

# Supporting Information

## Total OH reactivity of emissions from humans: in-situ measurement and budget analysis

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## Comparative reactivity method (CRM) operating procedures

The reference molecule used in CRM is pyrrole ( $C_4H_5N$ )<sup>1</sup>, which reacts with OH radicals at comparable rates with reactive species and is not commonly presented in the measured air. Pyrrole can be sensitively detected by PTR-MS due to its higher proton affinity than water. For CRM, three measurement modes were implemented to quantify the total OH reactivity: (1) pyrrole together with an OH radical scavenger<sup>2</sup> was introduced to define the initial pyrrole level (C1 mode); (2) the OH radical scavenger was stopped and the level of pyrrole after reaction with OH radicals was recorded (C2 mode); (3) finally sample air from the chamber was introduced into the reactor with the pyrrole, the resulting competition for the available OH leading to a third pyrrole level (C3 mode). Based on these three modes, the total reactivity ( $R$ ,  $s^{-1}$ ) was calculated using the following equation:

$$R = \frac{(C3 - C2)}{(C1 - C3)} \cdot C1 \cdot k_{Pyrrol + OH} \quad \text{Eq. (1)}$$

where  $C1$ ,  $C2$  and  $C3$  refer to previously mentioned pyrrole concentrations ( $\text{molecules cm}^{-3}$ ) in the corresponding mode and  $k_{Pyrrol + OH}$  refers to the rate constant of pyrrole reacting with OH radicals<sup>3</sup>. During an experiment, the OH reactivity measurement was switched between C2 mode and C3 mode every 5 minutes, and the C1 mode was usually measured at the end of the day. The pyrrole level measured by PTR-QMS was calibrated frequently using a gas standard (Westfalen AG, Germany).

## **Interference and corrections of OH reactivity data analysis**

- **Pyrrole photolysis**

The pen ray mercury lamp used for water photolysis would also lead to pyrrole photolysis, which would complicate the system<sup>1</sup>. Therefore, the initial pyrrole level (C1) was determined when the lamp was on, which already considered the loss of pyrrole due to photolysis.

- **Humidity correction**

As the OH radical concentration is dependent on the water vapor inside the reactor, any difference in humidity between the C2 and C3 modes must also be taken into account. The humidity correction was done by humidifying the air flow of CRM at different degrees under C2 mode<sup>1</sup>. The humidity was monitored by the ratio of  $m/z$  37 (water cluster) and  $m/z$ 19 (primary ions). Then a correction factor can be derived from the slope of humidity vs. C2 pyrrole level, with an error of 29%. The correction factor was then applied to the C2 level during measurements to correct the humidity difference between C2 mode and C3 mode. The correction of the C2 level was on average  $0.06 \pm 0.04$  ppb, leading to a reactivity of  $0.4 \pm 0.2$  s<sup>-1</sup>.

- **Correction factor for not being at pseudo-first-order conditions**

Equation (1), used to derive the OH reactivity, is based on the assumption of pseudo-first-order conditions. These conditions cannot be entirely fulfilled under normal operating conditions when maintaining a reasonable sensitivity. Therefore, a correction factor was applied as a function of the pyrrole/OH ratios. The method used to derive the correction factor is based on Michoud, et al. <sup>4</sup>. The correction factor was obtained from injecting known amount of a standard gas under different pyrrole/OH ratios conditions. A factor can be obtained from measured reactivity vs. calculated reactivity for that gas. Total of five standard gases with different rate constants reacting with the

OH radical including propane, propene, isoprene,  $\alpha$ -pinene and acetaldehyde were tested within the pyrrole/OH range observed during the entire campaign. A linear fit was applied among all the factors derived from the tests, resulting in a linear relationship between the correction factor and pyrrole/OH ratio ( $f = a[\text{pyrrole/OH}] + b$ ), with an error of 31%. Throughout the campaign, the pyrrole/OH ratio ranged from 2.0 - 3.0, which increased the OH reactivity by a factor of 1.3 to 2.7.

