

# Supplementary information for Secondary organic aerosol formation from gasoline vehicle emissions in a new mobile environmental reaction chamber

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## S1 Predicted photolysis rates at -7°C

Photolysis rates at -7°C for several gas phase species calculated using Eq. 3 and Eq. 4 (main text) are given in Table 4 (main text). Minor changes in absorption cross section as a function of temperature ( $\sigma(t)$ ) and quantum yield as a function of temperature ( $\Phi(t)$ ) were accounted for as described in the following sub-sections. For nitrous acid (HONO) and formaldehyde (HCHO), no literature data on how to account for the change in  $\sigma$  and  $\Phi$  as a function of temperature were found. Therefore the small change in photolysis rates in Table 4 are accounted for by the change in the emission fingerprint between 25°C and -7°C (see Fig. 3A, main text).

### S1.1 Nitrogen dioxide (NO<sub>2</sub>)

The absorption cross section,  $\sigma$ , of NO<sub>2</sub> as a function of temperature ( $T$ ) is given by the following parameterisation (DeMore et al., 1997), which was used to estimate  $\sigma(-7^\circ\text{C})$ :

$$\sigma(t) = \sigma(0^\circ\text{C}) + aT \quad , \quad (1)$$

with the parameter  $a$  tabulated in (DeMore et al., 1997).  $\Phi(t)$  is given in the literature at (Atkinson et al., 2004). An estimation of  $\Phi(-7^\circ\text{C})$  was calculated by interpolating the values given in the literature at  $25^\circ\text{C}$  and  $-29^\circ\text{C}$  (Atkinson et al., 2004).

### S1.2 Nitrate (NO<sub>3</sub>)

$\sigma(-7^\circ\text{C})$  of NO<sub>3</sub> was estimated by interpolating the values given in the literature at  $25^\circ\text{C}$  and  $-43^\circ\text{C}$  (Atkinson et al., 2004). For the photolysis reaction



$\Phi(t)$  is unity below 587 nm (Atkinson et al., 2004). For the photolysis pathway



and the photolysis pathway in Eq. 2 above 587 nm,  $\Phi(t)$  is given at  $25^\circ\text{C}$  and  $-43^\circ\text{C}$  in the literature (Johnston et al., 1996) and  $\Phi(-7^\circ\text{C})$  was estimated by interpolating  $\sigma(\lambda)$  between these values.

### S1.3 Ozone O<sub>3</sub>

The effect of temperature  $T$  on  $\sigma$  of O<sub>3</sub> is only small, decreasing by <1% between  $25^\circ\text{C}$  and  $-55^\circ\text{C}$  (Malicet et al., 1995), and was therefore neglected here. For the reaction



the main pathway of interest since O(<sup>1</sup>D) may react with water to produce OH radicals,  $\Phi(-7^\circ\text{C})$  as a function of wavelength  $\lambda$  was calculated using the following expression (Atkinson et al., 2004):

$$\begin{aligned} \Phi(\lambda T) = & \left\{ \frac{q1}{q1 + q2} \right\} \times A1 \times \exp \left\{ - \left( \frac{X1 - \lambda}{\omega1} \right)^4 \right\} + \left\{ \frac{q2}{q1 + q2} \right\} \times A2 \times \left\{ \frac{T}{300} \right\}^2 \\ & \exp \left\{ - \left( \frac{X2 - \lambda}{\omega2} \right)^2 \right\} + A3 \times \left\{ \frac{T}{300} \right\}^{1.5} \exp \left\{ - \left( \frac{X3 - \lambda}{\omega3} \right)^2 \right\} + c \quad , \end{aligned} \quad (5)$$

where

$$q(i) = \exp \left( \frac{vi}{RT} \right) \quad , \quad (6)$$

where  $R$  is the molar gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and using  $A1 = 0.8036$ ,  $A2 = 8.9061$ ,  $A3 = 0.1192$ ,  $X1 = 304.225$ ,  $X2 = 314, 957$ ,  $X3 = 310.737$ ,  $\omega1 = 5.576$ ,  $\omega2 = 6.601$ ,  $\omega3 = 2.187$ ,  $\nu1 = 0$ ,  $\nu2 = 825.518$ , and  $c = 0.0765$ .

