Supplement for "Secondary organic aerosol formation from idling gasoline passenger vehicle emissions investigated in a smog chamber"

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Methods and material

Heated inlet system

The raw exhaust was sampled from the exhaust pipe using a partial flow technique. The sample was taken through a flexible stainless steel tube with a length of 1.5 m and an inner diameter of 20 mm. The flexible tube was heated to 80 °C, which was higher than the exhaust temperature (typically 70 °C). Downstream the ejector the diluted exhaust was transferred to the smog chamber in a stainless steel pipe heated to 120 °C. The length of this pipe was 6 m and the inner diameter was 10 mm.

UV-spectrum

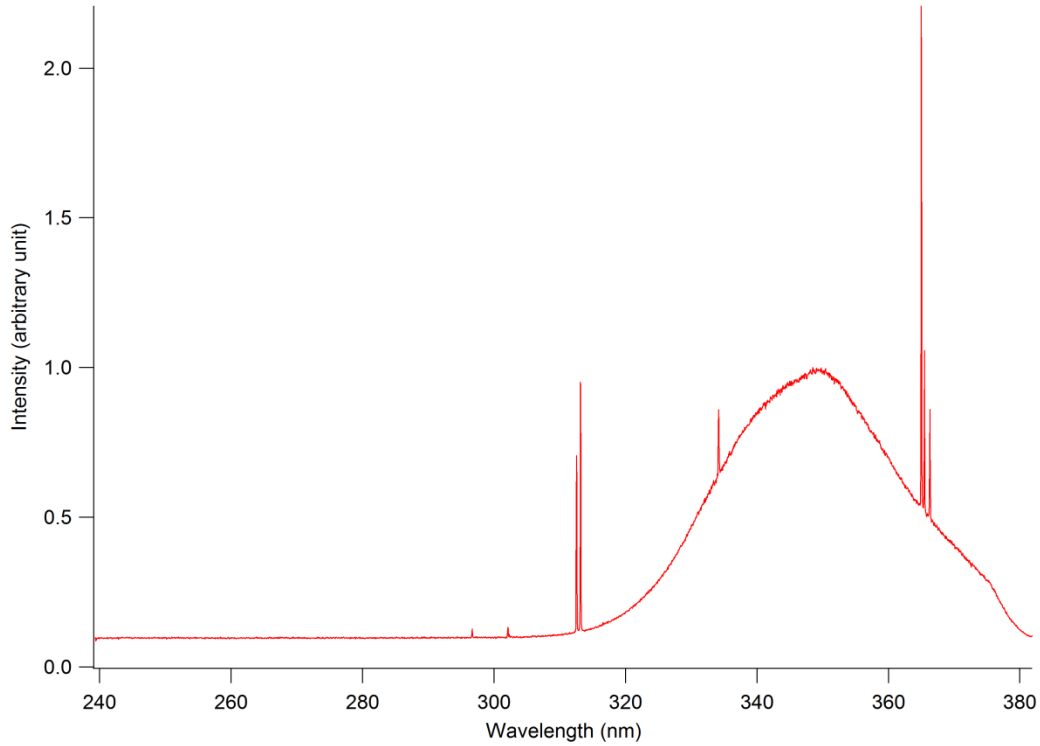

Figure S1. The measured UV-intensity spectrum from the black-lights used in the smog chamber.

Cleaning of the Teflon chamber

After a finished experiment the smog chamber was purged with filtered pressurized air. After this the chamber was cleaned with >1 ppm ozone for at least 5 h. During the cleaning procedure the UV-radiation was operated in 30 minute cycles without chamber cooling,

raising the smog chamber temperature to above 40 °C. This facilitates evaporation and degradation of organic contaminants on the chamber walls. The chamber was finally purged with dry pressurized air for several hours. Before each experiment, particle (AMS, SMPS) and gas (NO_x, O_3 and PTR-MS (when available) phase instruments sampled from the smog chamber to make sure that smog chamber was sufficiently clean. PTR-MS measurements during the blank experiment show a total concentration of light aromatics of less than 1 ppb.

