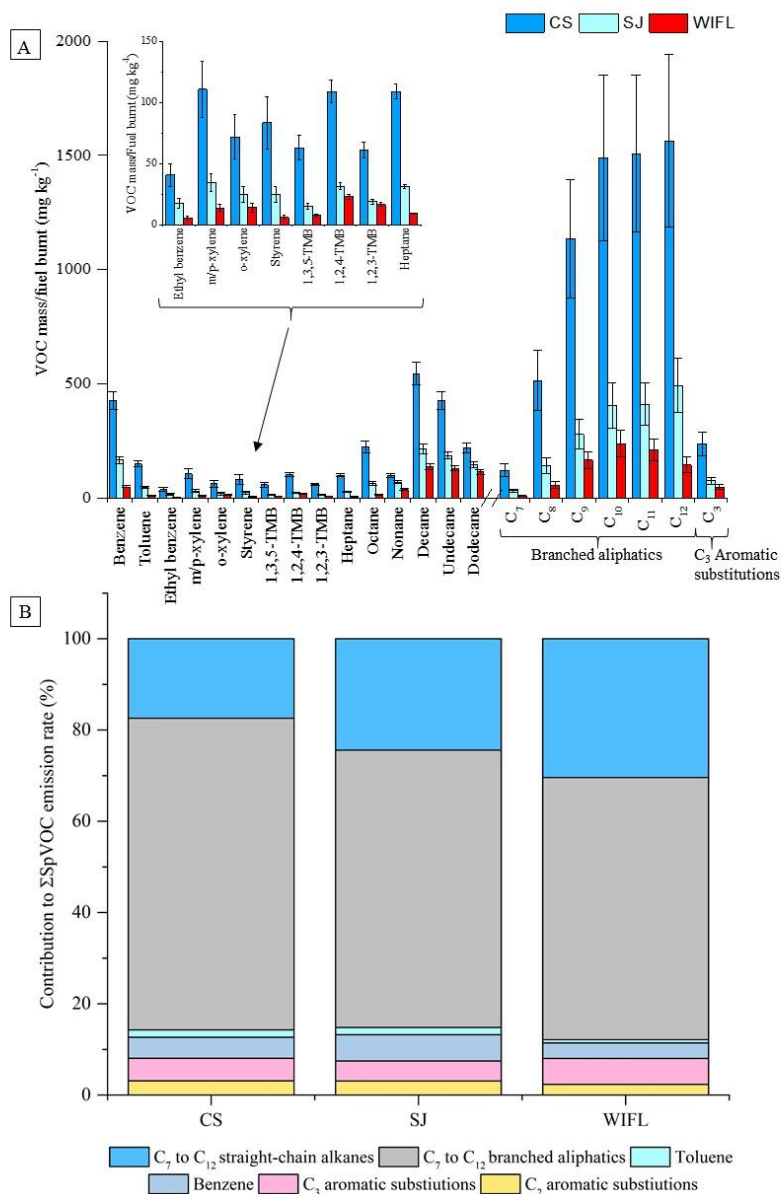


Figure 53 – Effect of different driving scenarios on measured VOC-IVOC emission rates (A) and the contribution of the individual and grouped compounds/VOCs to the ΣSpVOC total specified VOC emission rate (ΣSpVOC) (B). CS = cold-start (exp. 6), SJ = cold loaded (exp. 8), short journey, WIFL = warm idle following load (exp. 9, see text for further information). The emission rates of tridecane and the C₁₃ branched aliphatic grouping have not been included in (B) to allow direct comparison between other experiments where these species were not measured. Error bars represent the calculated uncertainty in the measured emission rates, see the SI section 1.1 for further information.

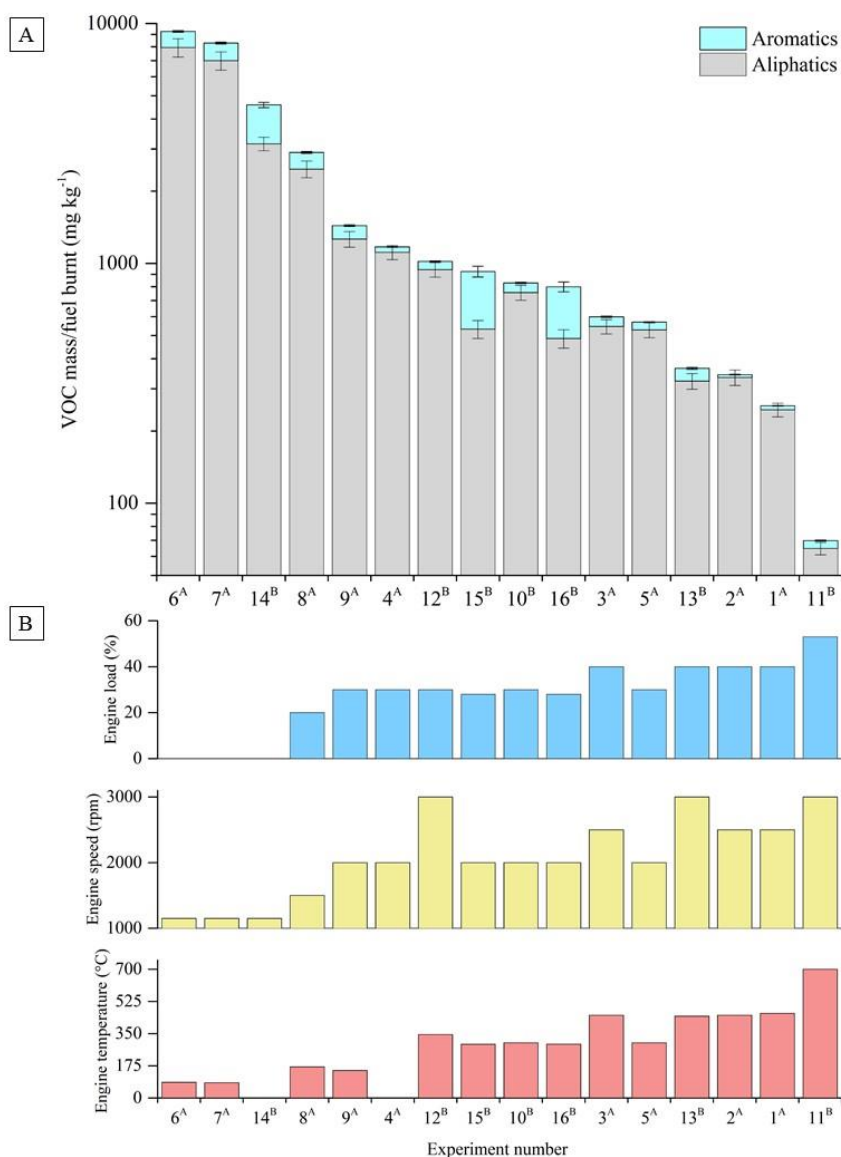


Figure 64 –Total speciated VOC-IVOC emission rate (Σ SpVOC) measured in each experiment (refer to Table 1) divided into aliphatic and aromatic emissions rates (A). Experiments ordered from left-to-right by decreasing VOC-IVOC emission rates.

5 Engine temperature, speed and load in each corresponding experiment is shown in (B). ^A = Fuel batch A used (see [sections 2.2 and 3.1.1, experimental section](#)). ^B = Fuel batch B used. No DOC in exp. 3. Sequence of engine conditions performed in exp. 99 (WIFL); 7 minutes of 2000 rpm and 28-30% load, followed by idling speed (1150 rpm) and 8 (see section 2.3 and SI Figure S2). 0% load prior to injection. No engine temperature measurement for exp. 4 and 14 (engine thermocouple unresponsive). Error bars represent the

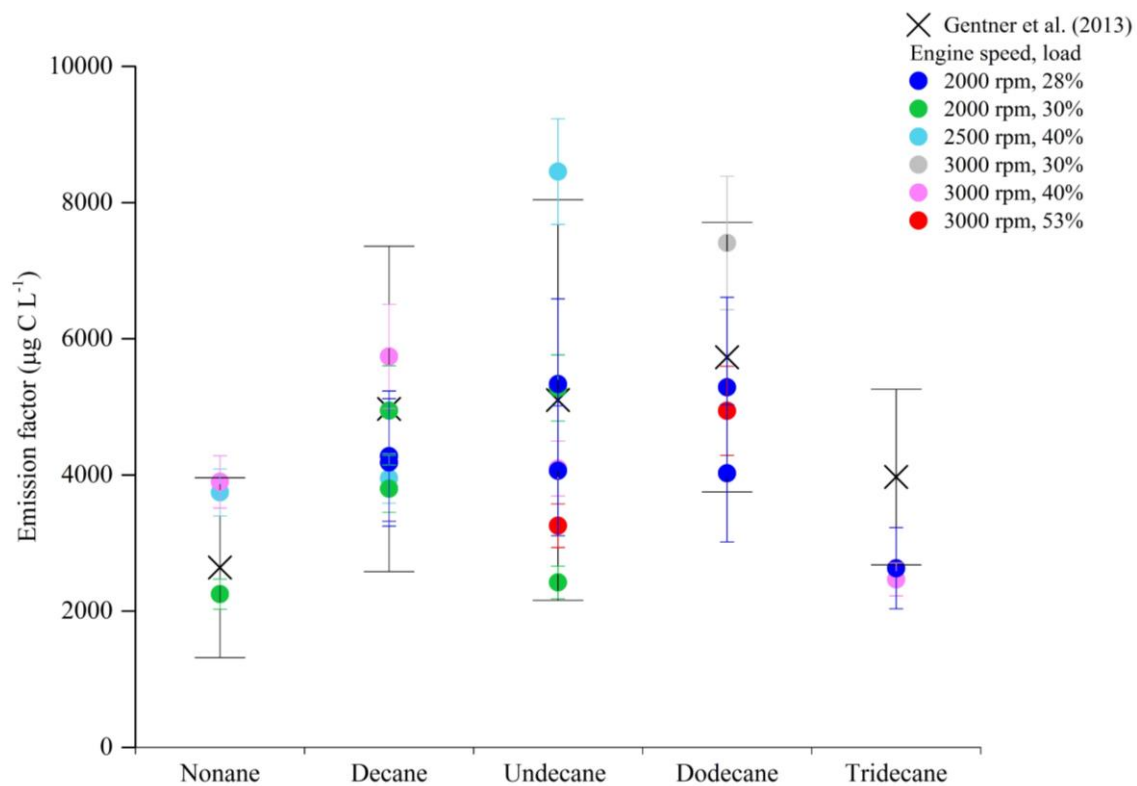


Figure 5 Comparison of n nonane to n tridecane emission factors obtained from different engine conditions in this study (coloured circles), with on road diesel emission factors from a highway tunnel in Oakland, California (Gentner et al., 2013) (black crosses) (A). Emission factors were calculated uncertainty in the measured emission rates, see the SI section using a liquid fuel density 852 g L^{-1} , and were weighted by carbon ($\mu\text{g C L}^{-1}$, see text for further information).