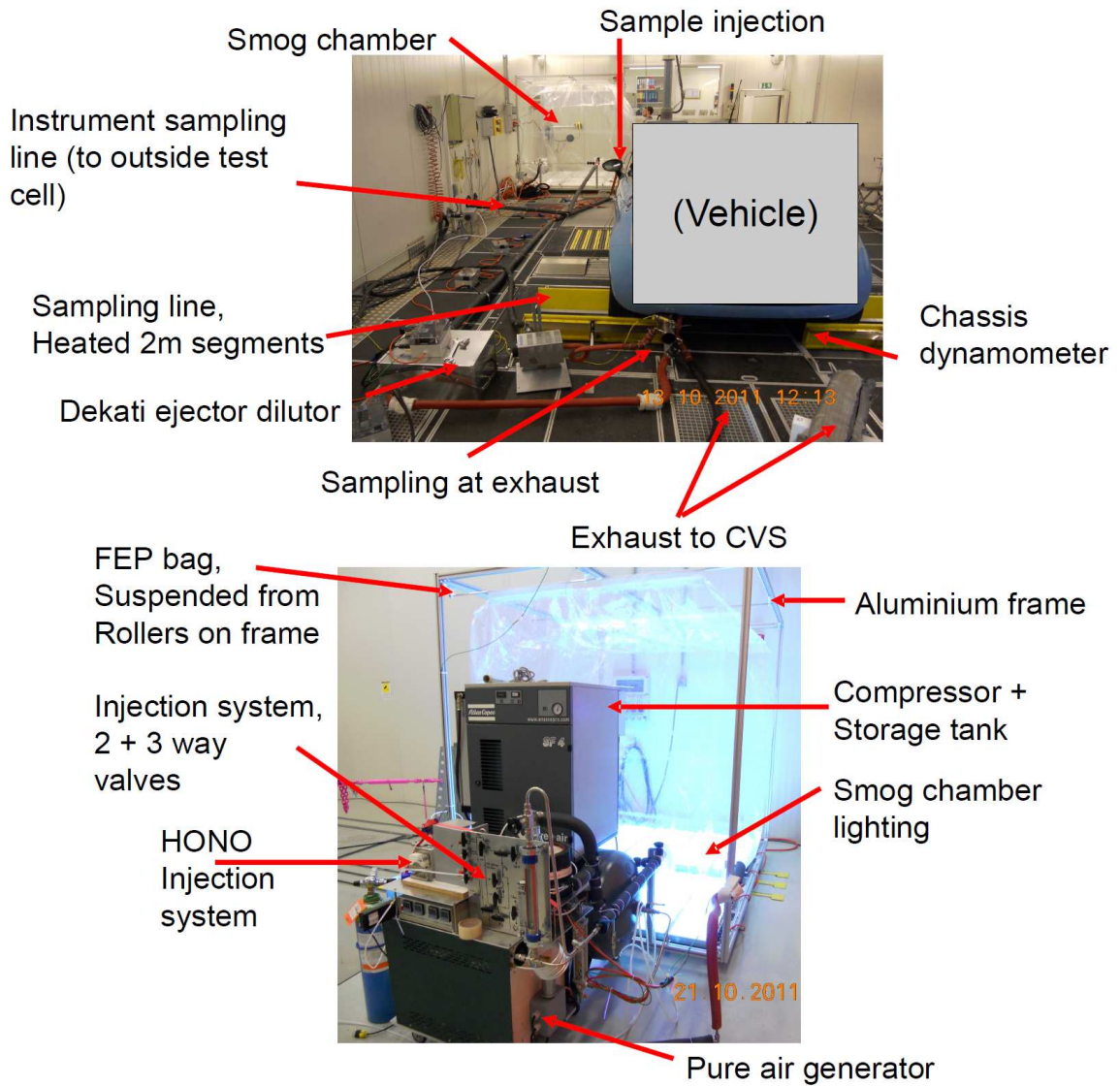
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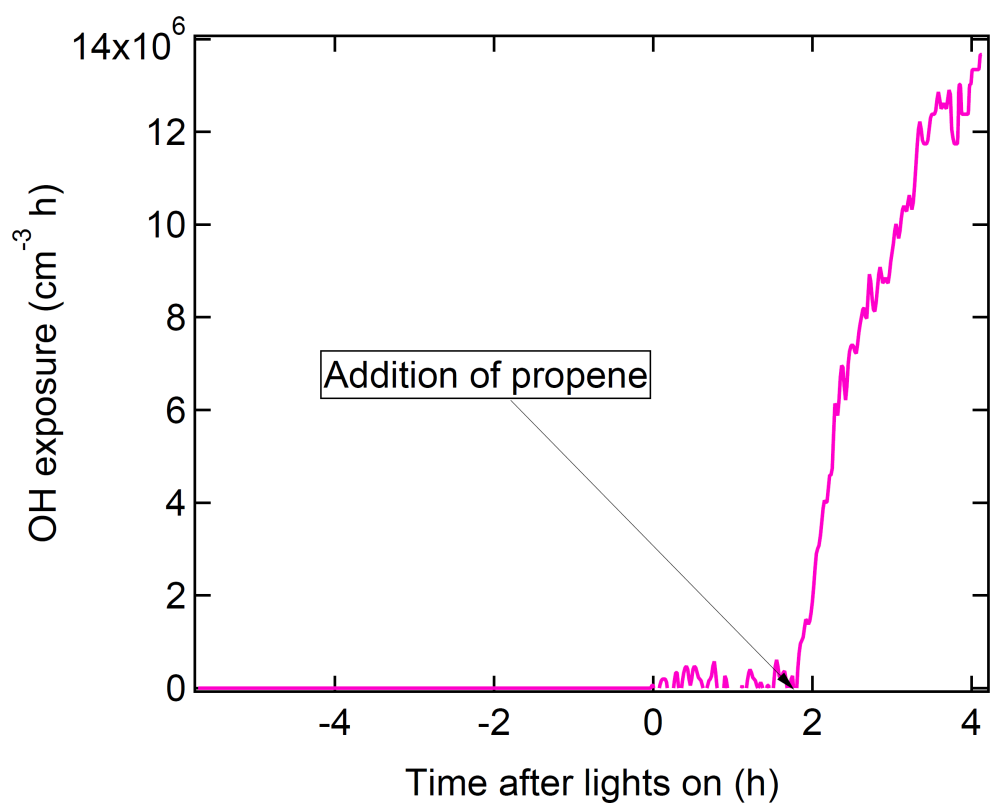
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