- **NO<sub>x</sub> interference**

Previous studies have also shown that NO<sub>x</sub> can potentially cause an interference to CRM measurements by producing OH radicals via reactions with HO<sub>2</sub> radicals. Relevant corrections should be applied if the measured conditions have abundant NO<sub>x</sub> (NO > 10ppb<sup>1</sup>) and it should be noted that NO has a more significant interference compared to NO<sub>2</sub> at the same level<sup>4-6</sup>. NO and NO<sub>2</sub> were continuously monitored by a chemiluminescence NO/NO<sub>x</sub> analyzer (ECO PHYSICS, model CLD 700 AL). The mixing ratios of NO and NO<sub>2</sub> in the occupied chamber were near or below the detection limit (1 ppb) for most of the time during the entire experimental period. By taking into account the dilution factor of the CRM (1.37), NO and NO<sub>2</sub> levels in the glass reactor would be lower than the detection limit most of the time. Therefore, NO<sub>x</sub> interference to the CRM could be neglected and no correction was applied. NO and NO<sub>2</sub> have OH rate constants comparable to some VOCs shown in Table S1 ( $9.70 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  and  $9.80 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  for NO and NO<sub>2</sub>, respectively<sup>7</sup>). The upper limit of the NO<sub>x</sub> contribution to the total reactivity (assuming 2 ppb of NO or NO<sub>2</sub>) would be 0.5 s<sup>-1</sup> (3.0% of the total reactivity under ozone-free condition and 1.5% under ozone-present condition). This is comparable to some top ten OH reactivity contributing species (Table 2). The NO<sub>x</sub> data were mostly at or below the detection limit and no clear trend can be observed due to human occupancy; the 2 ppb of NO<sub>x</sub> assumption

represents an upper limit estimate rather than a measurement. Therefore, NO<sub>x</sub> was not included in the calculation of OH reactivity in the study.

- **Ozone interference**

High level of ozone was also found to cause interference depending on the CRM system<sup>5</sup>. For ozone interference test, different levels of ozone (0 -110 ppb) was introduced to the empty chamber. The measured OH reactivity interference due to ozone was less than 3 s<sup>-1</sup> at the highest ozone level, which is lower than the limit of detection for CRM during this campaign (5 s<sup>-1</sup>). The ozone level in the chamber during the afternoon steady state when occupied was around 37 ppb, resulting in 1 s<sup>-1</sup> difference in the measured reactivity which was much smaller than the total uncertainty of the measured reactivity (16 – 22 s<sup>-1</sup>). As the ozone interference is negligible and extra uncertainty would be introduced from the correction factor, no correction was applied.

### **Calculations of precision and total uncertainty of CRM**

When a test gas is injected into the CRM at several known concentrations, the corresponding mean reactivity at each concentration can be obtained together with the standard deviation. By plotting the relative reactivity (standard deviation/mean reactivity,  $R_{relative}$ ) against the mean reactivity ( $R_{measured}$ ), an exponential curve is obtained that can be fit with the equation:

$$R_{relative} = a + b * \exp (c * R_{measured})$$

where parameters  $a$ ,  $b$  and  $c$  are derived from curve fitting and the relative reactivity defines the precision. For this study, results from test gases mentioned in “Correction factor for not being at pseudo-first-order conditions” were included to derive the fitting results. Based on the measured reactivity of real measurements, the precision can be calculated by applying this equation to each data point.

The accuracy of the CRM is the propagation of uncertainties from the pyrrole standard gas concentration, the dilution factors derived from flow measurements, the OH rate constant of pyrrole, the humidity correction, and the non-pseudo-first-order correction. Detailed numbers can be found in Table S1.