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The Effect of Varying Engine Conditions on Unregulated VOC-IVOC Diesel Exhaust Emissions

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Supplementary information

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1.1. Experimental reproducibility

The reproducibility of different engine conditions and exhaust dilution ratios on the measured VOC emission rates is discussed below. The VOC emissions rates from two cold start experiments (exp. 6 and 7, see Table 1) at 1150 rpm with 0% load, and two experiments (exp. 15 and 16) at 2000 rpm with 28% load (hereafter referred to as warm with load, WWL) are shown in the SI, Figures S1 and S2, respectively. These experiments were performed at similar exhaust dilution ratios. The VOC emission rates in both the cold start and WWL experiments displayed excellent reproducibility, considering the vast number of variables in these experiments (*e.g.* DOC hydrocarbon removal efficiency, fuel combustion *etc.*). The emission rates of all the VOCs except styrene in experiment 15, (below limit of detection, LOD) were within error. Furthermore, the contribution of the individual and grouped VOCs to the Σ SpVOC emission rate in each replicate experiment was also comparable, with all the VOC percentage contributions observed to be within error (see SI Tables S3 to S5). The VOC emission rates of two replicate experiments (exp. 1 and 2) with the use of different exhaust dilution ratios is shown in the SI, Figure S3. The engine conditions in these experiments were set to 2500 rpm with 40% load, with an exhaust dilution ratio of 166 and 313 for experiment 1 and 2, respectively. The VOC emission rates are relatively consistent between these experiments. Only one measurement of the exhaust emission was made in each of these experiments. The vast majority of experiments had a minimum of two replicate measurements of the exhaust emission, possibly accounting for the slight difference observed. The VOC emission rates from two replicate experiments (exp. 4 and 5) at the highest and lowest investigated exhaust dilution ratios is shown in the SI, Figure S4. These experiments investigated the extremes of the exhaust dilution ratio, with a dilution ratio of 1158 and 60 in exp. 4 and 5, respectively. The engine conditions in these experiments were set to 2000 rpm with 40% load. The VOC emission rates and exhaust composition showed some agreement between these experiments, but overall were rather inconsistent. The reason for the observed differences in these experiments is unclear. The engine thermocouple was unresponsive during one of the experiments (exp. 4) and consequently the engine temperature is unknown. This may account for the observed differences in the VOC emission rates (*e.g.* a lower temperature will decrease DOC HC removal efficiency, increasing VOC emission rates). In addition, it is uncertain if a steady state engine temperature was achieved before the exhaust was injected into the MAC. Nevertheless, no experiments have been compared in the following data with such large differences in the exhaust dilution ratios. Furthermore, where there is more than one experiment, the experiments with the closest dilution ratios have been compared.

2. Diesel fuel analysis: Fuel batch A and B

The emission rates from three cold start experiments, two using fuel batch A (exp. 6 and 7) and one using fuel batch B (exp. 14), are shown in the SI Figure S5. From Figure S5, it can be observed that there is a considerable difference in the emission rates of the C₇ to C₁₂-branched aliphatics between replicate experiments 6 and 7, and experiment 14. The emission rate of the C₇ to C₁₂-branched aliphatics decreased by a factor of ~4 with the use of fuel batch B (exp. 14). The excellent agreement of the emission rates between replicate cold start experiments 6 and 7, suggests the compositional differences observed in

experiment 14, is the result of a slight difference in the fuel composition between batches A and B. Comprehensive two-dimensional gas chromatography coupled to a time of flight mass spectrometer was used to further investigate any compositional differences between the fuel batches. The experimental method used for the analysis of the liquid diesel fuel is shown below in section 2.1. An extensive analysis of the liquid diesel fuel was not performed. The aim of this analysis was to investigate whether there were any apparent differences in the fuel composition that would prevent a direct comparison of the emission rates from fuel batches A and B. An extracted ion chromatogram for m/z 57 (dominant aliphatic fragment ion) from fuel batch A and B are shown in Figure S6 A and B, respectively. Both chromatograms have been normalised to the total peak area to allow direct comparison of peak intensity. The highlighted region in Figure S6 displays straight chain and branched aliphatics with a carbon number range of approximately C_7 to C_{12} . The carbon number range was determined using the NIST library. From Figure S6, it can be observed that the peak intensity in the chromatograms from fuel batches A and B are largely comparable, except for the highlighted region, where a slightly lower peak intensity is observed in Figure S6B (fuel batch B). As a result, the emission rates from experiments where two different fuel batches were used, have not been directly compared.

2.1 GC×GC TOFMS experimental method

Liquid fuel samples were analysed using comprehensive two dimensional gas chromatography (model 6890N, Agilent Technologies, UK) coupled to a time of flight mass spectrometer (Pegasus 4D, Leco, MI, USA) (GC×GC TOFMS). Compound separation was achieved using a primary 15 meter 5% phenyl polysilphenylene siloxane (BPX5, SGE, Ringwood, Australia), column with a 0.25 mm film thickness and 0.25 mm internal diameter, and a secondary 2 meter 50% phenyl polysilphenylene siloxane (BPX50, SGE, Ringwood, Australia) column with a 0.25 mm film thickness and 0.25 mm internal diameter. Samples were introduced into the GC×GC TOFMS using a Gerstel multipurpose sampler (MPS 2, Gerstel, USA) with dedicated controller (model C506, Gerstel, USA). A 1 μ L injection volume was used with a split ratio of 100:1. The transfer line was set to 270°C. Cryo jet modulation cooling was used to achieve comprehensive two dimensional separation. Helium (CP grade, BOC, UK) was used as the carrier gas with a constant flow rate of 1.5 ml min⁻¹. The oven starting temperature was set to 65°C with a 0.2 minute hold, followed by a temperature ramp of 4°C min⁻¹ to 240°C, with a further 10 minute hold. The modulator and secondary oven temperature was set to 15°C and 20°C above the oven temperature, respectively. The TOFMS acquisition rate was 50 spectra per second, with a scan range of m/z 35 to 500. The data was analysed using Leco ChromaTOF software version 4.51.6 (Leco, MI, USA). Compounds were identified using the National Institute of Standard and Technology (NIST) standard reference database (version 11).

3. Calculation of emission factors

The mixing ratios of the individual and grouped compounds/VOCs in the exhaust emissions were determined using either a NPL gas standard or the relative response factors (RRF) of liquid standards. The NPL gas standard consisted of 30

compounds~~VOCs~~ ranging from C₂ to C₈ with mixing ratios of 3 to 5 ppbv. In total, 11 compounds~~VOCs~~ in the NPL standard were used for quantification. A list of the speciated VOC-IVOCs~~VOCs~~, the calibration method and the compounds used for quantification are shown in the SI, Table S1. The response of an FID is assumed to be proportional to the number of carbon atoms present in a compound and is termed ‘effective carbon number’ (IOFI, 2011). The effective carbon was used to quantify the VOC-IVOC groupings, allowing multiple isomers in each group to be calibrated using one compound with the same number of carbon atoms. For example, the mixing ratio of the C₇ branched aliphatics was determined using heptane in NPL standard. The mixing ratio of styrene was also determined using the effective carbon number approach. The peak area of styrene was not direct measured but calculated by subtracting the peak area of the aromatic grouping with two carbon substitutions, from the sum of ethylbenzene, m/p-xylene and o-xylene, to give the peak area of the only other remaining compound in this group, styrene. The mixing ratio of styrene was determined using o-xylene. The mixing ratios of *n*-nonane to *n*-tridecane were determined using the RRFs from liquid standards. The RRF is an internal standardisation method commonly used with FIDs to determine an unknown concentration of a compound based on the peak area and concentration of an internal standard or reference compound (*e.g.* (IOFI, 2011; Tissot et al., 2012)). Liquid standards were prepared consisting of toluene, nonane, decane, undecane, dodecane and tridecane at known concentrations. Toluene was used as the reference compound, as it was much more resolved and easier to distinguish than the *n*-alkanes in the exhaust samples. The RRF was calculated as shown in Eq. 1 (IOFI, 2011); where A is the peak area of the reference compound (rc) (*i.e.* toluene) or the analyte (a) (*e.g.* nonane) and M is the concentration. Once the RRF had been determined, the unknown concentration of the analyte (*e.g.* nonane) or the VOC-IVOC grouping (using the effective carbon number approach) in the exhaust emissions were calculated using Eq.2. The mixing ratios of the individual and grouped compounds~~VOCs~~ were converted from ppbv to mg m⁻³, accounting for the molecular weight of the compound or grouping, and the average chamber temperature during the sampling period. The measured VOC-IVOC mass (mg) was determined by dividing the mixing ratio of the individual and grouped compounds in mg m⁻³ by the chamber volume (18 m³). Finally, the emission rates were calculated by dividing the measured VOC-IVOC mass by the amount of fuel burnt (mg kg⁻¹) (corrected for exhaust dilution, see Whitehead et al. (2017) for further information) in each experiment.

Eq. 1
$$\text{RRF} = \frac{A_a}{A_{rc}} \times \frac{M_{is}}{M_a}$$

Eq. 2
$$M_a = \frac{A_a}{A_{rc}} \times \frac{M_{is}}{\text{RRF}}$$

Table S1 – Calibration method and the compounds used for the quantification of the speciated ~~VOCs~~ VOC-IVOCs

<u>VOC-IVOCs</u>	Method of calibration	Calibration compound
Benzene	NPL	Benzene
Toluene	NPL	Toluene
Ethyl benzene	NPL	Ethyl benzene
m/p-xylene	NPL	m/p-xylene
o-xylene	NPL	o-xylene
Styrene	NPL	o-xylene
1,3,5-TMB	NPL	1,3,5-TMB
1,2,4-TMB	NPL	1,2,4-TMB
1,2,3-TMB	NPL	1,2,3-TMB
Heptane	NPL	Heptane
Octane	RRF	Octane
Nonane	RRF	Toluene-Nonane*
Decane	RRF	Toluene-Decane*
Undecane	RRF	Toluene-Undecane*
Dodecane	RRF	Toluene-Dodecane*
Tridecane	RRF	Toluene-Tridecane*
Branched Aliphatic Groupings		
C ₇	NPL	Heptane
C ₈	NPL	Octane
C ₉	RRF	Toluene-Nonane*
C ₁₀	RRF	Toluene-Decane*
C ₁₁	RRF	Toluene-Undecane*
C ₁₂	RRF	Toluene-Dodecane*
C ₁₃	RRF	Toluene-Tridecane*
Aromatic Substitution Groupings		
C ₂	NPL	o-xylene
C ₃	NPL	1,2,3-TMB

*RRF calculated from liquid standards using toluene as a reference compound (see text for further details).