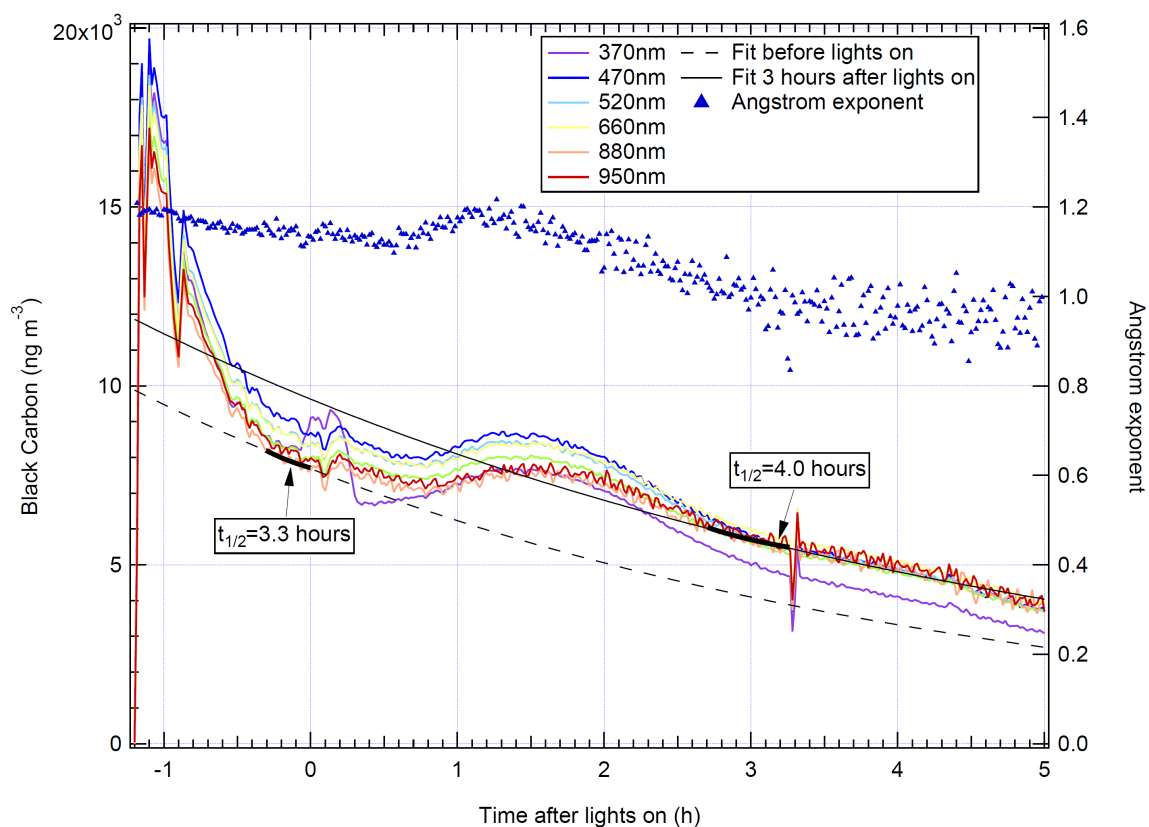
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**Figure S1: A) Labeled photograph of the smog chamber and sampling system as set up during sampling of emissions from a gasoline light duty vehicle at the vehicle emissions laboratory (VELA). B) Labeled photograph of the mobile smog chamber and injection system**