Vehicles

In total six gasoline passenger vehicles were tested at idling, the three cars selected represented three different European emission classes. All tested vehicles used three way catalysts. In the idling case, the cars were driven on a specified circuit until an engine temperature of 55 ±5 °C was reached. In this case neither the engine nor the catalyst had reached optimum operating temperature. Figure S2 shows the concentration of total-hydrocarbons during a cold idling experiment (I3), measured with a flame ionization detector (FID), calibrated with isobutene. In most experiments there was no systematic increase or decrease in the THC levels in the exhaust with time.

Table S1. Technical data of the three gasoline light duty vehicles used

European emission standard class	Power (kW)	Odometer (km)	Displacement (cm^3)	Weight (kg)
EURO2	118	220 000	1948	1400
EURO3	115	180 000	1998	1426
EURO4	48	60 000	998	1050

Table S2. Experimental conditions

Experiment	Total exhaust dilution	Ambient temperature °C
I1	31	-2
I2	109	-4
I3	90	-2
I4	78	-5
I5	27	3
S1	~1600	-5

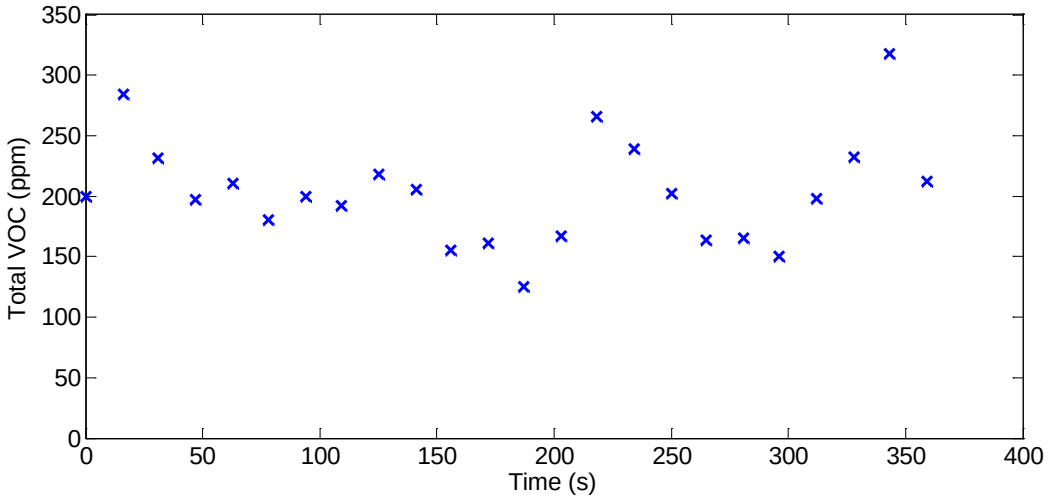

Figure S2: The concentration of total hydrocarbons in the undiluted exhaust as a function of time, experiment I3. The gasoline exhaust was added to the chamber for six minutes under idling conditions from an initial engine temperature of 55 °C using the Euro 2 vehicle.

Experimental procedure

During the experiments the surrounding steel chamber was constantly flushed with pure air (5 air exchanges h^{-1}). To avoid leaks into the smog chamber from the surrounding steel room, an overpressure was maintained in the smog chamber by manually elevating the floor and lowering the roof of the smog chamber.

Results

Figure S2 shows a comparison between PTR-MS and GC-MS measurements. The average ratio between the PTR-MS and GC-MS mixing ratio for each light aromatic is slightly lower

than 1 for toluene and xylenes, while it is higher for benzene and C_9 aromatics where the latter has an average ratio of 1.2.