Table S1 Uncertainties in the CRM

<b>Uncertainties from</b>	<b>Uncertainties (%)</b>
Pyrrole standard gas	10
Dilution factors	0.16
OH rate constant of pyrrole	14
Humidity correction	29
Non-pseudo-first-order correction	31
Propagated accuracy	46
Total uncertainty (mean and median)	50

### **Empty-chamber background**

The background obtained from the empty chamber before volunteers entered was in general very stable for calculated reactivity ( $3 \text{ s}^{-1}$  on average with a variability of 10%). For measured total reactivity, the background was typically around or under the detection limit ( $5 \text{ s}^{-1}$ ).

### **Definition of steady-state condition**

As the calculated reactivity has less uncertainty than measured reactivity, the steady-state condition was verified by the relative change of calculated reactivity during the 15 minutes before volunteers exited the chamber. This is to avoid any effect left due to requested movements by the volunteers (standing up and stretching) every hour during each experimental period. For all the experiments, the relative changes  $((\text{max}-\text{min})/\text{mean})$  were below 5% (0.8-5.0%, mean 2.1%), which is much less than the uncertainty of the calculated OH reactivity (21% - 45%, median and mean 29%). Therefore, the time period of 15 minutes is suitable to be considered as steady-state condition.

### **Adjustment method applied for OH reactivity per person comparison**

To be able to compare the OH reactivity per person ( $s^{-1}p^{-1}$ ) in the ICHEAR chamber experiments with other studies, the OH reactivity per person obtained from other studies were adjusted for the room volume and the air change rate (ACR) applied in the ICHEAR chamber experiments using the following equations:

$$RP_a = \frac{\text{Room volume (other studies)}}{22.5 \text{ m}^3} \times \frac{\text{ACR (other studies)}}{3.2 \text{ h}^{-1}} \times RP_b$$

where  $RP_a$  refers to the OH reactivity per person after the adjustment and  $RP_b$  refers to the OH reactivity per person before the adjustment, which is obtained from the total OH reactivity divided by the number of occupants in that environment.  $22.5 \text{ m}^3$  is the ICHEAR chamber volume and  $3.2 \text{ h}^{-1}$  is the ACR for the chamber. The per-person OH reactivity before the adjustment ( $RP_b$ ) for the other studies mentioned in Table 3 were estimated using reported values. For the museum gallery room study<sup>70</sup>,  $RP_b$  is derived from the incremental total OH reactivity ( $14 \text{ s}^{-1}$ ) during the high occupancy event (compared to the low occupancy condition) divided by the number of occupants (176 on average). For the classroom study<sup>71</sup> and cinema study<sup>72</sup>, the  $RP_b$  was calculated based on the VOC emission rates ( $\mu\text{g h}^{-1}p^{-1}$ ) reported in each work. As both studies used PTR-ToF-MS, some masses could only be assigned to chemical formulas instead of specific compounds. Therefore, we only included masses with specific compound assignments reported in those two studies to calculate the total OH reactivity per person. Those included VOCs were mostly measured during the present experiments as well. The emission rates were first converted to mixing ratios per person ( $\text{ppb p}^{-1}$ ) based on the indoor space volume and the ACR reported in each study. Then the total OH reactivity per person was calculated using Eq.1 in the main text. The estimated  $RP_b$  of those two studies may slightly underestimate the actual values as those masses without a specific

compound assignment (accounting for < 20% of the total VOC emission rates) were not included in the calculation.

