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

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Supplementary information

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 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 $\sum$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 injection 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 C_7 to C_{12} branched aliphatics between replicate experiments 6 and 7, and experiment 14. The emission rate of the C_7 to C_{12} 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 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}. 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 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 VOCs ranging from

C_2 to C_8 with mixing ratios of 3 to 5 ppbv. In total, 11 VOCs in the NPL standard were used for quantification. A list of the speciated 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 groupings, allowing multiple isomers in each group

5   to be calibrated using one compound with the same number of carbon atoms. For example, the mixing ratio of the C_7 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.

10   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. The RRF was calculated as shown in Eq. 1 (IOFI, 2011); where A is the peak area of the

15   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 grouping (using the effective carbon number approach) in the exhaust emissions were calculated using Eq.2. The mixing ratios of the individual and grouped 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 mass (mg) was determined by dividing the mixing ratio of the

20   individual and grouped compounds in mg m^{-3} by the chamber volume (18 m^3). Finally, the emission rates were calculated by dividing the measured VOC 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

$$RRF = \frac{A_a}{A_{rc}} \times \frac{M_{is}}{M_a}$$

25

Eq. 2

$$M_a = \frac{A_a}{A_{rc}} \times \frac{M_{is}}{RRF}$$

30

Table S1 – Calibration method and the compounds used for the quantification of the speciated VOCs

VOCs	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).

3.1 Uncertainty in emission rates

A propagation of errors was performed to determine the uncertainty in the measured VOC 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 VOCs ranged from 6 to 50%, with an average of 22%.

Table S2 – Measured emission rates of the individual VOCs 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. **t_R shift, tridecane not observed.

Table S3 – Measured emission rates of the grouped 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

**t_R shift, C_{13} aliphatic grouping not observed.

Table S4 – Percentage contribution of the individual VOCs to the ∑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. **t_R shift, tridecane not observed.