**Figure S2: OH exposure (cm<sup>-3</sup> h) in the smog chamber during Exp. 1. The addition of propene just before two hours after lights on was observed to significantly enhance photochemistry in the chamber.**



**Figure S3: Smog chamber black carbon (BC) concentration measured at different wavelengths using a prototype AE33 aethalometer as a function of time after lights on in the chamber after sampling emissions from a Euro 5 gasoline car. Also shown: particle half lives ( $t_{1/2}$ ) determined from a fit of BC measured at 880nm before lights on (dashed black line) and 3 hours after lights on (solid black line). The fitted region for each curve during each period is highlighted (thick black line) The Angstrom exponent value calculated for each measurement point is shown on the right axis (blue triangles).**

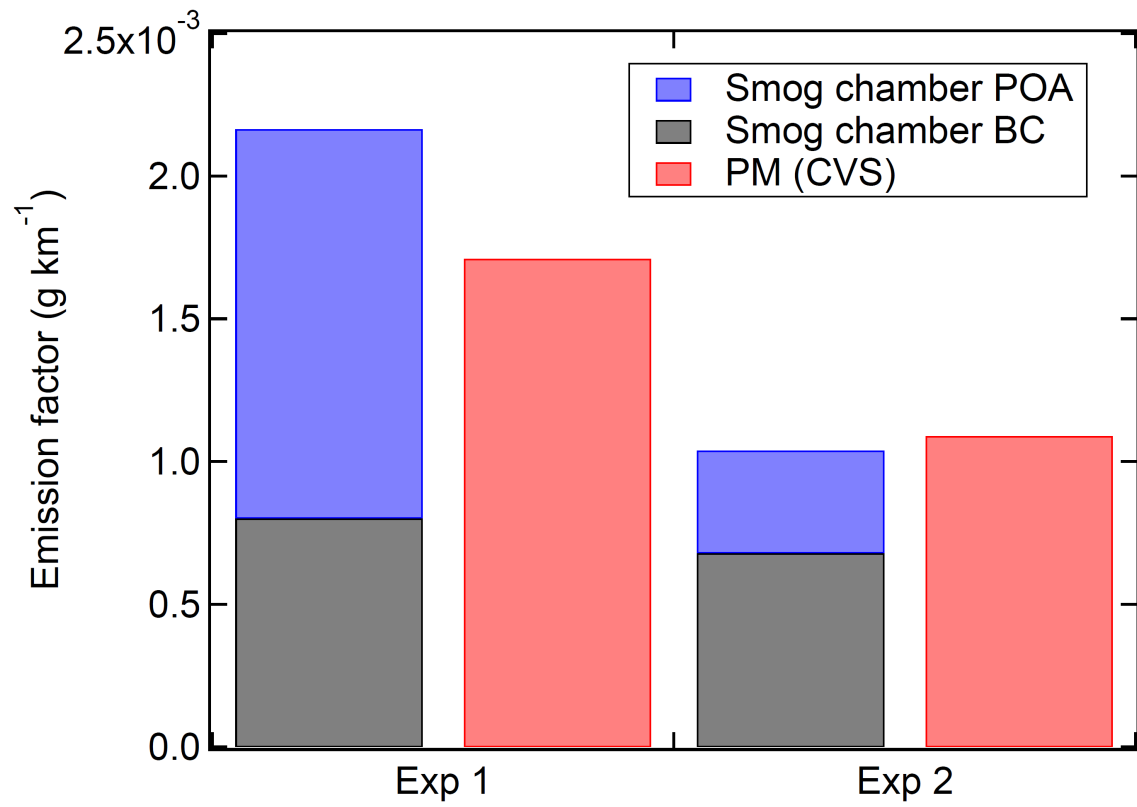


Figure S4: Primary aerosol emission factors for a Euro 5 gasoline light duty vehicle measured from the CVS and at the mobile smog chamber (sum of black carbon and primary organic aerosol).