### **Potential artifacts from decomposition of hydroperoxides**

It has been reported that metal surface can act as a catalyst for the decomposition of organic hydroperoxides, and that this is temperature dependent.<sup>73</sup> It has been further reported that with stainless tubing, the conversion rates for ISOPOOH to formaldehyde at room temperature were not significant (below 10%) but increased to 50% at 160 °C<sup>73</sup>. As the temperature in the ICHEAR chamber study was always less than ~ 31°C, this artifact on the stainless-steel chamber walls is not anticipated to be important. However, for the PTR-ToF-MS instrument, this interference may still exist as the drift tube was heated to 60 °C, converting a small amount of ISOPOOH to other products. Another important factor to consider is that in the ICHEAR chamber study, the main oxidant was ozone instead of OH radicals (which are the major oxidant outdoors). MVK and MACR, rather than ISOPOOH, are the major products of isoprene ozonolysis<sup>74</sup>. Furthermore, the reaction between ozone and isoprene is relatively slow ( $1.1 \times 10^{-3}$  ppb/h at 298 K)<sup>7</sup>; at the average ozone concentration (37 ppb) used in ICHEAR, the O<sub>3</sub>/isoprene reaction occurs at a rate ( $0.04 \text{ h}^{-1}$ ) substantially slower than the air change rate ( $3.2 \text{ h}^{-1}$ ). Hence, production of ISOPOOH via ozone reaction was quite small in ICHEAR. The formation of ISOPOOH, to the extent that it occurred in ICHEAR, was probably from isoprene/OH oxidation as OH radicals can be generated during the ozonolysis of unsaturated compounds. Assuming the extreme scenario that measured MVK/MACR were half decomposed from ISOPOOH, it would increase the calculated reactivity during ozone-present condition by  $0.6 \text{ s}^{-1}$  as ISOPOOH has a faster reaction rate constant compared to MVK/MACR ( $9.65 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ , averaged of (1,2)-ISOPOOH and (4,3)-ISOPOOH)<sup>75</sup>. The calculated increase of  $0.6 \text{ s}^{-1}$  is within the standard deviation of the total calculated reactivity



(1.4 s<sup>-1</sup>). Therefore, we judge that the interference should be small. In terms of reactivity measurement, as the PTR-QMS measured the air coming out of the glass reactor and temperature inside the reactor was around 35-40 °C, there should be no interference.

Table S2. List of compounds used in calculating the estimated OH reactivity.

Compound group	Protonated $m/z$ from PTR-MS	Formula assignment	Possible compound assignment	$k_{\text{Xi+OH}}$ ( $\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$ ) at 298K*	Remarks**	Reference
Hydrocarbons (HC)		C5H8	isoprene	$1.00 \times 10^{-10}$	Data from fast-GC	7 (IUPAC)
	79.053	C6H6	benzene	$1.20 \times 10^{-12}$	PTR calibrated	7 (IUPAC)
	93.070	C7H8	toluene	$5.60 \times 10^{-12}$	PTR calibrated	7 (IUPAC)
	105.070	C8H8	styrene	$5.80 \times 10^{-11}$		8
	107.086	C8H10	xylene	$1.70 \times 10^{-11}$ $(1.36 - 2.31) \times 10^{-11}$	PTR calibrated; k rate averaged from listed isomeric compounds	8
	119.086	C9H10	2-phenylpropene	$5.30 \times 10^{-11}$		9
	121.101	C9H12	trimethylbenzene	$4.06 \times 10^{-11}$ $(3.25 - 5.67) \times 10^{-11}$	PTR calibrated; k rate averaged from listed isomeric compounds	8
	133.101	C10H12	benzene,(2-methyl-1-propenyl)-	$3.30 \times 10^{-11}$		9
	137.132	C10H16	monoterpenes	$1.64 \times 10^{-10}$	PTR calibrated using $\alpha$ -pinene; k rate of limonene was taken	7 (IUPAC)
	OVOC Alcohols	33.034	CH4O	methanol	$9.00 \times 10^{-13}$	PTR calibrated
47.049		C2H6O	ethanol	$3.20 \times 10^{-12}$		7 (IUPAC)
OVOC Acids	43.018 61.029	C2H4O2	acetic acid	$8.00 \times 10^{-13}$		10
	73.029	C3H4O2	acrylic acid	$1.75 \times 10^{-11}$		11
	89.023	C3H4O3	pyruvic acid	$1.24 \times 10^{-13}$		12
OVOC Aromatics	95.049	C6H6O	phenol	$3.27 \times 10^{-11}$		13
	107.049	C7H6O	benzaldehyde	$1.20 \times 10^{-11}$		7 (IUPAC)
	109.029	C6H4O2	1,4-benzoquinone	$4.60 \times 10^{-12}$		14
	109.065	C7H8O	methylphenol/methoxybenzene/toluene-1,2-oxide 3/2-methyloxepin	$7.74 \times 10^{-11}$ $(2.54 - 21.0) \times 10^{-11}$	k rate averaged from listed isomeric compounds	15-17

