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*Supplement of*

## **Potential dual effect of anthropogenic emissions on the formation of biogenic secondary organic aerosol (BSOA)**

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### **S1 Experimental procedure for Pure $\alpha$ -pin experiments**

3 First, ammonium sulphate (AS) seed particles were fed into the chamber in an amount comparable to the primary particle mass loadings observed during vehicle exhaust experiments. Then, for Pure  $\alpha$ -pin high NO<sub>x</sub> experiments, NO and NO<sub>2</sub> were introduced into the chamber so that NO<sub>x</sub> concentration and NO<sub>2</sub>-to-NO ratio were comparable to Mixed experiments. For Pure  $\alpha$ -pin NO<sub>x</sub> free experiments, no NO<sub>x</sub> was added. After that ~3  $\mu$ l of butanol-d<sub>9</sub> and ~1  $\mu$ l (5 ppbv) of  $\alpha$ -pinene were injected into the chamber. In high NO<sub>x</sub> experiments, propene was added before switching the BL-lamps on to adjust the VOC-to-NO<sub>x</sub> ratio. Last, H<sub>2</sub>O<sub>2</sub> was introduced into the chamber for OH-radical generation. After BL-lamps were switched on the  
8 photochemistry period was continued for 4 hours.

### **S2 Details from fragmentation of vehicle emitted aromatic VOCs inside the PTR-ToF-MS**

With the PTR-MS technique, when H<sub>3</sub>O<sup>+</sup> ions are used for ionization, separation of any isomeric compounds cannot be achieved. This causes problems in accounting for the degree of fragmentation, if information about the structure of the compounds is missing because some isomers go through higher fragmentation than others. Moreover, if the degree of  
21 fragmentation is not known or cannot be estimated, the quantification of measured compound is not possible without high uncertainties. For example, some aromatic compounds inside the drift tube of the PTR-ToF-MS undergo fragmentation while the others do not, even if they would have same elemental composition (Gueneron et al., 2015). Therefore, the degree of

fragmentation depends on the structure of the compound and the drift tube settings (mainly E/N value) (Gueneron et al., 2015;Kari et al., 2018).

Based on previous studies we can be sure that SOA precursors measured in this study from gasoline exhaust are mainly comprised of isomers of the compounds that do not go through substantial fragmentation inside the drift tube. For example, previous studies have identified the composition of gasoline exhaust showing that xylene isomers dominate over ethyl benzene detected at integer  $m/z$  107, and trimethylbenzene isomers dominate over other isomers of C3-benzenes detected at integer  $m/z$  121 (Schmitz et al., 2000;Schauer et al., 2002;Nordin et al., 2013;Platt et al., 2013;Gueneron et al., 2015). As the aromatic VOCs having only methyl substituents do not undergo fragmentation inside the PTR-ToF-MS, under the settings we operated the PTR-ToF-MS, we were able to quantitate them. Moreover, some of the detected oxygenated aromatics, such as benzaldehyde, do not go through substantial fragmentation inside the PTR-ToF-MS under the settings we operated the PTR-ToF-MS during the measurement campaign (Warneke et al., 2003;Maleknia et al., 2007;Schwarz et al., 2009). Therefore, for several SOA precursors measured with the PTR-ToF-MS we can be confident that substantial fragmentation inside the PTR-ToF-MS did not occur, and we were able to quantify these compounds without high uncertainties. However, we cannot assume that the fragmentation of all SOA precursors is unsubstantial, because we cannot identify their molecular structures or get information about the structure from literature that would enable us to estimate the degree of fragmentation they may undergo inside the drift tube. These species were mainly oxygenated aromatics, hence for these SOA precursors the calculated reacted concentrations may be incorrect that underestimates the predicted SOA mass from reactions between OH-radicals and these SOA precursors, while the fragmentation overestimates the concentration of benzene and toluene reported because the fragments of many larger aromatics possess their structural form in addition to small alkanes and alkenes present for example at mass integers  $m/z$  41 and 43 (Gueneron et al., 2015).