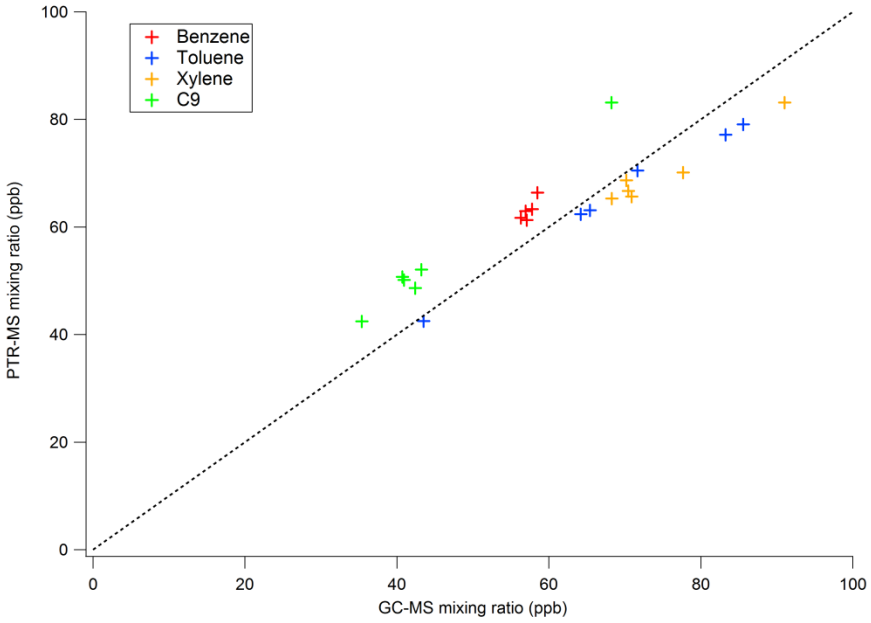

Figure S3. A comparison between PTR-MS and GC-MS for C_6-C_9 aromatics measured in the smog chamber. The broken line shows a ratio of 1.

The PTR-MS method is based on reactions of hydronium ions (H_3O^+) with gaseous compounds having a larger proton affinity than that of H_2O, which results in a non-dissociative proton transfer to a majority of the VOCs. The PTR-MS consists of a discharge ion source to produce the primary ions, a drift-tube reactor, where the proton transfer reaction between H_3O^+ and the target VOC takes place and a quadrupole mass spectrometer for the detection of reagent and product ions. Evidence of weak fragmentation of C_7 and C_8 compounds was found as suggested by a slightly larger ratio of PTR-MS to GC-MS for benzene than for toluene and xylenes (Jobson et al., 2010).

Table S3. Chemical composition of the gasoline fuel and the undiluted gasoline exhaust.

Compound	Fuel (ng μg^{-1})	Exhaust[a] (mg m^{-3})
methyl tert-butyl ether (MTBE)	12.3	-
ethyl tert-butyl ether (ETBE)	0.5	-
benzene	11.7	13.96
toluene	117.9	16.02
ethylbenzene	19.0	2.83
p/m-xylene	72.2	14.49
o-xylene	21.1	5.90
propylbenzene	5.0	1.06
3-ethyltoluene	13.6	4.32
4-ethyltoluene	5.8	1.99
1,3,5-trimethylbenzene	6.8	2.42
2-ethyltoluene	4.6	1.76
1,2,4-trimethylbenzene	18.8	10.95
1,2,3-trimethylbenzene	3.2	1.72
2,2,4-trimethylpentane	112.4	1.14
hexane	68.3	2,13
heptane	20.7	2.67
octane	4.0	1.17
sulfur	<0.01	-
ethanol	5 vol%	-

[a]Undiluted concentrations, average for experiment I1-I3

Table S4. $f43$ and $f44$ fractions, reacted mass fractions and yield relative to m-xylene for the pure precursors presented in figure 8. These were used for calculations of the expected $f43$ and $f44$ of gasoline exhaust assuming that all SOA originated from C_6-C_9 light aromatic compounds.

Compound	$f43$	$f44$	Reacted mass fraction of (C_6-C_9) LA (average of I1 and I2)	Reference
benzene	0.03	0.12	0.011	Ng et al., 2010
toluene	0.130	0.120	0.115	Chhabra et al., 2011
ethylbenzene	0.023	0.122	0.016	Sato et al., 2010
m/o/p-xylene	0.170	0.095	0.344[a]	Exp. P2 this study
1,3,5-trimethylbenzene	0.175	0.055	0.100	Ng et al., 2010
1,2,4-trimethylbenzene	0.197	0.088	0.230	Derived from experiment P1
1,2,3-trimethylbenzene	0.197	0.088	0.047	Assumed to be same as 1,2,4-tmb
2/3/4-ethyltoluene and propyl benzene	0.110	0.105	0.137	Assumed as the mean of ethylbenzene and 1,2,4-trimethylbenzene
naphthalene[b]	0.01	0.1	-	Chhabra et al., 2011

[a]All xylenes are assumed to have the same $f43$ and $f44$ as measured for m-xylene in exp. P2.