OVOC Aromatics	121.065	C <sub>8</sub> H <sub>8</sub> O	tolualdehyde	$1.60 \times 10^{-11}$		8
	123.044	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	p-benzoquinone, 2-methyl-	$2.35 \times 10^{-11}$		14
	123.081	C <sub>8</sub> H <sub>10</sub> O	dimethylphenol	$8.48 \times 10^{-11}$		16
	125.060	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	4-methoxyphenol /3-methoxyphenol/2-methoxyphenol	$8.94 \times 10^{-11}$ $(7.44-9.80) \times 10^{-11}$	k rate averaged from listed isomeric compounds	16
	135.081	C <sub>9</sub> H <sub>10</sub> O	dimethylbenzaldehyde	$2.74 \times 10^{-11}$ $(2.46-3.70) \times 10^{-11}$	k rate averaged from listed isomeric compounds	18
	137.060	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	1,4-benzodioxane	$2.52 \times 10^{-11}$		19
	149.096	C <sub>10</sub> H <sub>12</sub> O	2,4,5-trimethylbenzaldehyde	$4.27 \times 10^{-11}$		20
OVOC Carbonyls	31.018	CH <sub>2</sub> O	formaldehyde	$9.37 \times 10^{-12}$		8
	45.033	C <sub>2</sub> H <sub>4</sub> O	acetaldehyde	$1.50 \times 10^{-11}$	PTR calibrated	7 (IUPAC)
	57.034	C <sub>3</sub> H <sub>4</sub> O	acrolein	$2.00 \times 10^{-11}$		21
	59.048	C <sub>3</sub> H <sub>6</sub> O	acetone	$1.80 \times 10^{-13}$	PTR calibrated	7 (IUPAC)
	71.048	C <sub>4</sub> H <sub>6</sub> O	methyl vinyl ketone (MVK)/methacrolein (MACR)/isoprene hydroxy hydroperoxide (ISOPOOH)	$2.45 \times 10^{-11}$ $(2.0 -2.9) \times 10^{-11}$	PTR calibrated; k rate averaged from MVK and MACR	7 (IUPAC)
	73.064	C <sub>4</sub> H <sub>8</sub> O	methyl ethyl ketone	$1.10 \times 10^{-12}$	PTR calibrated	7 (IUPAC)
	75.044	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	hydroxyacetone	$3.00 \times 10^{-12}$		22
	83.049	C <sub>5</sub> H <sub>6</sub> O	4-oxopentanal fragment; methylfuran	$2.00 \times 10^{-11}$	k rate of 4OPA was taken	23
	85.028	C <sub>4</sub> H <sub>4</sub> O <sub>2</sub>	butenedial	$5.21 \times 10^{-11}$		24
	85.065	C <sub>5</sub> H <sub>8</sub> O	2-pentenal	$4.37 \times 10^{-11}$		25
	87.044	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	1,4-butanedial	$5.70 \times 10^{-11}$	k rate of 4-hydroxy-2-butenal was taken	26
	87.081	C <sub>5</sub> H <sub>10</sub> O	pentanal	$2.80 \times 10^{-11}$		8
	97.020	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	2 or 3-furancarboxaldehyde	$4.18 \times 10^{-11}$ $(3.50-4.85) \times 10^{-11}$	k rate averaged from listed isomeric compounds	27
	97.065	C <sub>6</sub> H <sub>8</sub> O	2,4-hexadienal	$5.90 \times 10^{-11}$		28
99.045	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	4-oxo-2-pentenal	$5.58 \times 10^{-11}$		24	