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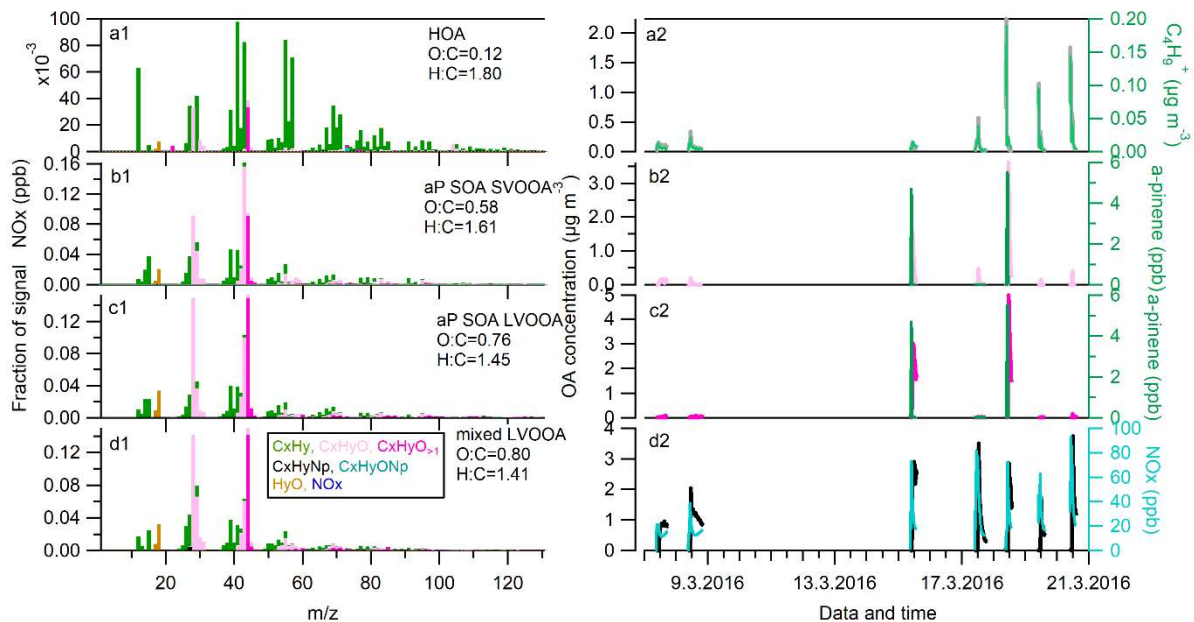


Figure S1. PMF factor solutions to the high-resolution mass spectra: profiles (left panels) and time series (right panels). Tracers were selected to correlate with the factor time series.

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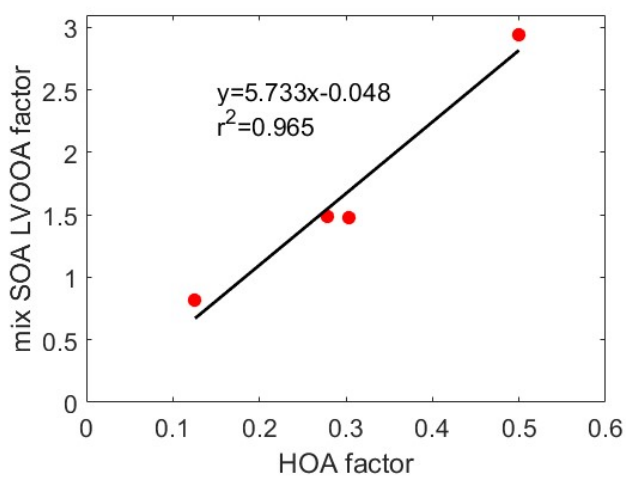
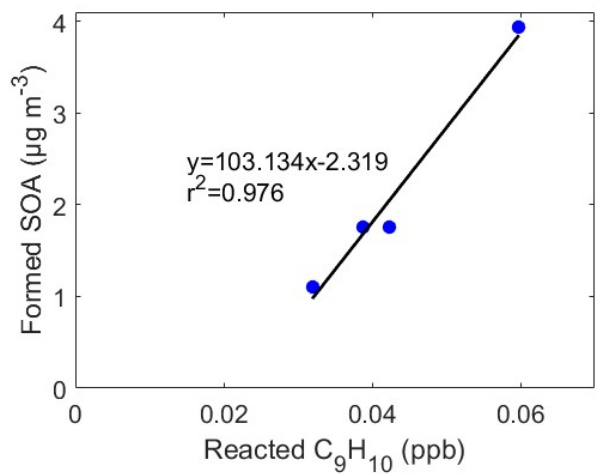


Figure S2. HOA factor as a function of mix\_SOA\_LVOOA factor in Pure Vehicle experiments.