13.1 Uncertainty in emission rates

A propagation of errors was performed to determine the uncertainty in the measured VOC-IVOC emissions rates. The propagation of errors included; (i) the standard deviation in the replicate measurements of the calibration standard and the reported uncertainty in the standard VOC mixing ratios, (ii) standard deviation of the replicate measurements of the liquid standards used for the calculation of the RRF (where applicable), and (iii) a 5% standard deviation in the chamber volume. An additional 20% error was also included for the emission rates obtained from three-dimensional integration using GC Image software. This additional error was included to account for the inability of the automated peak integration software to distinguish closely eluting peaks. The software was observed to draw a straight line through two closely eluting peaks, rather than following the peak curvature, effecting the measured volume. The variability in the emission rates between one- and three-dimensional integration was estimated by measuring the emission rate of toluene in the exhaust samples using both integration methods. Toluene was selected due to its importance in the RRF calculation (reference compound) and because it was observed to elute near to an unknown compound in some experiments (*i.e.* model compound). The average variability in the emission rate of toluene between the two integration methods was determined to be 20.7%. Overall, the uncertainty in the measured emission rates of the individual and grouped compounds/VOCs ranged from 6 to 50%, with an average of 22%.

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Table S2 – Exhaust injection times, GC×GC-FID sampling duration and the number of exhaust measurements made in each of the experiments.

<u>Experiment number*</u>	<u>Exhaust injection time (HH:MM)</u>	<u>Exhaust sampling start time (HH:MM)</u>	<u>Exhaust sampling end time (HH:MM)</u>	<u>Sampling duration (HH:MM)</u>	<u>Number of samples collected</u>
<u>1</u>	<u>11:44</u>	<u>11:53</u>	<u>12:20</u>	<u>00:26</u>	<u>1</u>
<u>2</u>	<u>10:44</u>	<u>11:06</u>	<u>11:33</u>	<u>00:26</u>	<u>1</u>
<u>3</u>	<u>11:47</u>	<u>12:05</u>	<u>12:58</u>	<u>00:53</u>	<u>2</u>
<u>4</u>	<u>11:26</u>	<u>11:35</u>	<u>12:28</u>	<u>00:52</u>	<u>2</u>
<u>5</u>	<u>11:00</u>	<u>11:20</u>	<u>12:13</u>	<u>00:53</u>	<u>2</u>
<u>6</u>	<u>10:58</u>	<u>10:58</u>	<u>12:44</u>	<u>01:46</u>	<u>4</u>
<u>7</u>	<u>11:52</u>	<u>12:05</u>	<u>12:58</u>	<u>00:52</u>	<u>2</u>
<u>8</u>	<u>14:23</u>	<u>14:30</u>	<u>15:23</u>	<u>00:53</u>	<u>2</u>
<u>9</u>	<u>17:09</u>	<u>17:09</u>	<u>18:02</u>	<u>00:53</u>	<u>2</u>
<u>10</u>	<u>12:16</u>	<u>12:21</u>	<u>13:40</u>	<u>01:18</u>	<u>3</u>
<u>11</u>	<u>15:26</u>	<u>15:25</u>	<u>16:44</u>	<u>01:18</u>	<u>3</u>
<u>12</u>	<u>11:37</u>	<u>11:56</u>	<u>12:49</u>	<u>00:52</u>	<u>2</u>
<u>13</u>	<u>15:34</u>	<u>15:53</u>	<u>16:45</u>	<u>00:52</u>	<u>2</u>
<u>14</u>	<u>13:53</u>	<u>14:02</u>	<u>14:28</u>	<u>00:26</u>	<u>1</u>
<u>15</u>	<u>11:04</u>	<u>11:13</u>	<u>12:05</u>	<u>00:52</u>	<u>2</u>
<u>16</u>	<u>11:26</u>	<u>11:38</u>	<u>12:31</u>	<u>00:52</u>	<u>2</u>

*See Table 1 for corresponding experimental numbers.

Table S3 – Measured emission rates of the individual VOC-IVOCs in each experiment (mg kg⁻¹)

Exp. Nu.	Benzene	Toluene	Ethyl benzene	m/p-xylene	o-xylene	Styrene*	1,3,5-TMB	1,2,4-TMB	1,2,3-TMB	Heptane	Octane	Nonane	Decane	Undecane	Dodecane	Tridecane
1	2.0±0.2	0.8±0.1	0.3±0.1	0.4±0.1	-	-	-	-	3.2±0.3	0.7±0.04	1.0±0.1	1.6±0.1	5.5±0.5	30.7±2.8	125.6±11.5	**
2	1.9±0.2	1.6±0.1	0.1±0.01	0.1±0.03	0.2±0.1	-	-	-	-	0.5±0.03	-	2.4±0.2	7.3±0.7	32.3±3.0	156.6±14.4	**
3	19.5±1.7	3.9±0.4	1.6±0.4	3.0±0.6	2.2±0.5	2.7±0.7	2.3±0.4	2.4±0.2	1.9±0.2	2.4±0.1	5.0±0.6	11.7±1.1	33.8±3.1	49.8±4.6	137.6±12.6	**
4	42.7±3.8	1.4±0.1	-	2.3±0.5	1.2±0.3	4.1±1.0	-	1.3±0.1	-	0.5±0.03	4.3±0.5	15.9±1.5	78.9±7.2	120.6±11.1	273.8±25.1	**
5	33.4±3.0	1.4±0.1	0.3±0.1	1.0±0.2	0.6±0.1	0.6±0.2	0.4±0.1	0.8±0.1	0.7±0.1	1.7±0.1	7.5±0.8	18.1±1.7	62.2±5.7	52.9±4.9	52.0±4.8	**
6	427.9±38.3	149.6±14.1	37.5±8.6	105.7±22.0	62.7±9.2	82.8±21.0	57.6±9.2	103.2±9.0	59.0±6.1	100.3±5.8	224.6±25.6	98.7±9.1	543.9±50.0	425.8±39.1	219.4±20.2	**
7	504.2±45.1	142.2±13.4	29.1±6.7	92.8±19.4	50.1±8.6	80.0±20.3	54.0±8.6	91.9±8.0	44.8±4.6	90.8±5.2	190.3±21.7	80.2±7.4	527.0±48.4	370.1±34.0	193.7±17.8	**
8	166.7±14.9	46.3±4.4	15.9±3.6	31.1±6.5	18.4±2.5	23.6±6.0	15.5±2.5	23.7±2.1	13.9±1.4	27.2±1.6	64±37.3	69.0±6.3	214.7±19.7	186.7±17.2	146.5±13.5	**
9	48.8±4.4	10.3±1.0	3.4±0.8	11.2±2.3	14.3±1.3	4.6±1.2	7.9±1.3	18.5±1.6	6.9±0.7	5.3±0.3	13.9±1.6	37.2±3.4	136.3±12.5	130.3±12.0	114.2±10.5	**
10	47.2±4.2	3.9±0.4	2.3±0.5	3.4±0.7	1.3±0.2	1.6±0.4	1.0±0.2	1.9±0.2	-	3.5±0.2	8.8±1.0	42.1±4.1	102.8±13.7	55.4±5.5	44.5±5.9	19.4±1.9
11	1.3±0.1	1.2±0.1	0.1±0.01	0.3±0.1	0.2±0.04	0.6±0.2	0.1±0.02	0.1±0.01	-	1.5±0.1	0.8±0.1	1.2±0.1	3.4±0.5	9.3±0.9	15.4±2.0	5.9±0.6
12	25.5±2.3	5.1±0.5	2.1±0.5	8.9±1.8	3.7±0.9	2.5±0.6	3.8±0.6	5.5±0.5	1.1±0.1	3.7±0.2	15.1±1.7	47.2±4.6	76.2±10.1	53.2±5.3	43.5±5.8	65.8±6.5
13	9.2±0.8	3.2±0.3	1.8±0.4	5.0±1.0	2.1±0.5	1.5±0.4	1.8±0.3	2.8±0.2	0.8±0.1	3.1±0.2	6.7±0.8	12.5±1.2	20.5±2.7	16.1±1.6	8.7±1.2	11.4±1.1
14	458.4±78.7	188.9±32.9	67.6±18.8	195.7±52.4	84.2±22.9	35.7±9.7	39.0±4.3	148.7±24.7	43.0±7.3	79.1±22.2	164.7±26.9	263.9±25.9	408.2±54.3	271.3±26.8	297.7±39.4	168.9±16.6
15	184.9±28.8	16.3±3.1	9.4±2.4	28.1±14.1	14.5±4.3	-	14.5±5.4	32.4±14.1	10.9±4.3	11.7±2.2	36.4±6.5	49.2±10.7	22.7±5.1	31.8±7.5	34.4±8.6	18.6±4.2
16	146.6±22.8	13.0±2.5	5.0±1.3	13.5±6.8	10.6±3.1	2.0±0.6	17.2±6.5	29.8±13.0	10.0±4.0	9.0±1.7	33.1±5.9	47.0±10.2	23.2±5.2	24.2±5.7	26.2±6.6	13.9±3.2

*The emission rate of styrene calculated by subtracting the emission rate of ethyl benzene, m/p-xylene and o-xylene from the emission rate of the single-ring aromatic group with two carbon substitutions. **_{tr} shift, tridecane not observed.

Table S4S3 – Measured emission rates of the grouped VOC-IVOCs VOCs in each experiment (mg kg⁻¹)

Exp. Nu.	Branched Aliphatics							Aromatic Substitutions
	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₃
1	1.3±0.3	7.4±1.9	4.4±1.0	9.1±2.2	22.1±5.0	35.7±8.6	**	2.9±0.6
2	1.3±0.3	3.7±0.9	6.7±1.5	17.3±4.2	32.0±7.3	74.4±17.9	**	5.2±1.1
3	4.4±1.0	18.8±4.8	46.8±10.7	76.8±18.8	72.0±16.4	86.4±20.8	**	14.2±3.1
4	4.1±0.9	34.6±8.8	108.8±24.9	170.4±41.7	175.9±40.2	124.0±29.9	**	6.9±1.5
5	3.4±0.8	27.6±7.0	71.7±16.4	90.8±22.2	71.0±16.2	69.4±16.7	**	1.8±0.4
6	122.4±27.6	514.5±130.5	1135.2±259.7	1488.5±363.9	1507.2±344.1	1563.7±376.7	**	237.6±52.5
7	99.3±22.4	492.4±124.9	1013.8±232.0	1528.6±373.7	1210.9±276.4	1204.3±290.1	**	201.2±44.5
8	32.6±7.4	142.2±36.1	278.9±63.8	405.9±99.2	410.7±93.8	492.8±118.7	**	75.0±16.6
9	9.1±2.1	56.4±14.3	166.3±38.0	238.0±58.2	211.2±48.2	144.7±34.9	**	48.7±10.8
10	7.2±1.6	30.8±7.8	92.4±21.1	151.5±37.0	94.9±21.7	54.8±13.2	47.3±10.9	10.3±2.3
11	0.9±0.2	0.9±0.2	1.9±0.4	3.4±0.8	5.5±1.3	8.7±2.1	6.0±1.4	1.3±0.3
12	8.2±1.8	66.3±16.8	111.2±25.4	158.1±38.7	105.2±24.0	105.6±25.4	82.5±19.0	19.1±4.2
13	6.3±1.4	25.2±6.4	39.6±9.1	55.5±13.6	41.1±9.4	41.6±10.0	34.5±8.0	14.0±3.1
14	97.7±25.1	276.9±69.8	350.8±93.2	402.2±112.4	286.2±75.9	83.0±22.9	**	166.1±42.4
15	15.0±4.1	108.9±26.6	77.9±24.5	48.5±13.6	49.3±14.6	11.5±3.6	15.6±4.3	82.8±30.7
16	10.9±3.0	105.2±25.7	73.9±23.2	45.7±12.8	45.6±13.5	12.5±3.9	15.4±4.3	65.2±24.2

**_{tr} shift, C₁₃ aliphatic grouping not observed.

Table S584 – Percentage contribution of the individual compoundsVOCs to the Σ SpVOC emission rate in each experiment.

