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# Supplement of

# Technical note: Use of an atmospheric simulation chamber to investigate the effect of different engine conditions on unregulated VOC-IVOC diesel exhaust emissions

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#### 1. Calculation of emission factors

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The mixing ratios of the individual and grouped compounds 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 ranging from C<sub>2</sub> to C<sub>8</sub> with mixing ratios of 3 to 5 ppbv. In total, 11 compounds in the NPL standard were used for quantification. A list of the speciated VOC-IVOCs, 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 C<sub>7</sub> 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 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 were converted from ppbv to mg m<sup>-3</sup>, 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<sup>-3</sup> by the chamber volume (18 m<sup>3</sup>). Finally, the emission rates were calculated by dividing the measured VOC-IVOC mass by the amount of fuel burnt (mg kg<sup>-1</sup>) (corrected for exhaust dilution, discussed in a separate publication) in each experiment.

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

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

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

VOC-IVOCs	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 <sub>7</sub>	NPL	Heptane
$C_8$	NPL	Octane
C9	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 <sub>2</sub>	NPL	o-xylene
$C_3$	NPL	1,2,3-TMB

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

## 1.1 Uncertainty in emission rates

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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 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 VOC-IVOCs ranged from 6 to 50% with an average of 22%.

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

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

<sup>\*</sup>See Table 1 for corresponding experimental numbers.

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

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<sub>R</sub> shift, tridecane not observed.

Table S4 – Measured emission rates of the grouped VOC-IVOCs in each experiment (mg kg<sup>-1</sup>)

	Branched Aliphatics											
Exp. Nu.	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>3</sub>				
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				

<sup>\*\*</sup>t<sub>R</sub> shift, C<sub>13</sub> aliphatic grouping not observed.

 $\textbf{Table S5} - \text{Percentage contribution of the individual compounds to the } \sum SpVOC\text{-}IVOC \text{ emission rate in each experiment.}$ 

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

<sup>\*</sup>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<sub>R</sub> shift, tridecane not observed.

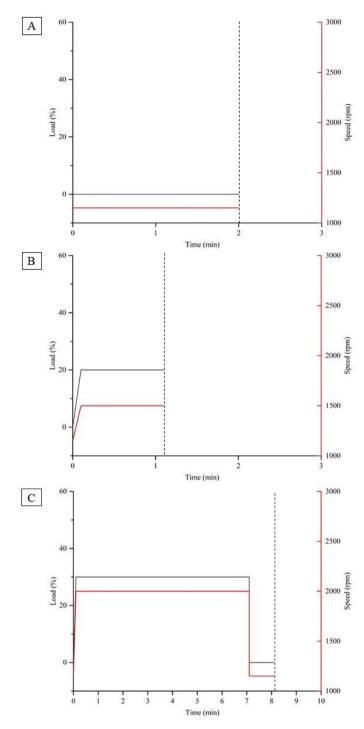
 $\textbf{Table S6} \text{ - Percentage contribution of grouped compounds to } \underline{\sum} SpVOC\text{-}IVOC \text{ emission rate in each experiment}$ 

		Aliphatic Grouping										
Exp. Nu.	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>3</sub>					
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 S7 – Emission rates of the speciated aromatic and aliphatic compounds and their percentage contribution to the  $\sum SpVOC$ -IVOC emission rate in each experiment

		Exhaust composition (mg kg <sup>-1</sup> )	Percentage exhaust composition (%)*			
Exp. Nu.	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	

<sup>\*</sup>To allow for direct comparison between experiments, the percentage exhaust composition does not include tridecane and the C<sub>13</sub> branched aliphatic grouping.



**Figure S1** – Engine speeds and loads performed in driving scenario experiments, (A) cold-start (exp. 6, see Table 1) (B) 'cold loaded' (exp. 8) and, (C) 'warm idle following load' (exp. 9). Black line = engine load (primary y-axis). Red line = engine speed (secondary y-axis). Dashed line = exhaust emissions injected into the MAC.

## 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.

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