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**Figure S3. Reacted concentration of C<sub>9</sub>H<sub>10</sub> as a function of formed SOA in Pure Vehicle experiments.**

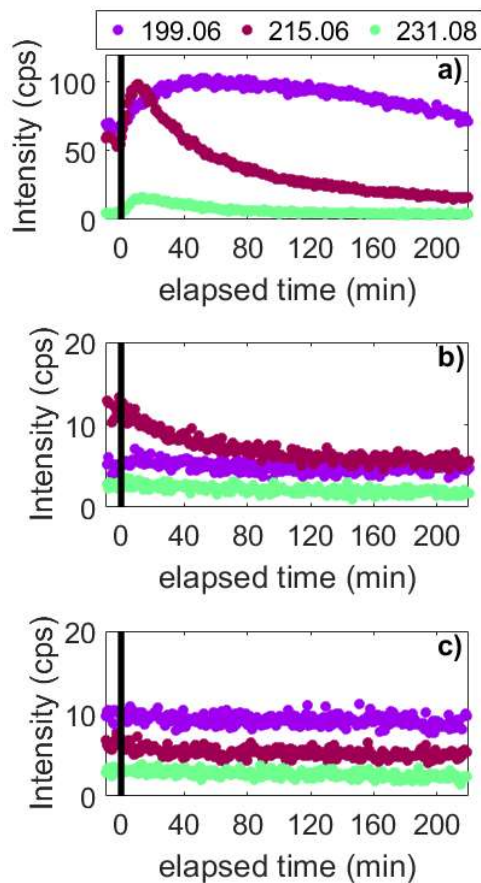


Figure S4. Temporal evolution of acetate-ToF-CIMS measured oxidation products formed when  $\alpha$ -pinene and gasoline vehicle exhaust were both present in the chamber during the photochemistry (panel a)). Panels b) and c) show the evolution of same compounds during Pure Vehicle and Pure  $\alpha$ -pin high NOx experiments to demonstrate the absence of these compounds when only  $\alpha$ -pinene or gasoline vehicle exhaust were present inside the chamber during the photochemistry period. At time zero the photochemistry experiment was started when BL lamps were switched on.

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**Table S1.** Organic compounds calibrated for FTIR that were used to calculate THC values from the raw exhaust.

Gas	Formula	Range	Unit
Methane	CH <sub>4</sub>	1000	ppm
Ethane	C <sub>2</sub> H <sub>6</sub>	200	ppm
Propane	C <sub>3</sub> H <sub>8</sub>	200	ppm
Butane	C <sub>4</sub> H <sub>10</sub>	200	ppm
Pentane	C <sub>5</sub> H <sub>12</sub>	200	ppm
Hexane	C <sub>6</sub> H <sub>14</sub>	200	ppm
Heptane	C <sub>7</sub> H <sub>16</sub>	200	ppm
Octane	C <sub>8</sub> H <sub>18</sub>	200	ppm
Acetylene	C <sub>2</sub> H <sub>2</sub>	200	ppm
Ethylene	C <sub>2</sub> H <sub>4</sub>	200	ppm
Propene	C <sub>3</sub> H <sub>6</sub>	200	ppm
1,3-Butadiene	C <sub>4</sub> H <sub>6</sub>	200	ppm
Benzene	C <sub>6</sub> H <sub>6</sub>	200	ppm
Toluene	C <sub>7</sub> H <sub>8</sub>	200	ppm
m-Xylene	C <sub>8</sub> H <sub>10</sub>	200	ppm
o-Xylene	C <sub>8</sub> H <sub>10</sub>	200	ppm
p-Xylene	C <sub>8</sub> H <sub>10</sub>	200	ppm
1,2,3-Trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	200	ppm
1,2,4-Trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	200	ppm
1,3,5-Trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	200	ppm
Formic acid	CH <sub>2</sub> O <sub>2</sub>	200	ppm
Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	200	ppm
Formaldehyde	CH <sub>2</sub> O	200	ppm
Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	200	ppm



**Table S1 continues.** Organic compounds calibrated for FTIR that were used to calculate THC values from the raw exhaust.