Exp. Nu.	Exp. Date	Benzene	Toluene	Ethyl benzene	m/p-xylene	o-xylene	Styrene*	1,3,5-TMB	1,2,4-TMB	1,2,3-TMB	Heptane	Octane	Nonane	Decane	Undecane	Dodecane
1	30.07.14	0.8±0.1	0.3±0.03	0.1±0.03	0.2±0.03	-	0.007±0.002	-	-	1.3±0.1	0.3±0.02	0.4±0.05	0.6±0.1	2.2±0.2	12.1±1.1	49.3±4.5
2	31.07.14	0.5±0.05	0.5±0.04	0.01±0.003	0.0±0.01	0.1±0.02	0.004±0.001	-	-	-	0.2±0.01	-	0.7±0.1	2.1±0.2	9.4±0.9	45.6±4.2
3	01.08.14	3.3±0.03	0.6±0.1	0.3±0.1	0.5±0.1	0.4±0.1	0.5±0.1	0.4±0.1	0.4±0.04	0.3±0.03	0.4±0.02	0.8±0.1	2.0±0.2	5.6±0.5	8.3±0.8	23.0±2.1
4	05.08.14	3.6±0.3	0.1±0.01	-	0.2±0.04	0.1±0.03	0.3±0.1	-	0.1±0.01	-	0.0±0.002	0.4±0.04	1.4±0.1	6.7±0.6	10.3±0.9	23.4±2.1
5	08.08.14	5.9±0.5	0.2±0.02	0.05±0.01	0.2±0.04	0.1±0.03	0.1±0.03	0.1±0.01	0.1±0.01	0.1±0.01	0.3±0.02	1.3±0.1	3.2±0.3	10.9±1.0	9.3±0.9	9.1±0.8
6	06.08.14	4.6±0.4	1.6±0.2	0.4±0.1	1.1±0.2	0.7±0.2	0.9±0.2	0.6±0.1	1.1±0.1	0.6±0.1	1.1±0.1	2.4±0.3	1.1±0.1	5.9±0.5	4.6±0.4	2.4±0.2
7	07.08.14	6.1±0.5	1.7±0.2	0.4±0.1	1.1±0.2	0.6±0.2	1.0±0.2	0.7±0.1	1.1±0.1	0.5±0.1	1.1±0.1	2.3±0.3	1.0±0.1	6.4±0.6	4.5±0.4	2.3±0.2
8	06.08.14 (2)	5.7±0.5	1.6±0.1	0.5±0.1	1.1±0.2	0.6±0.2	0.8±0.2	0.5±0.1	0.8±0.1	0.5±0.05	0.9±0.1	2.2±0.3	2.4±0.2	7.4±0.7	6.4±0.6	5.0±0.5
9	06.08.14 (3)	3.4±0.3	0.7±0.05	0.2±0.1	0.8±0.2	1.0±0.3	0.3±0.1	0.5±0.1	1.3±0.1	0.5±0.05	0.4±0.02	1.0±0.1	2.6±0.2	9.5±0.9	9.1±0.8	7.9±0.7
10	13.11.14 (1)	6.2±0.6	0.5±0.2	0.3±0.1	0.5±0.1	0.2±0.04	0.2±0.05	0.1±0.02	0.2±0.02	-	0.5±0.03	1.2±0.1	5.5±0.5	13.5±1.8	7.3±0.7	5.8±0.8
11	13.11.14 (2)	2.3±0.2	2.1±0.06	0.1±0.02	0.4±0.1	0.3±0.1	1.0±0.3	0.2±0.04	0.2±0.01	-	2.6±0.2	1.4±0.2	2.1±0.2	5.9±0.8	16.0±1.6	26.5±3.5
12	14.11.14 (1)	2.9±0.3	0.6±0.1	0.2±0.06	1.0±0.2	0.4±0.1	0.3±0.1	0.4±0.1	0.6±0.05	0.1±0.01	0.4±0.02	1.7±0.2	5.4±0.5	8.7±1.2	6.1±0.6	5.0±0.7
13	14.11.14 (2)	2.9±0.3	1.0±0.7	0.6±0.1	1.6±0.3	0.7±0.2	0.5±0.1	0.6±0.1	0.9±0.1	0.2±0.03	1.0±0.06	2.1±0.2	3.9±0.4	6.4±0.9	5.0±0.5	2.7±0.4
14	25.11.14	10.4±1.8	4.3±0.4	1.5±0.4	4.4±1.2	1.9±0.5	0.8±0.2	0.9±0.1	3.4±0.6	1.0±0.2	1.8±0.5	3.7±0.6	6.0±0.6	9.3±1.2	6.2±0.6	6.8±0.9
15	01.10.15	20.7±3.2	1.8±0.3	1.1±0.3	3.2±1.6	1.6±0.5	-	1.6±0.6	3.6±1.6	1.2±0.5	1.3±0.2	4.1±0.7	5.5±1.2	2.5±0.6	3.6±0.8	3.9±1.0
16	29.09.15	19.1±3.0	1.7±7.0	0.6±0.2	1.8±0.9	1.4±0.4	0.3±0.1	2.2±0.8	3.9±1.7	1.3±0.5	1.2±0.2	4.3±0.8	6.1±1.3	3.0±0.7	3.2±0.7	3.4±0.9

*The emission rate of styrene calculated by subtracting the emission rate of ethyl benzene, m/p-xylene and o-xylene from the emission rate of the single-ring aromatic group with two carbon substitutions. **_{tr} shift, tridecane not observed.

Table S6S5 - Percentage contribution of grouped compoundsVOCs to Σ SpVOC emission rate in each experiment

Exp. Nu.	Aliphatic Grouping						Aromatic Substitutions
	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₃
1	0.5±0.1	2.9±0.7	1.7±0.4	3.6±0.9	8.7±2.0	14.0±3.4	1.1±0.3
2	0.4±0.1	1.1±0.3	1.9±0.4	5.0±1.2	9.3±2.1	21.7±5.2	1.5±0.3
3	0.7±0.2	3.1±0.8	7.8±1.8	12.8±3.1	12.0±2.7	14.4±3.5	2.4±0.5
4	0.3±0.1	3.0±0.7	9.3±2.1	14.5±3.6	15.0±3.4	10.6±2.5	0.6±0.1
5	0.6±0.1	4.8±1.2	12.6±2.9	16.0±3.9	12.5±2.8	12.2±2.9	0.3±0.1
6	1.3±0.3	5.6±1.4	12.2±2.8	16.1±3.9	16.3±3.7	16.9±4.1	2.6±0.6
7	1.2±0.3	5.9±1.5	12.2±2.8	18.4±4.5	14.6±3.3	14.5±3.5	2.4±0.5
8	1.1±0.3	4.9±1.2	9.6±2.2	14.0±3.4	14.2±3.2	17.0±4.1	2.6±0.6
9	0.6±0.1	3.9±1.0	11.6±2.6	16.6±4.0	14.7±3.4	10.1±2.4	3.4±0.7
10	0.9±0.2	4.0±1.0	12.1±2.8	19.9±4.9	12.5±2.8	7.2±1.7	1.4±0.3
11	1.5±0.3	1.6±0.4	3.2±0.7	5.8±1.4	9.5±2.2	15.0±3.6	2.2±0.5
12	0.9±0.2	7.6±1.9	12.8±2.9	18.2±4.4	12.1±2.8	12.1±2.9	2.2±0.5
13	2.0±0.4	7.9±2.0	12.4±2.8	17.4±4.2	12.9±2.9	13.0±3.1	4.4±1.0
14	2.2±0.6	6.3±1.6	8.0±2.1	9.1±2.5	6.5±1.7	1.9±0.5	3.8±1.0
15	1.7±0.5	12.2±3.0	8.7±2.7	5.4±1.5	5.5±1.6	1.3±0.4	9.3±3.4
16	1.4±0.4	13.7±3.3	9.6±3.0	5.9±1.7	5.9±1.7	1.6±0.5	8.5±3.1

Table S786 – Emission rates of the speciated aromatic and aliphatic compounds~~VOCs~~ and their percentage contribution to the Σ SpVOC emission rate in each experiment

Exp. Nu.	Exhaust composition (mg kg ⁻¹)			Percentage exhaust composition (%)*	
	Aromatic	Aliphatic	Total Speciated	Aromatic	Aliphatic
1	9.6±0.8	245.1±15.8	254.7±15.8	3.8±0.3	96.2±6.2
2	9.1±1.2	334.5±24.7	343.6±24.7	2.6±0.3	97.4±7.2
3	53.7±3.8	545.4±37.2	599.0±37.4	9.0±0.6	91.0±6.2
4	59.8±4.3	1111.8±75.8	1171.7±75.9	5.1±0.4	94.9±6.5
5	40.9±3.0	528.1±37.9	569.0±38.0	7.2±0.5	92.8±6.7
6	1323.7±76.7	7944.2±695.1	9267.9±699.3	14.3±0.8	85.7±7.5
7	1290.3±73.1	7001.4±612.0	8291.7±616.3	15.6±0.9	84.4±7.4
8	430.0±25.3	2471.6±197.8	2901.6±199.4	14.8±0.9	85.2±6.8
9	174.6±12.7	1262.9±94.9	1437.5±95.7	12.1±0.9	87.9±6.6
10	73.1±4.9	755.3±54.0	828.5±54.3	9.6±0.6	90.4±6.9
11	5.1±0.4	64.8±3.8	69.9±3.8	8.8±0.6	91.2±6.0
12	77.3±5.4	941.6±65.1	1018.9±65.4	8.9±0.6	91.1±7.1
13	42.1±3.5	322.9±24.0	365.0±24.2	13.2±1.1	86.8±7.1
14	1427.4±116.1	3150.8±201.2	4578.1±232.3	32.4±2.6	67.6±4.5
15	393.6±47.4	531.5±45.7	925.2±65.9	44.2±5.3	55.8±5.1
16	312.9±37.4	486.0±42.9	798.9±56.9	40.7±4.9	59.3±5.5

*To allow for direct comparison between experiments, the percentage exhaust composition does not include tridecane and the C₁₃ branched aliphatic grouping.