OVOC Carbonyls	99.081	C6H10O	cis-3-hexenal; (2e)-2-hexenal; 2-pentenal, 2-methyl-	$4.64 \times 10^{-11}$ $(3.93 - 6.60) \times 10^{-11}$	k rate averaged from listed isomeric compounds	29-31
	101.060	C5H8O2	4-oxopentanal (4-OPA)	$2.00 \times 10^{-11}$		23
	101.096	C6H12O	hexanal	$3.00 \times 10^{-11}$		8
	103.075	C5H10O2	1-hydroxy-2-methyl-3-butanone	$1.62 \times 10^{-11}$		32
	109.101 127.112	C8H14O	6-methyl-5-hepten-2-one (6-MHO)	$1.57 \times 10^{-10}$		33
	111.081	C7H10O	4-methylenehex-5-enal/(3z)-4-methylhexa-3,5-dienal/(3e)-4-methylhexa-3,5-dienal/4-methylcyclohex-3-en-1-one	$1.69 \times 10^{-10}$ $(1.10 - 3.10) \times 10^{-10}$	k rate averaged from listed isomeric compounds	34
	113.096	C7H12O	(e)-2-hepten-1-al	$4.39 \times 10^{-11}$		25
	115.112	C7H14O	2, 3-dimethylpentanal; heptanal	$3.20 \times 10^{-11}$ $(2.96 - 4.20) \times 10^{-11}$	k rate averaged from listed isomeric compounds	35, 36
	127.076	C7H10O2	3-methyl-3-hexene-2,5-dione	$9.40 \times 10^{-11}$		20
	129.127	C8H16O	octanal	$3.00 \times 10^{-11}$	k rate estimated, same as hexanal	
	139.112	C9H14O	bicyclo[2.2.1]heptan-2-one, 3,3-dimethyl-/sabinaketone/ bicyclo[3.1.1]heptan-2-one, 6,6-dimethyl-	$8.85 \times 10^{-12}$ $(5.15 - 14.3) \times 10^{-12}$	k rate averaged from listed isomeric compounds	37, 38
	123.117 141.127	C9H16O	trans-2-nonenal	$4.35 \times 10^{-11}$		30
	125.132 143.143	C9H18O	nonanal	$3.60 \times 10^{-11}$		39
	153.127	C10H16O	camphor	$3.80 \times 10^{-12}$		40
	155.154	C10H18O	geraniol; citronellal	$1.90 \times 10^{-10}$ $(1.50 - 2.31) \times 10^{-10}$	k rate averaged from listed isomeric compounds	41, 42

OVOC Carbonyls	137.097 155.107	C <sub>9</sub> H <sub>14</sub> O <sub>2</sub>	4-methyl-4-octene-1,8-dial (4-MOD)	$1.57 \times 10^{-10}$	k rate estimated, same as 6-MHO	
	139.148 157.159	C <sub>10</sub> H <sub>20</sub> O	C <sub>10</sub> aliphatic carbonyls (decanal)	$3.60 \times 10^{-11}$	k rate estimated, same as nonanal	
	151.112 169.123	C <sub>10</sub> H <sub>16</sub> O <sub>2</sub>	4-methyl-8-oxo-noennal (4-MON)	$1.57 \times 10^{-10}$	k rate estimated, same as 6-MHO	
	171.175	C <sub>11</sub> H <sub>22</sub> O	C <sub>11</sub> aliphatic carbonyls (undecanal)	$3.60 \times 10^{-11}$	k rate estimated, same as nonanal	
	177.164 195.175	C <sub>13</sub> H <sub>22</sub> O	geranyl acetone	$1.57 \times 10^{-10}$	k rate estimated, same as 6-MHO	
		C <sub>3</sub> H <sub>6</sub> O	propanal	$2.00 \times 10^{-11}$	Data from fast-GC	7 (IUPAC)
OVOC others	69.034	C <sub>4</sub> H <sub>4</sub> O	furan	$4.04 \times 10^{-11}$		43
	89.060	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	acetic acid, ethyl ester; formic acid, 1-methylethyl ester	$2.04 \times 10^{-12}$ $(1.69 - 2.4) \times 10^{-12}$	k rate averaged from listed isomeric compounds	44, 45
	111.044	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	aromatic phenol/e,z- and e,e-2,4-hexadienedial/2- furancarboxaldehyde, 5- methyl-/1,2- dihydroxybenzene/1,4- benzenediol/1,3- benzenediol	$5.19 \times 10^{-11}$ $(0.44 - 10.3) \times 10^{-11}$	k rate averaged from listed isomeric compounds	14, 46, 47
	113.060	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	formic acid, tert-butyl ester/butanoic acid, methyl ester/formic acid, butyl ester/propanoic acid, 2- methyl-, methyl ester/	$2.63 \times 10^{-12}$ $(0.68 - 3.82) \times 10^{-12}$	k rate averaged from listed isomeric compounds	48-52
	115.075	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>	ethyl crotonate/3-methyl- 2,4-pentanedione/2,5- hexanedione/methacrylic acid ethyl ester	$3.25 \times 10^{-11}$ $(0.67 - 4.96) \times 10^{-11}$	k rate averaged from listed isomeric compounds	53-56