Gas	Formula	Range	Unit
Methanol	CH <sub>3</sub> OH	500	ppm
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	500	ppm
Propanol	C <sub>3</sub> H <sub>7</sub> OH	500	ppm
Methyl tertiary butyl ether	C <sub>5</sub> H <sub>12</sub> O	200	ppm

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**Table S2.** SOA precursors applied for predicted SOA calculation.

Suggested name <sup>1</sup>	Formula	SOA mass Yield Lower estimate	SOA mass Yield Higher estimate	References for SOA mass yields and possible proxy for yield
Benzene	C <sub>6</sub> H <sub>6</sub>	0.156	0.281	(Ng et al., 2007)
Toluene	C <sub>7</sub> H <sub>8</sub>	0.08	0.32	(Ng et al., 2007;Hildebrandt et al., 2009)
Phenol	C <sub>6</sub> H <sub>6</sub> O	0.34	0.34	(Chhabra et al., 2011)
Styrene	C <sub>8</sub> H <sub>8</sub>	0.035	0.059	(Ng et al., 2007), Xylene
Benzaldehyde	C <sub>7</sub> H <sub>6</sub> O	0.08	0.32	(Ng et al., 2007), Toluene
Xylene	C <sub>8</sub> H <sub>10</sub>	0.035	0.059	(Ng et al., 2007)
C <sub>9</sub> -aromatic	C <sub>9</sub> H <sub>8</sub>	0.049	0.065	(Li et al., 2016), Trimethylbenzene
C <sub>9</sub> -aromatic	C <sub>9</sub> H <sub>10</sub>	0.049	0.065	(Li et al., 2016), Trimethylbenzene
Methyl-benzaldehyde	C <sub>8</sub> H <sub>8</sub> O	0.08	0.32	(Ng et al., 2007), Toluene
Trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	0.049	0.065	(Li et al., 2016)
Naphtalene	C <sub>10</sub> H <sub>8</sub>	0.2	0.222	(Chan et al., 2009;Chhabra et al., 2010)
C <sub>10</sub> -aromatic	C <sub>10</sub> H <sub>12</sub>	0.049	0.065	(Li et al., 2016), Trimethylbenzene
Oxygen containing C <sub>8</sub> -aromatic	C <sub>8</sub> H <sub>6</sub> O <sub>2</sub>	0.111	0.111	(Chhabra et al., 2011), Syringol
Oxygen containing C <sub>9</sub> -aromatic	C <sub>9</sub> H <sub>10</sub> O	0.111	0.111	(Chhabra et al., 2011), Syringol
C <sub>10</sub> -aromatic	C <sub>10</sub> H <sub>14</sub>	0.049	0.065	(Li et al., 2016), Trimethylbenzene
C <sub>11</sub> -aromatic	C <sub>11</sub> H <sub>14</sub>	0.2	0.222	(Chan et al., 2009;Chhabra et al., 2010), Naphtalene
Oxygen containing C <sub>10</sub> -aromatic	C <sub>10</sub> H <sub>12</sub> O	0.111	0.111	(Chhabra et al., 2011), Syringol
C <sub>11</sub> -aromatic	C <sub>11</sub> H <sub>16</sub>	0.049	0.065	(Li et al., 2016), Trimethylbenzene
C <sub>12</sub> -aromatic	C <sub>12</sub> H <sub>18</sub>	0.049	0.065	(Li et al., 2016), Trimethylbenzene
Oxygen containing C <sub>10</sub> -aromatic	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	0.111	0.111	(Chhabra et al., 2011), Syringol

<sup>1</sup> Suggested name is based on the identified molecular structure and literature