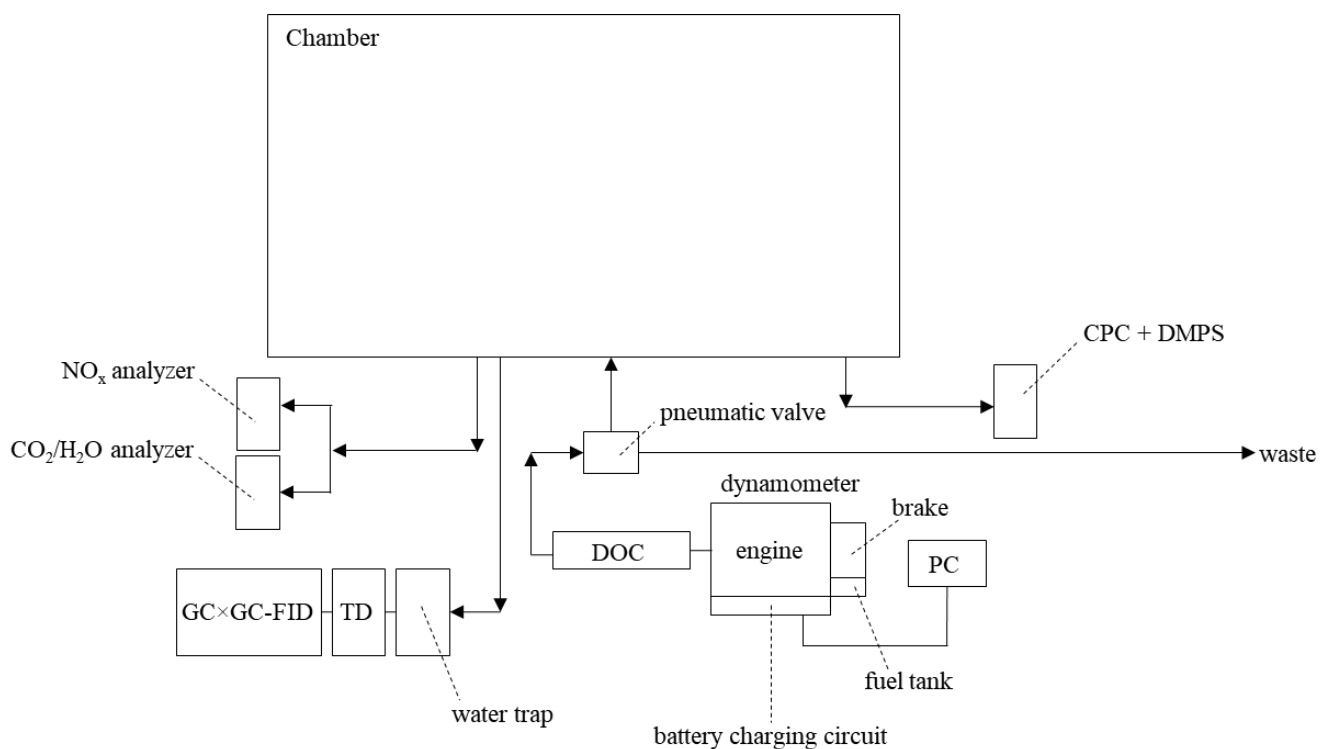


Figure 1 – Schematic of dynamometer and sampling system. Arrows display air flow direction. CPC = condensation particle counter. DMPS = differential mobility particle sizer. DOC = diesel oxidative catalyst. TD = thermal desorption unit. GCxGC-FID = comprehensive two-dimensional gas chromatography flame ionisation detector. See experimental Section 2, for further information.

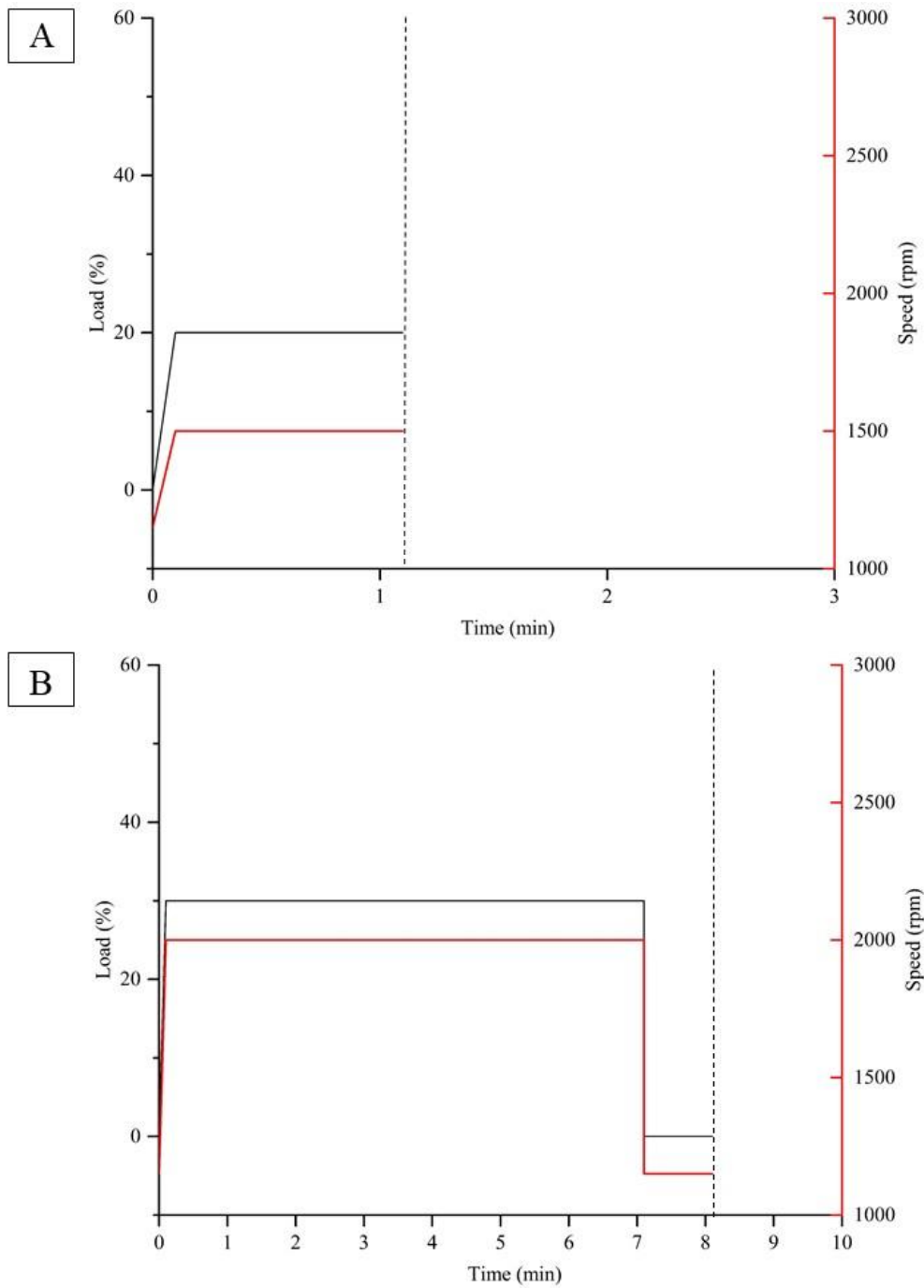
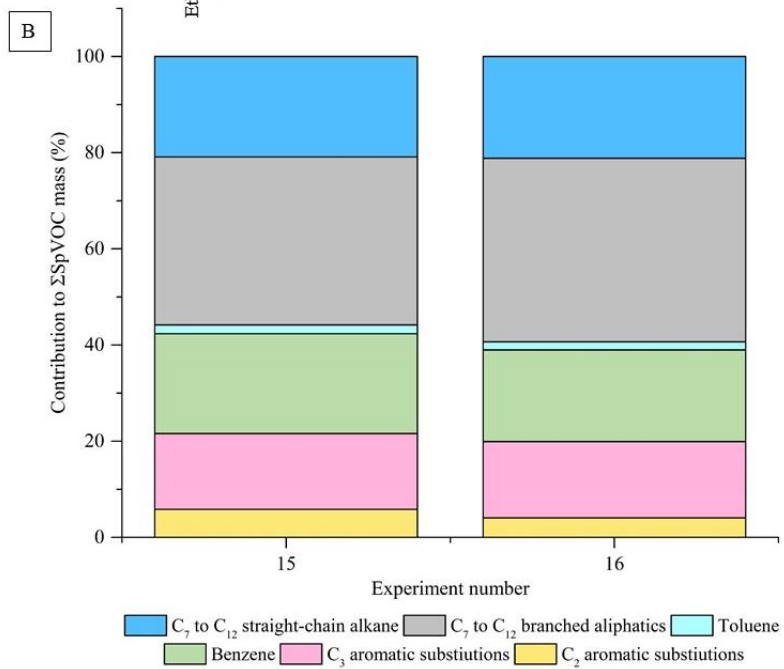
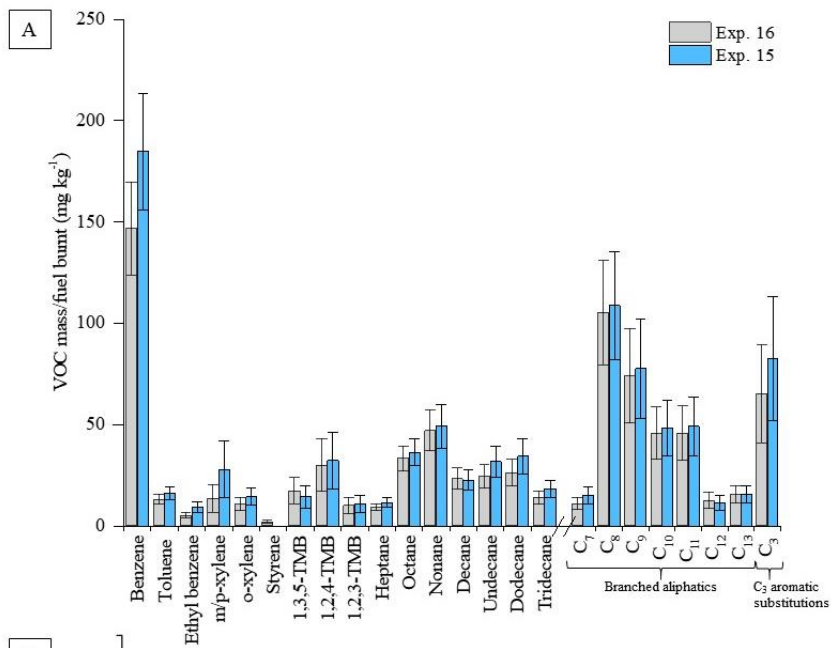


Figure S2 – Sequence of engine speeds and loads performed in driving scenario experiments, (A) ‘short journey’ (exp. 8, see Table 1) and, (B) ‘warm idle following load’ (exp. 9, see Table 1). Dashed line = exhaust emissions injected into the MAC. Black line = engine load (primary y-axis). Red line = engine speed (secondary y-axis).