Table S5 - Percentage contribution of grouped VOCs to ∑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 S6 – Emission rates of the speciated aromatic and aliphatic VOCs and their percentage contribution to the $\sum$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 C$_{13}$ branched aliphatic grouping.
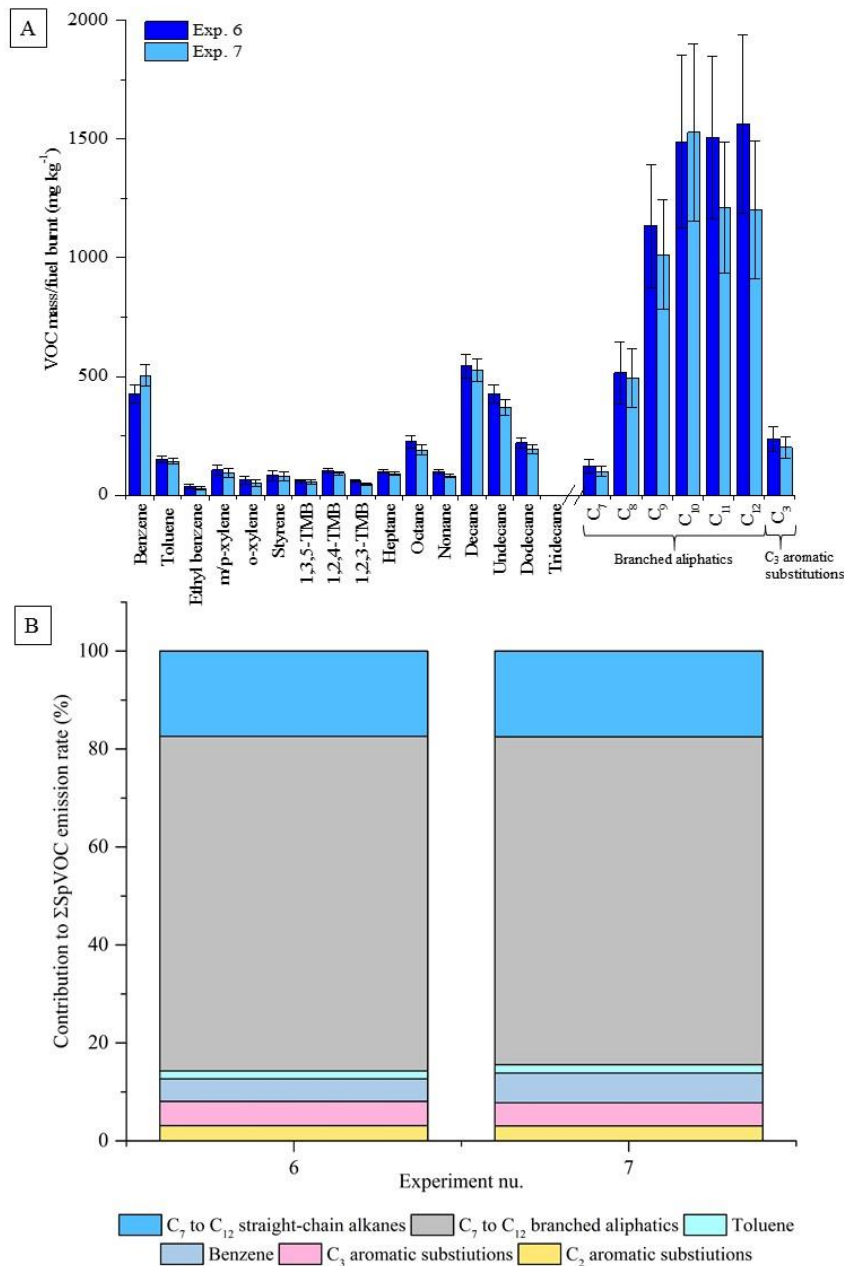
Figure S1 – Comparison of measured VOC emission rates in repeat cold-start experiments (exp. 6 and 7) (A). Comparison of the percentage contribution of the individual and grouped VOCs to the $\sum$SpVOC emission rates in exp. 6 and 7 (B). The emission rates of tridecane and the C_{13} branched aliphatic grouping has not been