OVOC others	117.091	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	butanoic acid, 2-methyl-, methyl ester/methyl valerate/acetic acid, butyl ester/isobutyl acetate/propanoic acid, propyl ester/butanoic acid, ethyl ester	$4.17 \times 10^{-12}$ ( $0.56 - 6.33$ ) $\times 10^{-12}$	k rate averaged from listed isomeric compounds	48, 49, 52, 57-59
	129.091	C <sub>7</sub> H <sub>12</sub> O <sub>2</sub>	n-butyl acrylate/4-pentenyl acetate	$3.28 \times 10^{-11}$ ( $2.28 - 4.33$ ) $\times 10^{-11}$	k rate averaged from listed isomeric compounds	60, 61
	143.107	C <sub>8</sub> H <sub>14</sub> O <sub>2</sub>	1-hydroxy-6-methyl-5-hepten-2-one (OH-6MHO)	$6.60 \times 10^{-11}$	k rate of butyl methacrylate was taken	60
Nitrogen containing	42.033	C <sub>2</sub> H <sub>3</sub> N	acetonitrile	$2.20 \times 10^{-14}$	PTR calibrated	7 (IUPAC)
		NH <sub>3</sub>	ammonia	$1.57 \times 10^{-13}$	Data from Picarro	7 (IUPAC)
	46.029	CH <sub>3</sub> NO	formamide/formaldoxime	$2.97 \times 10^{-12}$ ( $1.50 - 4.44$ ) $\times 10^{-12}$	k rate averaged from listed isomeric compounds	62, 63
	70.065	C <sub>4</sub> H <sub>7</sub> N	butyronitrile	$2.56 \times 10^{-13}$		64
	74.024	C <sub>2</sub> H <sub>3</sub> NO <sub>2</sub>	nitroethene	$1.20 \times 10^{-12}$		65
Sulfur containing	49.011	CH <sub>4</sub> S	methanethiol	$3.30 \times 10^{-11}$		7 (IUPAC)
	63.026	C <sub>2</sub> H <sub>6</sub> S	dimethyl sulfide	$4.80 \times 10^{-12}$	PTR calibrated	7 (IUPAC)
	91.057	C <sub>4</sub> H <sub>10</sub> S	tert-butylthiol; 2-butanethiol; 1-propanethiol, 2-methyl-; 1-butanethiol;	$4.22 \times 10^{-11}$ ( $2.91 - 5.60$ ) $\times 10^{-11}$	k rate averaged from listed isomeric compounds	66
	95.016	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub> S	dimethyl sulfone	$3.00 \times 10^{-13}$		67

IUPAC: preferred values recommend by IUPAC were taken.

\* rate constant ranges listed in parentheses refer to the range of rate constants of listed isomeric compounds.