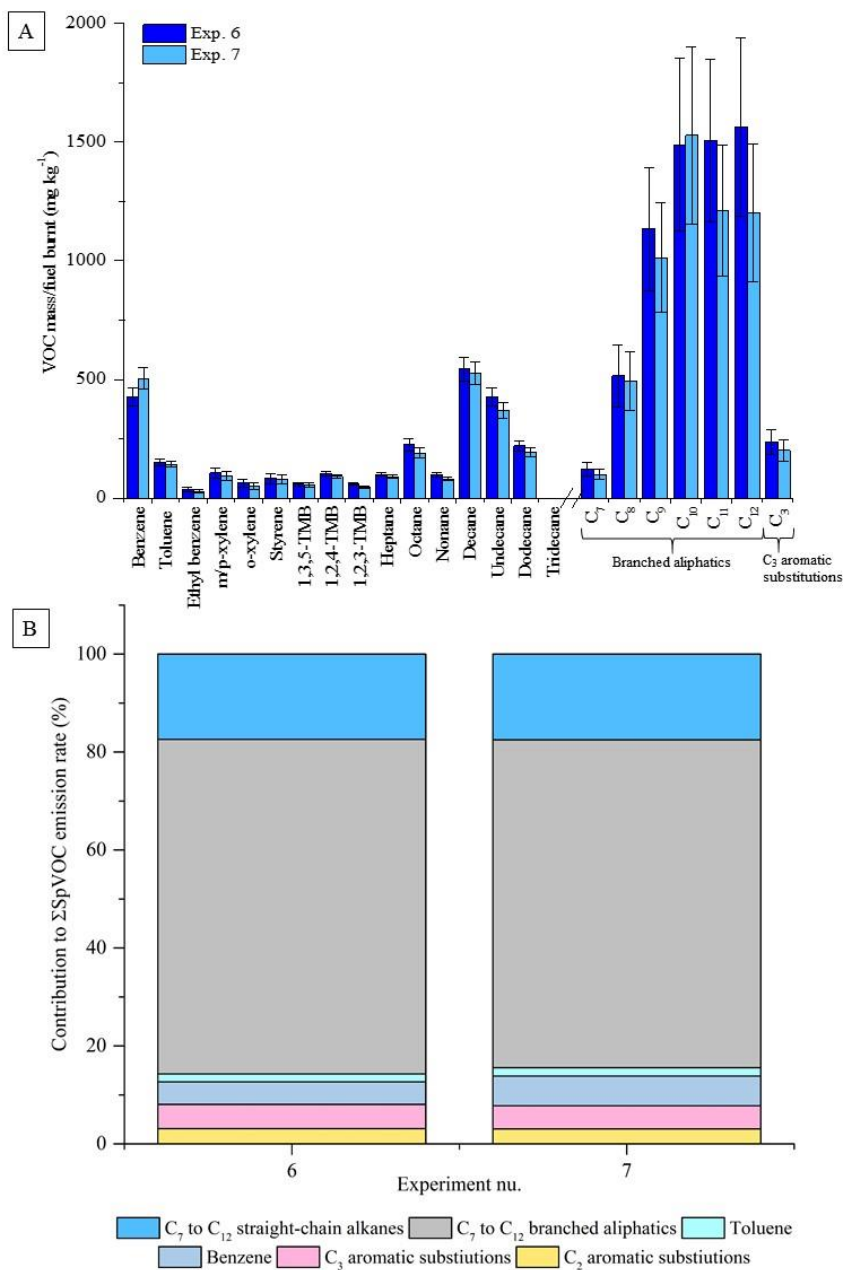


Figure S1— Comparison of measured VOC emission rates in repeat cold-start experiments (exp. 6 and 7) (A). Comparison of the percentage contribution of the individual and grouped VOCs to the Σ SpVOC emission rates in exp. 6 and 7 (B). The emission rates of tridecane and the C₁₃-branched aliphatic grouping has not been included in (B) to allow direct comparison between other experiments where these species were not measured.

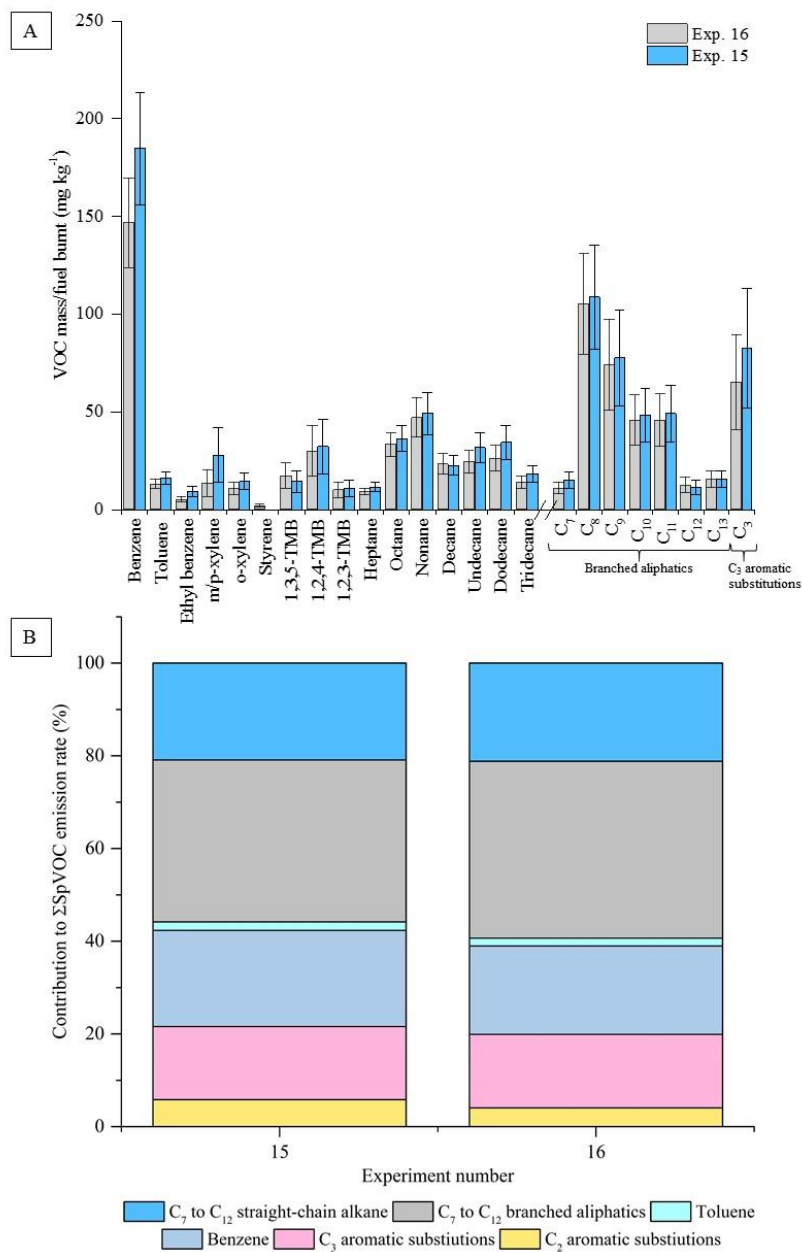
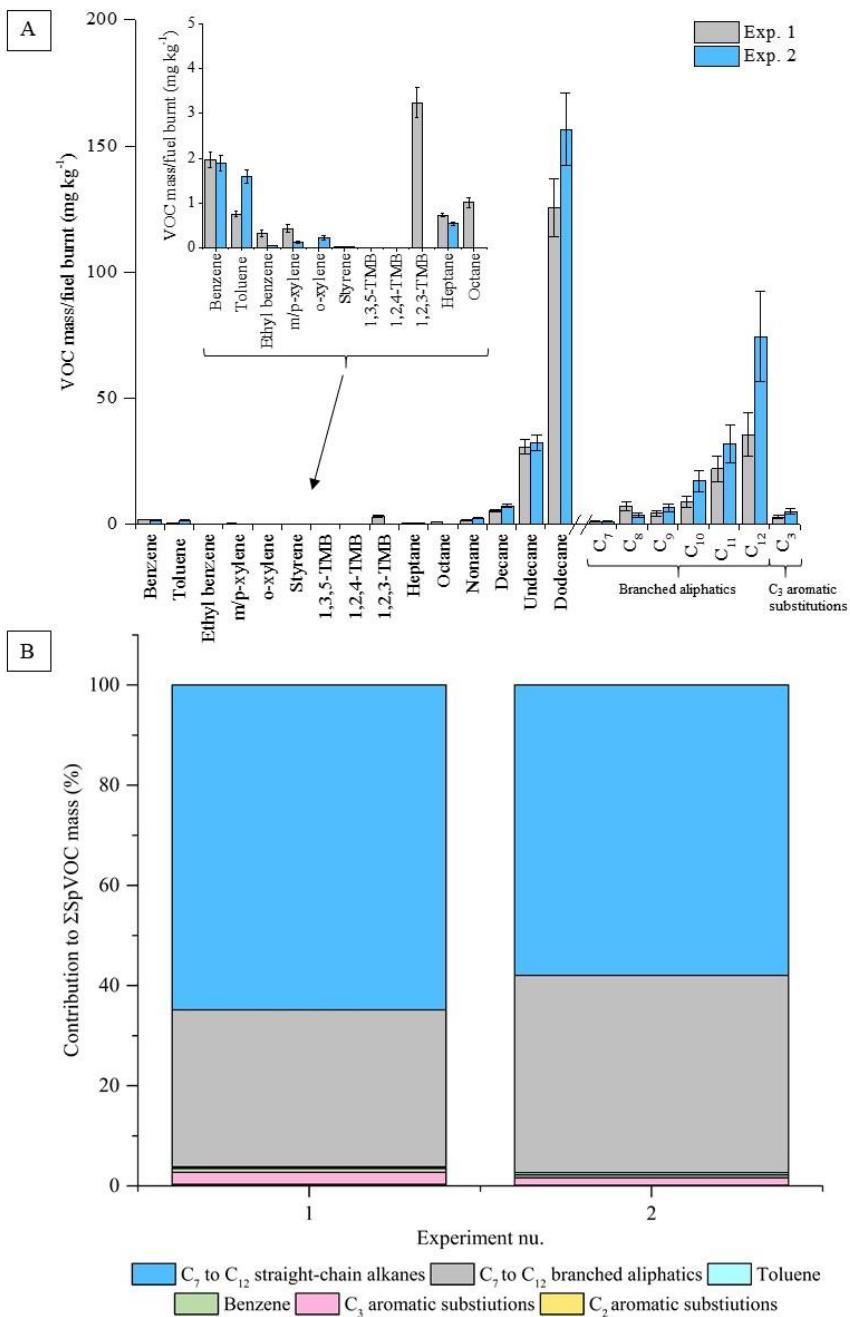


Figure S3S2 – Comparison of measured VOC-IVOC emission rates in ~~replicate~~repeat WWL experiments (exp. 15 and 16, 2000 rpm, 30% load) (A). Comparison of the percentage contribution of the individual and grouped ~~compounds~~VOCs to the ΣSpVOC emission rates in exp. 15 and 16 (B). The emission rates of tridecane and the C₁₃ branched aliphatic grouping has not been included in (B) to allow direct comparison between other experiments where these species were not measured. Error bars represent the calculated uncertainty in the measured emission rates, see the SI section 1.1 for further information.