included in (B) to allow direct comparison between other experiments where these species were not measured.
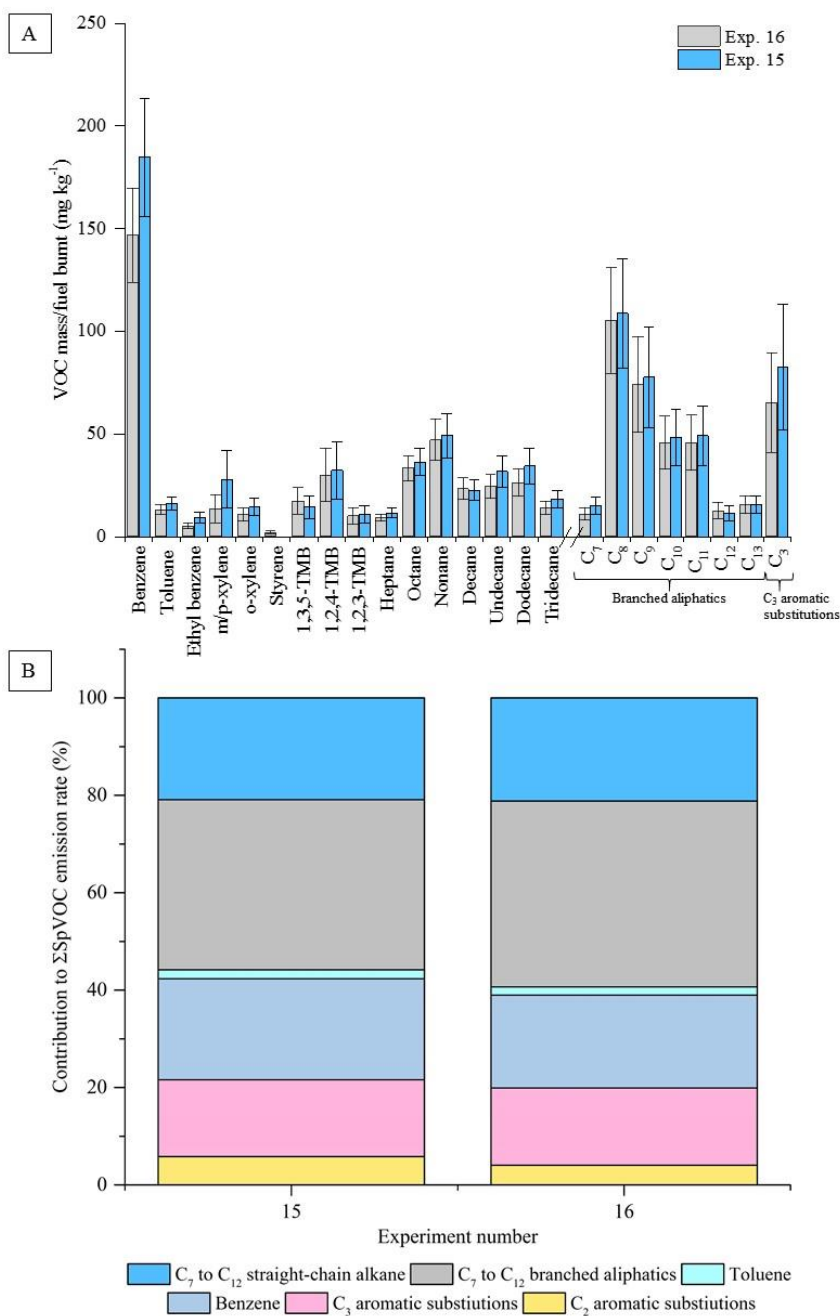
Figure S2 – Comparison of measured VOC emission rates in repeat WWL experiments (exp. 15 and 16) (A). Comparison of the percentage contribution of the individual and grouped VOCs to the $\sum$SpVOC emission rates in exp. 15 and 16 (B). The emission rates of tridecane and the C_{13} branched aliphatic grouping has not been included in (B) to allow direct comparison between other experiments where these species were not measured.
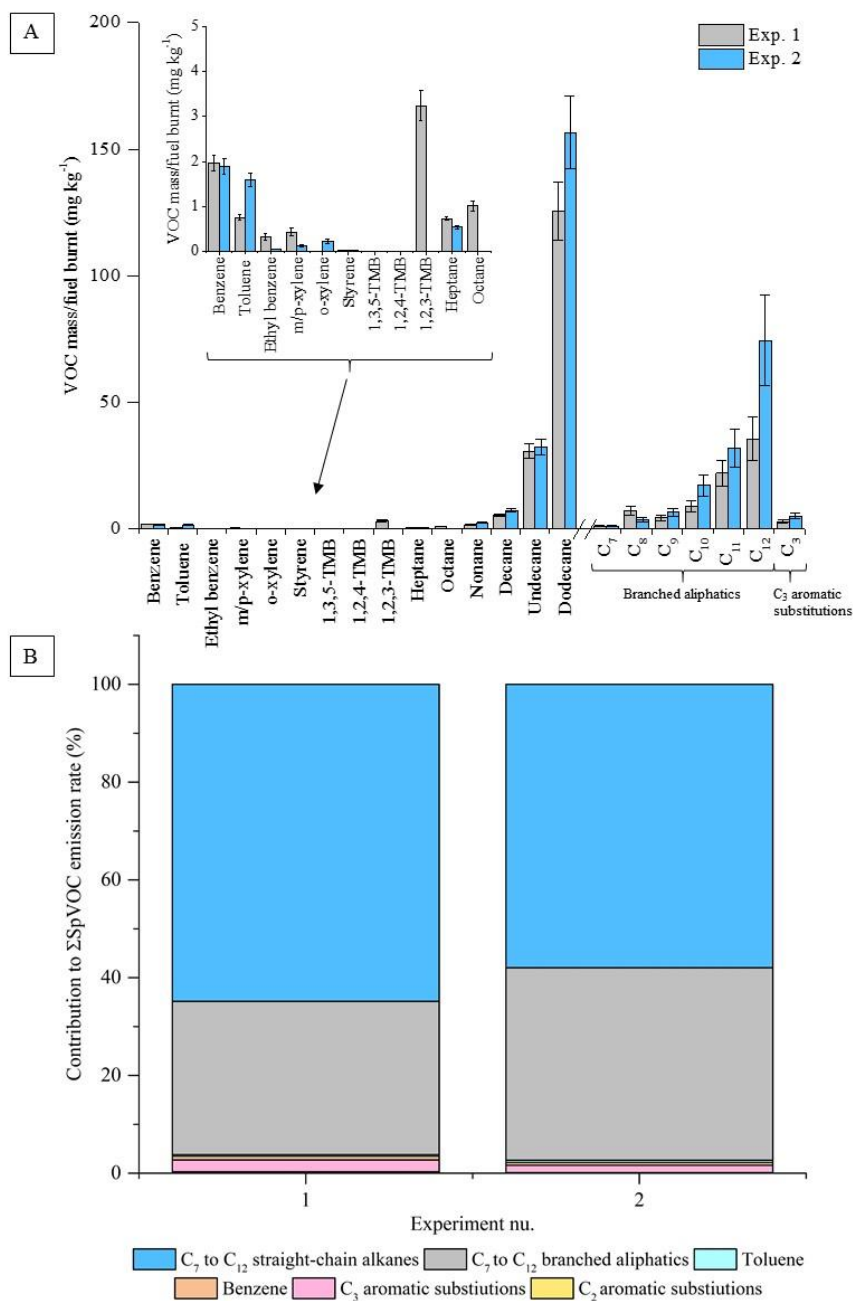