[b]Not included in calculation, given here for reference.

Expected $f43$ and $f44$ assuming additive SOA composition and yield for C_6-C_9 Light aromatics

First we note that the $f43$ and $f44$ fractions for m-xylene in experiment P2 were within 0.02 of values from several studies in the literature (Ng et al. 2010, Chhabra et al. 2011, Loza et al. 2012) suggesting that these measurements are typically repeatable between instruments and set-ups. In Table S4 we list literature values for the most important C_6-C_9 light aromatic precursors, for compounds with no available literature data we had to make assumptions based on the structure of the component. For example, the three xylene isomers were assumed to have the same $f43$ and $f44$ fractions as found for m-xylene. This is suported by a study

with the potential aerosol mass chamber which showed that the $f43$ and $f44$ fractions of SOA from p- and m- xylene varied by less than 0.01 (Kang et al. 2011). The $f43$ and $f44$ values for 1,2,4-trimethylbenzene were derived from experiment P1 (precursor mixture of 1,2,4 TMB, m-xylene and toluene), where 1,2,4 TMB constituted more than 60% of the reacted light aromatics. We used the $f43$, $f44$ and yields for toluene and m-xylene given in Table S4 and assumed that the mixed SOA was additive in terms of yield and composition.

Finally, we estimated the expected $f43$, $f44$ in each gasoline exhaust experiment if assuming additive yield and composition. The SOA contribution from each component was first calculated from the reacted mass fraction and yield using the high and low yield aromatic classes from Odum et al. (1997). Then the $f43$ and $f44$ fractions were calculated as the weighted sum of the thirteen different components in table S4. The resulting "expected" $f43$ and $f44$ are given in table S5.

Table S5. The expected and measured $f43$ and $f44$ for the six gasoline exhaust experiments. The expected $f43$ and $f44$ figures are based on the assumption that the SOA was produced only from light aromatics (C_6-C_9) and that the mass spectra of the gasoline exhaust can be calculated as the weighted mean of the SOA from each precursor. The $f43$ and $f44$ figures for 13 pure C_6-C_9 light aromatic precursors (table S4) are used together with the GC-MS data of the reacted concentration for those precursors to calculate the expected $f43$ and $f44$. Benzene, toluene, ethyl-benzene, propyl benzene and the ethyl-toluenes were assumed to have twice as high yield as m-xylene (Odum et al., 1997).

Exp.	Expected $f43$	Expected $f44$	Measured[a] $f43$	Measured[a] $f44$	Maximum fraction of C_6-C_9 contribution to SOA[b]
I1	0.145	0.099	0.088	0.114	0.61
I2	0.148	0.097	0.090	0.130	0.61
I3	0.158	0.093	0.086	0.090	0.54
I4	0.138	0.103	0.080	0.130	0.58
I5	0.157	0.097	0.081	0.107	0.52
S1	0.142	0.101	0.148	0.095	1.04

[a]POA subtracted

[b]Based on the ratio between the measured and expected $f43$.

Table S6. Estimations of potential SOA formed from C_{10}, C_{11} light aromatics and naphthalene. For C_{10} light aromatics, the reacted concentration was estimated from PTR-MS measurements. For C_{11} light aromatics and naphthalene the initial concentration was first estimated using PTR-MS and the reacted concentration was calculated using $k_{OH} = 5.67*10^{-11}$ (C_{11}) and $k_{OH} = 2.44*10^{-11}$ (naphthalene) (The Master Chemical Mechanism). The yield curves for C_{10} and C_{11} were assumed to be identical to m-xylene (according to the fit in figure 5), while the yield for naphthalene is assumed to be three times the yield for m-xylene.