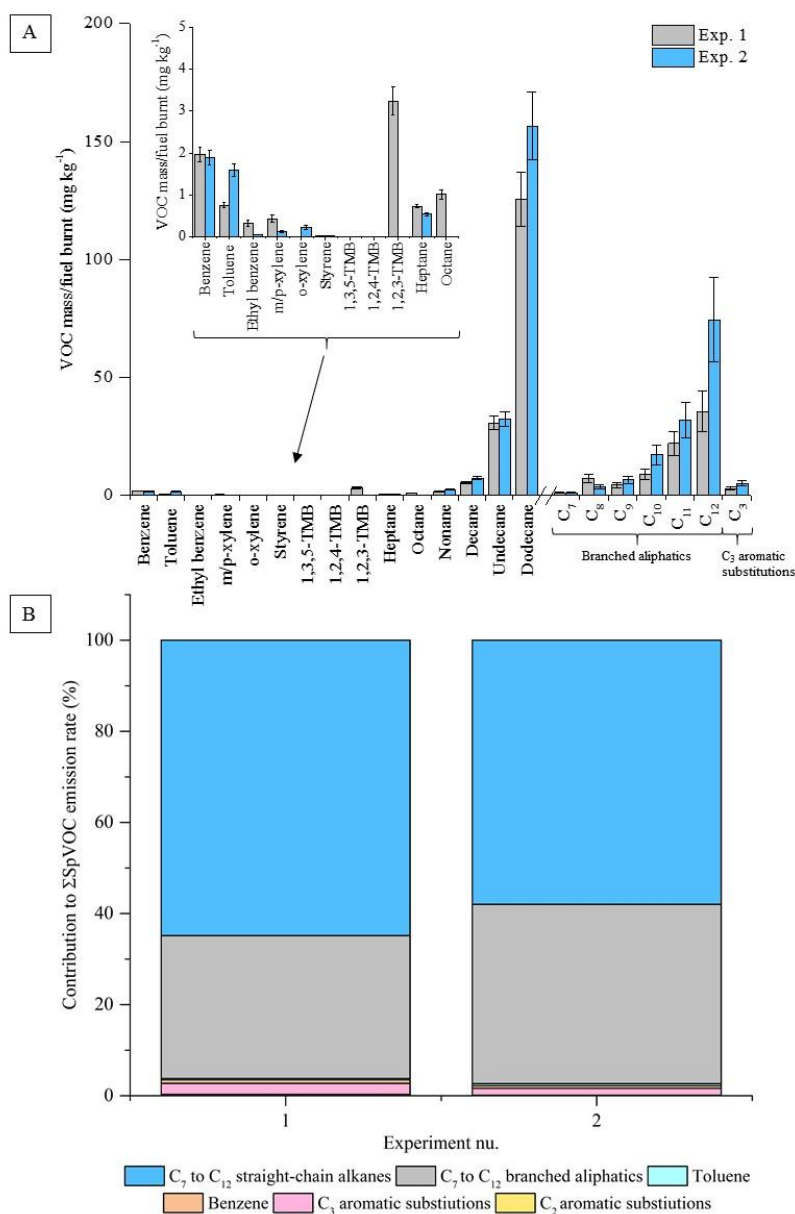
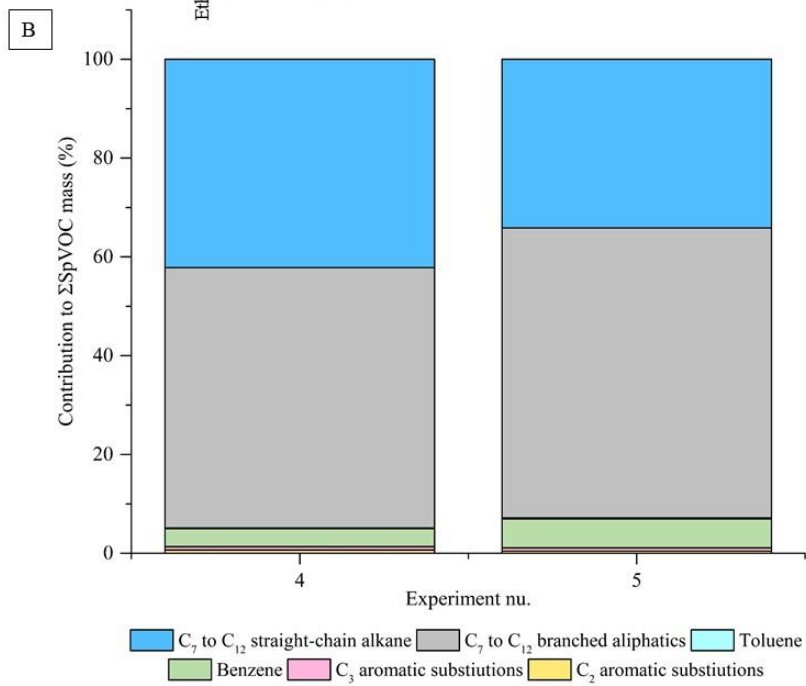
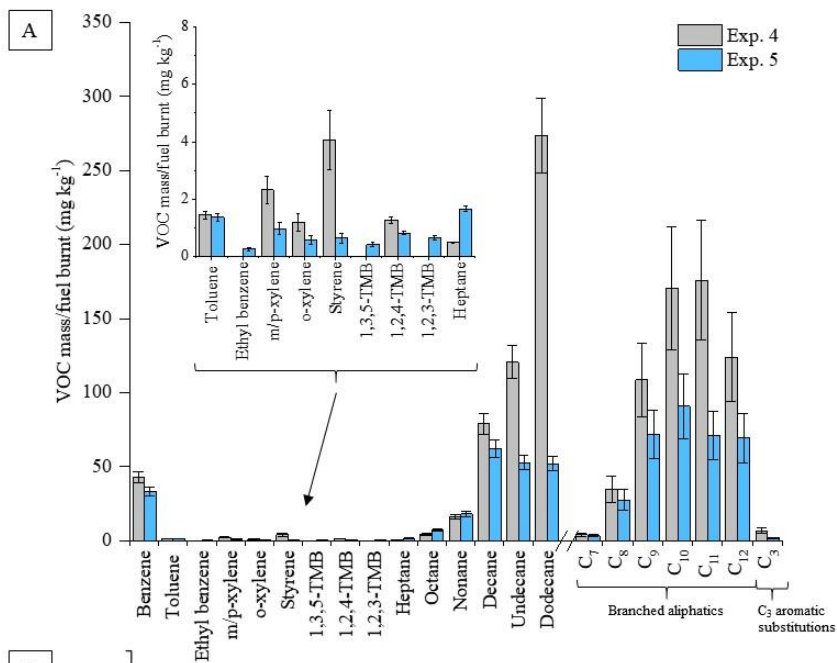


Figure S4S3 – Comparison of measured VOC-IVOC emission rates in replicate warm high load repeat experiments 1 and 2 (exp. 1 and 2, 2500 rpm, 40% load) (A). Comparison of the percentage contribution of the individual and grouped compounds VOCs to the Σ SpVOC emission rates in exp. 1 and 2 (B). The emission rates of tridecane and the C₁₃ branched aliphatic grouping has not been included in (B) to allow direct comparison between other experiments where these species were not measured. Error bars represent the calculated uncertainty in the measured emission rates, see the SI section 1.1 for further information.