Figure S3 – Comparison of measured VOC emission rates in repeat experiments 1 and 2 (2500 rpm, 40% load) (A). Comparison of the percentage contribution of the individual and grouped VOCs to the $\sum$SpVOC emission rates in exp. 1 and 2 (B). The emission rates of tridecane and the C_{13} branched aliphatic grouping has not been included in (B) to allow direct comparison between other experiments where these species were not measured.
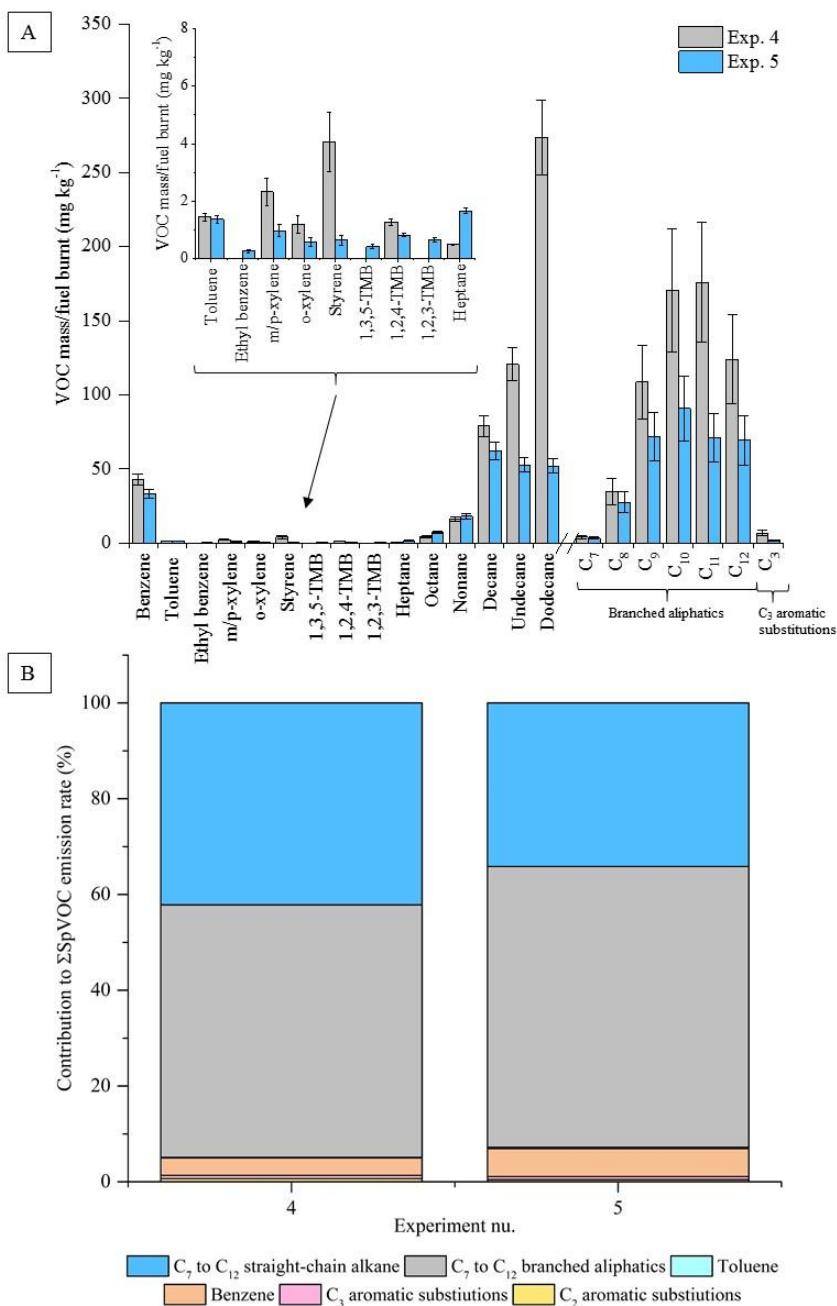
Figure S4 – Comparison of measured VOC emission rates in repeat experiments 4 and 5 (2000 rpm, 40% load) (A). Comparison of the percentage contribution of the individual and grouped VOCs to the $\sum$SpVOC emission rates in exp. 4 and 5 (B). The emission rates