Exp. Id	Initial concentration of C_{10}/ C_{11}/ naphthalene (ppb)	Reacted conc. C_{10}/ C_{11}/ naphthalene (µg m^{-3})	Estimated formed SOA C_{10}/ C_{11}/ naphthalene (µg m^{-3})
I1	13.4/1.1/2.8	30.7/2.6/3.6	2.5/0.2/0.9
I2	17.7/1.6/4.4	40.1/5.9/6.0	4.6/0.7/2.1
S1	4.4/0.2/0.2	12.6/0.4/0.2	0.8/<0.1/<0.1

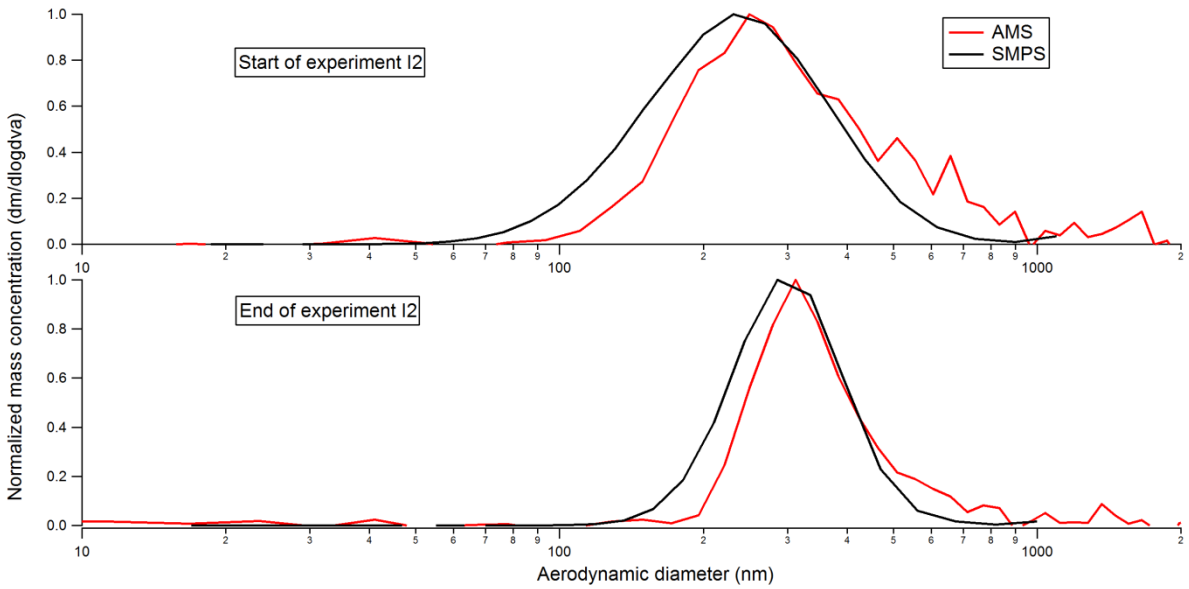

Figure S4. The normalized mass size distribution for SMPS and AMS at the start (before UV lights) and end of experiment I2. The SMPS volume size distribution is converted to mass size distribution by multiplying the volume with the density of the mixture calculated from

the AMS-data. The SMPS mobility diameter size channels have been converted to vacuum aerodynamic diameters also using the density of the mixture.