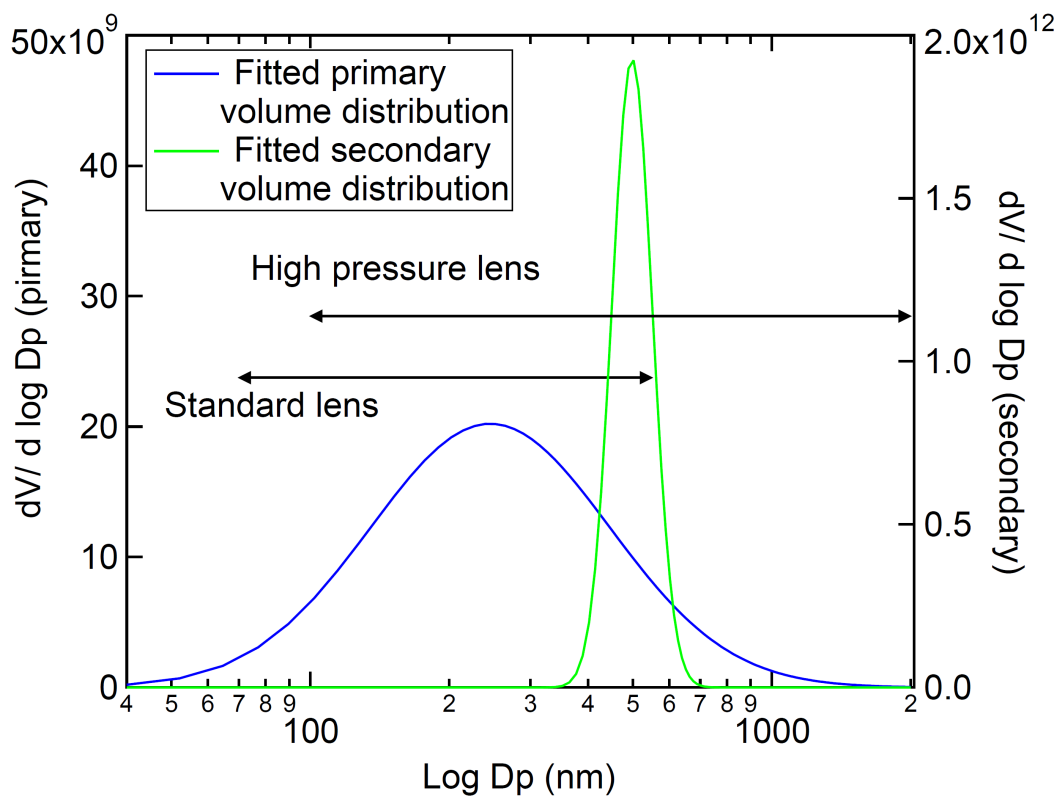


Figure S5: Example lognormal fitted scanning mobility particle sizer (SMPS) volume distributions of primary (blue) and aged aerosol (green) from a gasoline light duty vehicle measured from the mobile smog chamber. The size cut-offs for the standard AMS lens and for the high pressure lens used in this study are given by the arrows. By using the large lens around 40 nm are cut from the lower edge of the volume distribution (<10%) while no part of the higher edge is cut. The standard lens would cut a small portion at both sides of the primary aerosol volume distribution. For the secondary aerosol the standard lens would cut a small portion of the larger particles, while none are cut by the large lens. Therefore, while both lenses could reasonably be used to measure the aging of aerosol from this vehicle, the high pressure lens is slightly better suited.



**Table S1: Technical details of the Euro 5 gasoline light duty vehicle used in this study**

Displacement	Power	Odometer	Gasoline	Fuel system	Weight
875cm <sup>3</sup>	62.5kW	1376km	CEC RF-02-99 oxy 0.8-1.2	Multipoint port	830 kg

**Table S2: Certified properties of the gasoline fuel used in the gasoline light duty vehicle during the driving cycle from which emissions were sampled into the mobile smog chamber**



 		<b>Gasoline CEC-RF-02-99</b> <b>JRC</b>		<b>VELA</b>	
Supplier		Haltermann Products			
Gasoline Reference		<b>CEC Legis. Fuel RF-02-99, Ohygen Cont. 0.8-1.2%</b>			
Batch		<b>QE29513AJ6</b>			
<b>Certificate of analysis</b>					
Analysis	Unit <sup>t</sup>	Result	Limits		Method
		QE29513AJ6	Min	Max	
RON	-----	99.20	95.00	-----	EN 25164
MON	-----	87.50	85.00	-----	EN 25163
Density @ 15°C	kg/m <sup>3</sup>	759.20	-----	-----	ISO 12185
Density @ 4°C	kg/m <sup>3</sup>	-----	-----	-----	-----
Density @ 15°C	kg/m <sup>3</sup>	759.20	748.00	762.00	ISO 3675
RVP	kPa	59.80	56.00	60.00	EN 12
Distillation IBP	°C	35.50	24.00	40.00	ISO 3405
Dist.100°C	%vol	51.60	49.00	57.00	ISO 3405
Dist.150°C	%vol	84.80	81.00	87.00	ISO 3405
Distillation FBP	°C	193.50	190.00	215.00	ISO 3405
Dist. Residue	%vol	1.00	-----	2.00	ISO 3405
Oxidation Stability	min >	1.2000	-----	-----	ISO 7536
Olefins	%vol	4.20	-----	10.00	ASTM D1319
Aromatics	%vol	29.60	28.00	40.00	ASTM D1319
Saturates	%vol	61.30	-----	-----	ASTM D1319
Benzene	%vol	0.20	-----	1.00	EN 12177
Oxygenates	%vol	4.90	-----	-----	EN 1601
tested by subcontractor					
Oxygen Content	% wt	0.9	0.80	1.20	EN 1601
tested by subcontractor					
Hydrogen	% wt	13.16	-----	-----	ASTM D3343
Carbon	% wt	85.95	-----	-----	ASTM D3343
C:H Ratio [H=1]	-----	6.53	-----	-----	ASTM D3343