of tridecane and the C_{13} branched aliphatic grouping has not been included in (B) to allow direct comparison between other experiments where these species were not measured.
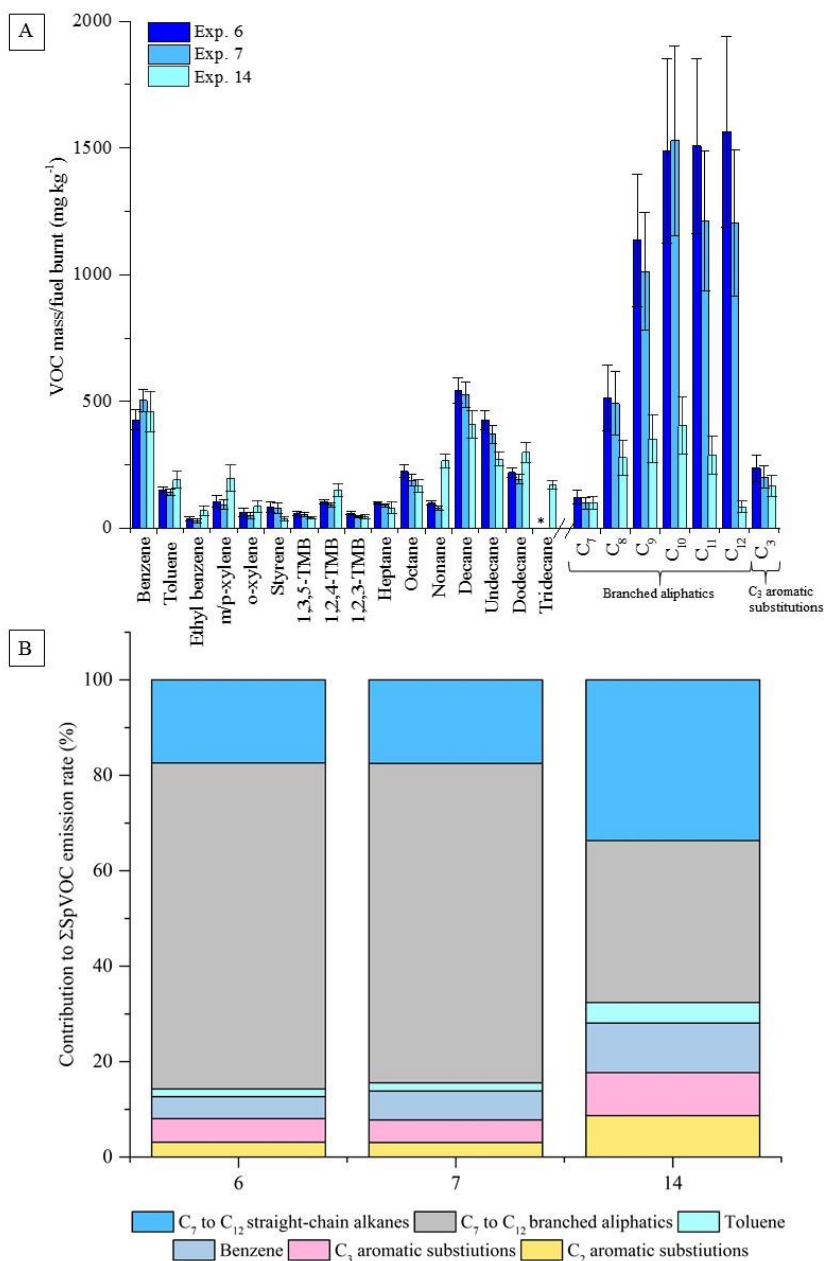
Figure S5 – Comparison of measured VOC emissions rates in repeat cold-start experiments 6 and 7 (fuel batch A) with cold-start experiment 14 (fuel batch B) (A). Comparison of the percentage contribution of the individual and grouped VOCs to the $\sum$SpVOC emission rates in experiments 6, 7, 14 (B). The emission rates of tridecane and the C_{13} branched aliphatic grouping has not been included in (B) to allow direct comparison between other experiments where these species were not measured.