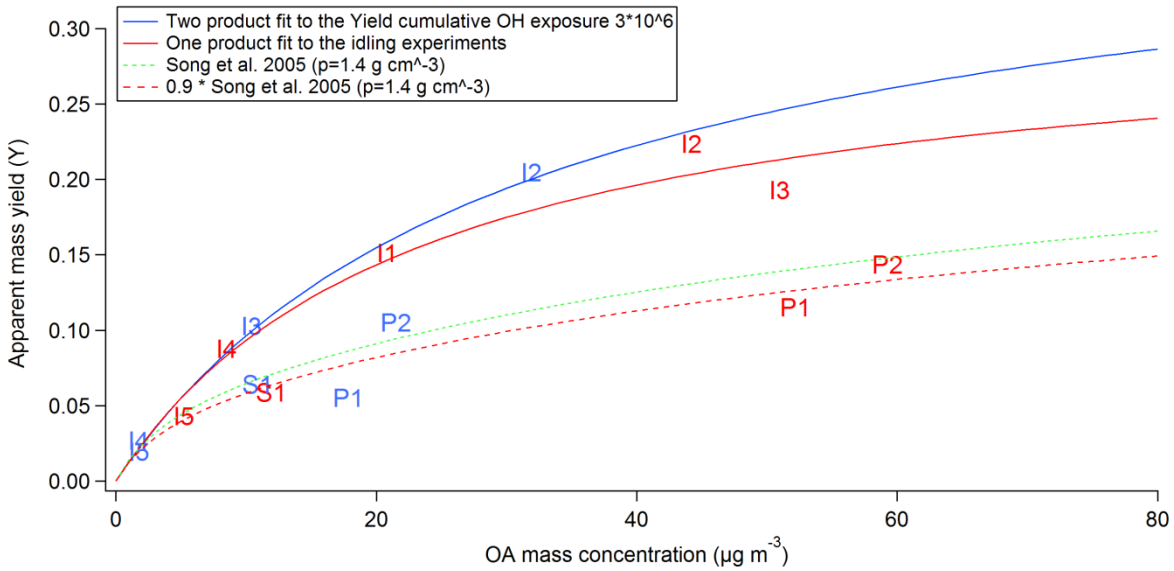

Figure S5. The apparent mass yield for the gasoline exhaust and precursor experiment, end of each experiment (red symbols) and at a cumulative OH exposure of 3 * 10^6 cm^{-3} h (blue symbols). A one product fit (red solid line) is applied to the yield data at the end of the idling experiments (same as figure 5 in the main paper). A two product fit is applied to the yield data at cumulative OH exposure of 3 * 10^6 cm^{-3} h (blue solid line) the fitting parameters is a1=0.3799, a2=0.048, k1=0.0332 and k2= 0.0035. The green and red broken lines are a two product fit to the m-xylene yield from Song et al. (2005), (assuming a SOA density of 1.4 g cm^{-3}).

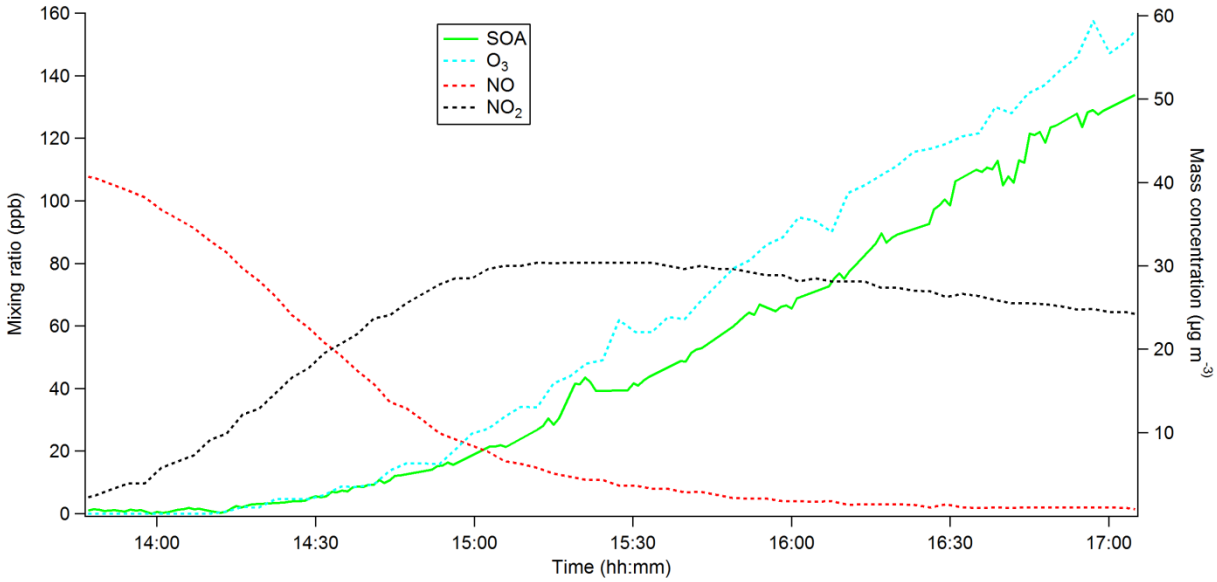

Figure S6. Ozone, NO, NO_2 concentrations together with the wall loss corrected SOA mass concentration as a function of time in experiment I3. The data shows evidence of SOA production in the presence of NO, in contrast to the precursor experiments (e.g. Fig 3). UV-lights were turned on at 13:42.

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