Table S3: Selected vehicle and test cell parameters

Experiment	Test Cell		Oil temperature (°C)		Catalyst temperature (°C)	
	Temperature (°C)	RH (%)	Initial	Final	Minimum	Maximum
Exp. 1	24.0	50.2	23.0	88.6	29.7	197.5
Exp. 1	22.1	50.0	23.0	88.1	26.1	201.7

**Table S4: Emission factors ( $\text{mg km}^{-1}$ ) and percentage contribution of hydrocarbon measured in the emissions from the Euro 5 gasoline light duty vehicle during experiments 1 and 2 using Fourroer transform infra red spectroscopy (FTIR, tailpipe) and gass chromatogrphy flame ionisation detection (GC-FIC, CVS).**

Compound	EF <sub>KM</sub> (mg)		%	
	Exp. 1	Exp. 2	Exp. 1	Exp.2
<b>C1 Hydrocarbons</b>				
Methane	8.0		5.0	
Formaldehyde	0.9		0.6	
<b>C2 Hydrocarbons</b>				
Ethane	1.8	1.3		
Ethene	6.4	6.1		
Ethyne	7.1	6.8		
<b>C3 Hydrocarbon</b>				
Propane	0.1	0.1		
Propene	2.0	1.7		
<b>C4 Hydrocarbon</b>				
Isobutane	0.2	0.2		
n-Butane	0.5	0.4		
Trans-2-butene	0.2	0.1		
1-butene	0.3	0.2		
Cis-2-butene	0.1	0.1		
1,3-butadiene	0.3	0.2		
<b>C5 Hydrocarbon</b>				
2-methylbutane	1.8	1.1		
n-pentane	0.7	0.5		
trans-2-pentene	0.1	0.0		
1-pentene	0.4	0.2		
Isoprene	0.2	0.0		

**Table S4: Emission factors and percentage contribution of hydrocarbon measured in the emissions from the Euro 5 gasloibe light duty vehicle during experiments 1 and 2, continued**

Compound	EF <sub>KM</sub> (mg)		%	
	Exp. 1	Exp. 2	Exp. 1	Exp. 2
<b>C6 Hydrocarbon</b>				
2-methylpentane	0.9	0.3		
n-hexane	0.2	0.1		
<b>C7 Hydrocarbon</b>				
n-heptane	0.3	0.0		
<b>C8 Hydrocarbon</b>				
2,2,4-trimethylpentane	1.0	0.1		
n-octane	0.2	0		
<b>Aromatic hydrocarbon</b>				
Benzene	1.8	0.2		
Toluene	2.2	0.3		
ethylbenzene	0.7	0.1		
m/p-xylene	2.9	0.5		
o-xylene	1.2	0.2		
1,2,3-trimethylbenzene	0.9	0.2		
1,3,5-trimethylbenzene	1.4	0.3		
1,2,4-trimethylbenzene	0.6	0		
<b>Unknown</b>				

\* From FTIR, two experiment average.