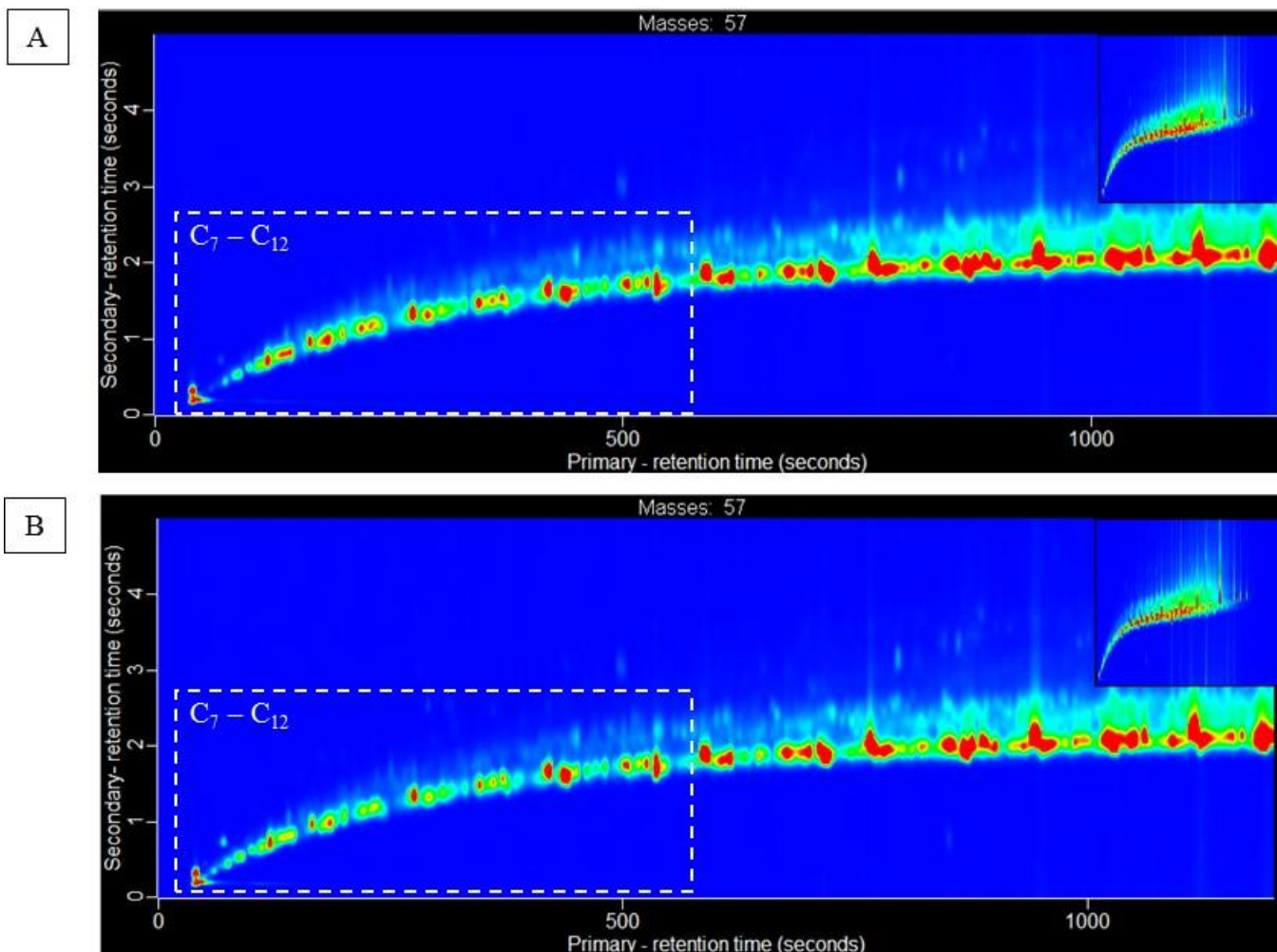
Figure S6 – Extracted ion chromatogram of *m/z* 57 (dominate aliphatic fragment ion) for the liquid diesel fuel samples analysed using GC×GC-TOFMS. A = Fuel batch A (see text for further information). B = Fuel batch B. Chromatogram axis, x = primary, first dimension separation (boiling point, increasing from left-to-right), y = secondary, 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. Dashed box highlights an approximate carbon number range of C_7 to C_{12}, determined from the library identification of individual compounds.

4. References

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