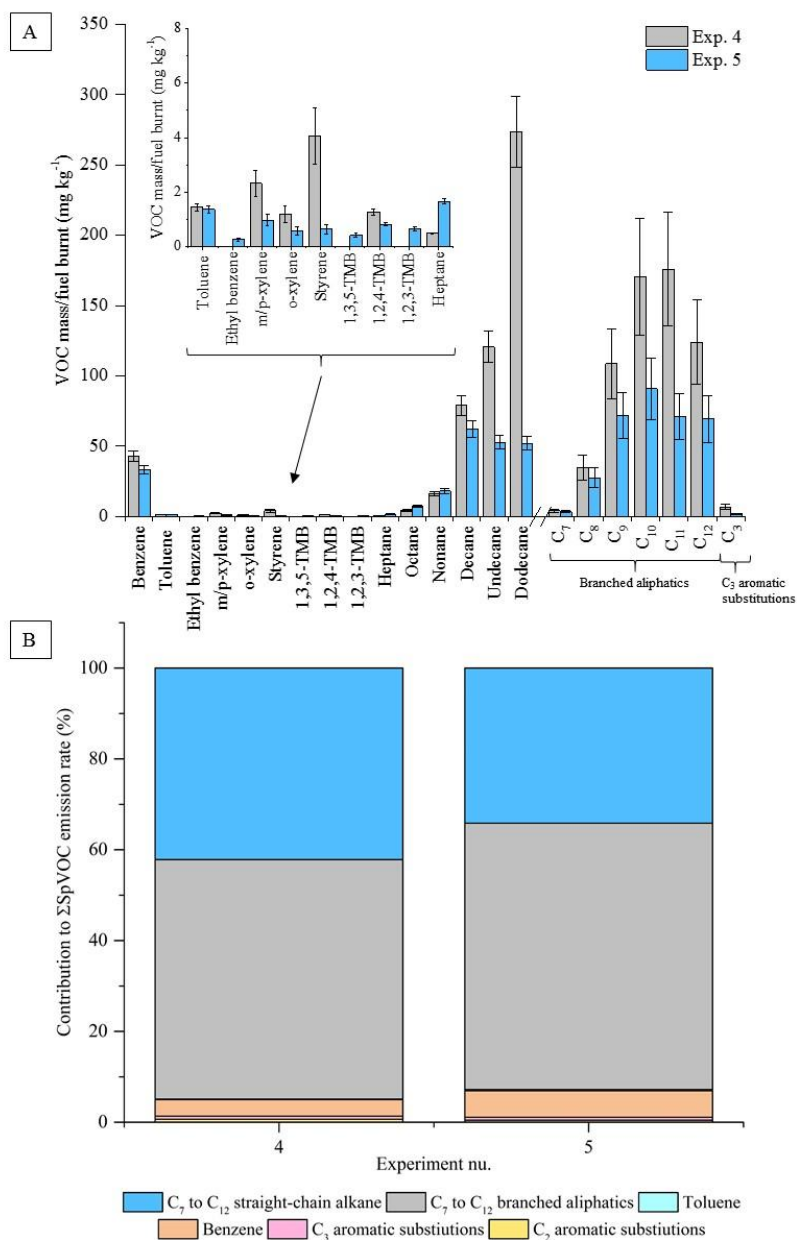


Figure S584 – Comparison of measured VOC-IVOC emission rates in replicate warm with load repeat experiments 4 and 5 (2000 rpm, 3040% load) (A). Comparison of the percentage contribution of the individual and grouped compounds/VOCs to the ΣSpVOC emission rates in exp. 4 and 5 (B). The emission rates of tridecane and the C₁₃ branched aliphatic grouping has not been included in (B) to allow direct comparison between other experiments where these species were not measured. Error bars represent the calculated uncertainty in the measured emission rates, see the SI section 1.1 for further information.

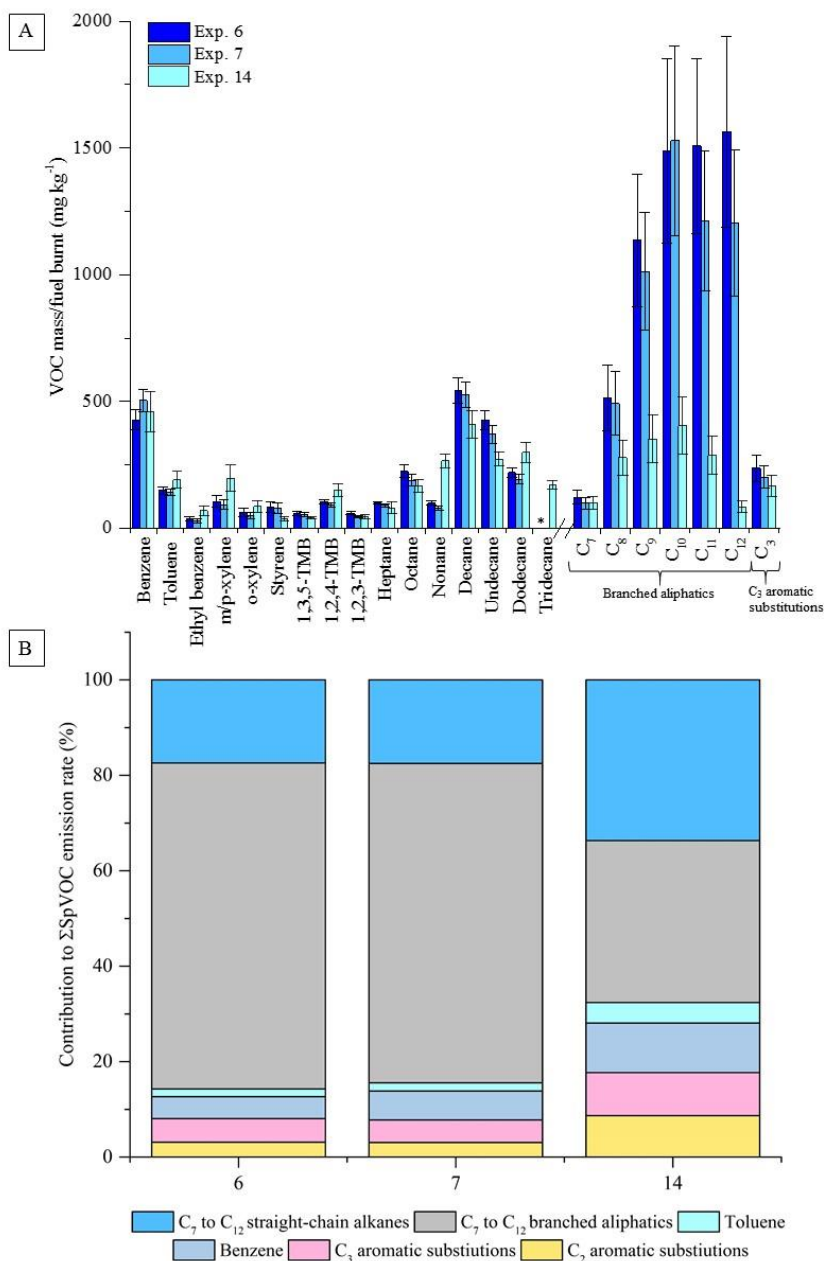


Figure S5— Comparison of measured VOC emissions rates in repeat cold-start experiments 6 and 7 (fuel batch A) with cold-start experiment 14 (fuel batch B) (A). Comparison of the percentage contribution of the individual and grouped VOCs to the Σ SpVOC emission rates in experiments 6, 7, 14 (B). The emission rates of tridecane and the C₁₃-branched aliphatic grouping has not been included in (B) to allow direct comparison between other experiments where these species were not measured.

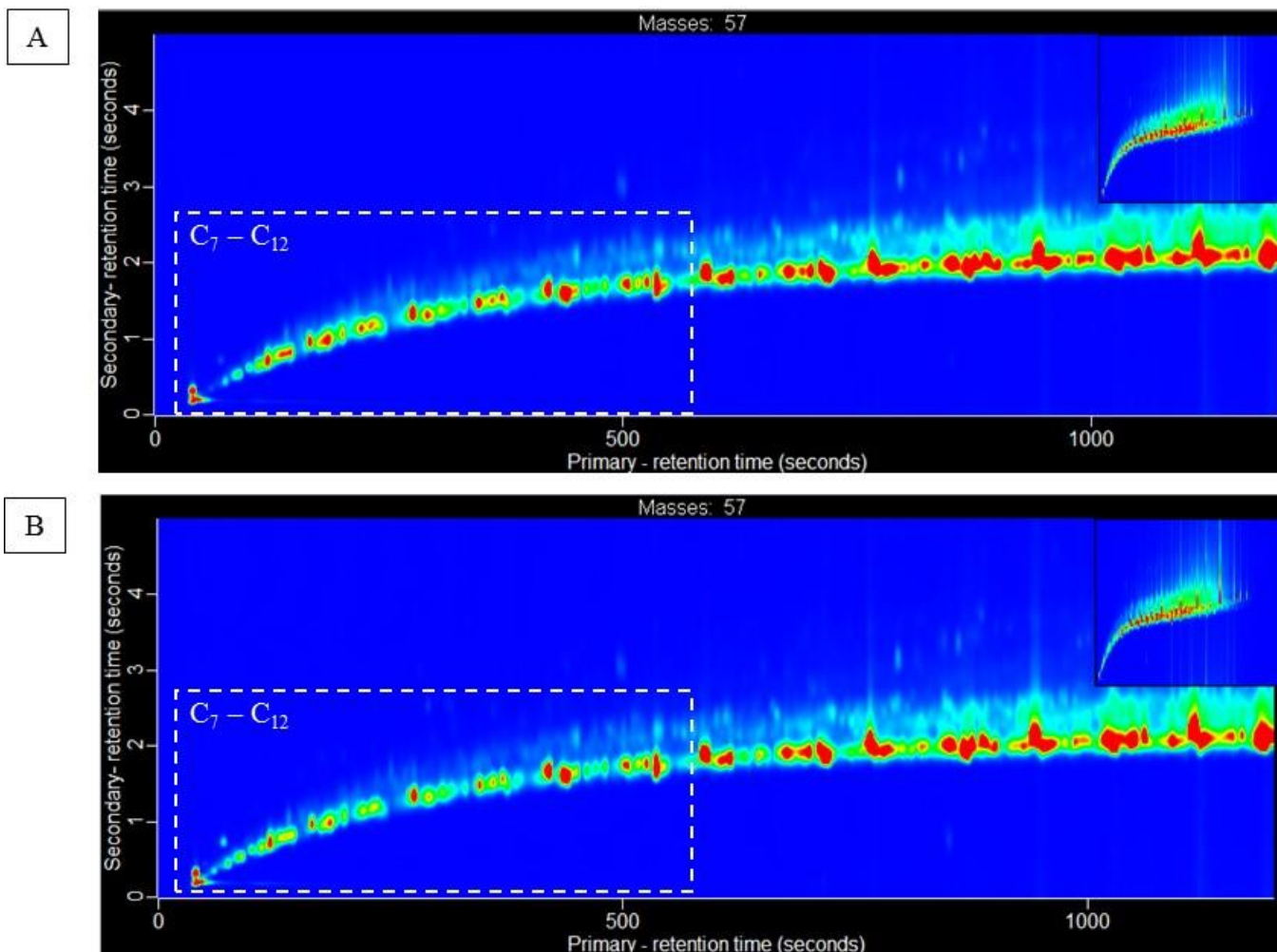


Figure S6 – Extracted ion chromatogram of m/z 57 (dominate aliphatic fragment ion) for the liquid diesel fuel samples analysed using GC \times GC-TOFMS. A = Fuel batch A (see [section 3.1.1](#) for further information). B = Fuel batch B. Chromatogram axis, x = primary column, first dimension separation (boiling point, increasing from left-to-right), y = secondary column, second dimension separation (polarity, increasing from bottom-to-top). Colour scale represents peak intensity, increasing from blue to red. Chromatograms have been normalised to allow direct comparison of peak intensity between chromatograms. Dashed box highlights an approximate carbon number range of C₇ to C₁₂, determined from the [NIST](#) library identification of individual compounds.

4. References

IOFI: Guidelines for the quantitative gas chromatography of volatile flavouring substances, from the Working Group on Methods of Analysis of the International Organization of the Flavor Industry (IOFI), *Flavour and Fragrance Journal*, 26, 297-299, 10.1002/ffj.2061, 2011.

Tissot, E., Rochat, S., Debonneville, C., and Chaintreau, A.: Rapid GC-FID quantification technique without authentic samples using predicted response factors, *Flavour and Fragrance Journal*, 27, 290-296, 10.1002/ffj.3098, 2012.