\*\*Compounds without mentioning as “PTR calibrated”, “fast-GC” nor “Picarro” refer to the mixing ratios of species measured by PTR-ToF-MS were calculated based on theoretic method using a constant rate coefficient ( $2.0\text{E-}9 \text{ cm}^3\text{s}^{-1}$ ) for the reactions with  $\text{H}_3\text{O}^+$ <sup>68</sup>, except for 6-MHO where a known rate coefficient ( $3.8\text{E-}9 \text{ cm}^3\text{s}^{-1}$ ) was used<sup>69</sup>.

Table S3. Top ten species contributing to the calculated OH reactivity of breath emissions (Experiment 12, adult group A3) under ozone-free and ozone-present conditions.

	Mass (H <sup>+</sup> )	Compounds	OH Reactivity (s <sup>-1</sup> )	Fraction
<b>Ozone-free</b>	*	isoprene	11.9	95.3%
	33.034	methanol	0.15	1.2%
	137.132	limonene	0.09	0.7%
	59.048	acetone	0.08	0.6%
	69.034	furan	0.04	0.3%
	61.029	acetic acid	0.04	0.3%
	87.044	1,4-butanedial	0.03	0.2%
	127.112	6MHO	0.02	0.2%
	91.057	C4H10S	0.02	0.2%
	63.026	DMS	0.01	0.1%
		<b>Sum of top 10 species</b>	<b>12.3</b>	<b>99.1%</b>
		<b>Sum of all species</b>	<b>12.5</b>	
<b>Ozone-present</b>	*	isoprene	11.2	82.5%
	87.044	1,4-butanedial	0.5	3.4%
	101.096	4OPA	0.3	2.0%
	45.034	acetaldehyde	0.2	1.5%
	127.112	6MHO	0.1	0.9%
	*	propanal	0.1	0.9%
	71.049	C4H6O	0.1	0.8%
	33.034	methanol	0.1	0.8%
	69.034	furan	0.1	0.7%
	61.029	acetic acid	0.1	0.7%
		<b>Sum of top 10 species</b>	<b>12.8</b>	<b>94.3%</b>
		<b>Sum of all species</b>	<b>13.5</b>	

\*isoprene and propanal data were obtained from fast-GC

Table S4. Top ten species contributing to the calculated OH reactivity of dermal emissions (Experiment 13, adult group A3) under ozone-free and ozone-present conditions.

	Mass (H <sup>+</sup> )	Compounds	OH Reactivity (s <sup>-1</sup> )	Fraction
<b>Ozone-free</b>	45.034	acetaldehyde	0.7	15.1%
	69.070	isoprene	0.3	7.2%
	127.112	6MHO	0.3	7.0%
	95.049	phenol	0.3	6.6%
	137.133	limonene	0.3	6.3%
	#	ammonia	0.2	4.6%
	121.065	tolualdehyde	0.2	4.5%
	91.057	C4H10S	0.2	4.3%
	87.044	1,4-butanedial	0.2	4.1%
	71.049	C4H6O	0.2	3.8%
	<b>Sum of top 10 species</b>	<b>2.9</b>	<b>63.4%</b>	
	<b>Sum of all species</b>	<b>4.6</b>		
<b>Ozone-present</b>	127.112	6MHO	13.2	41.8%
	101.096	4OPA	3.6	11.3%
	87.044	1,4-butanedial	1.5	4.6%
	45.034	acetaldehyde	1.3	4.1%
	157.159	decanal	0.7	2.3%
	143.143	nonanal	0.7	2.3%
	141.127	nonenal	0.7	2.2%
	143.107	OH-6MHO	0.7	2.2%
	137.133	limonene	0.6	2.0%
	195.186	geranal acetone	0.5	1.7%
	<b>Sum of top 10 species</b>	<b>23.5</b>	<b>74.5%</b>	
	<b>Sum of all species</b>	<b>31.5</b>		

#ammonia data was from Picarro.



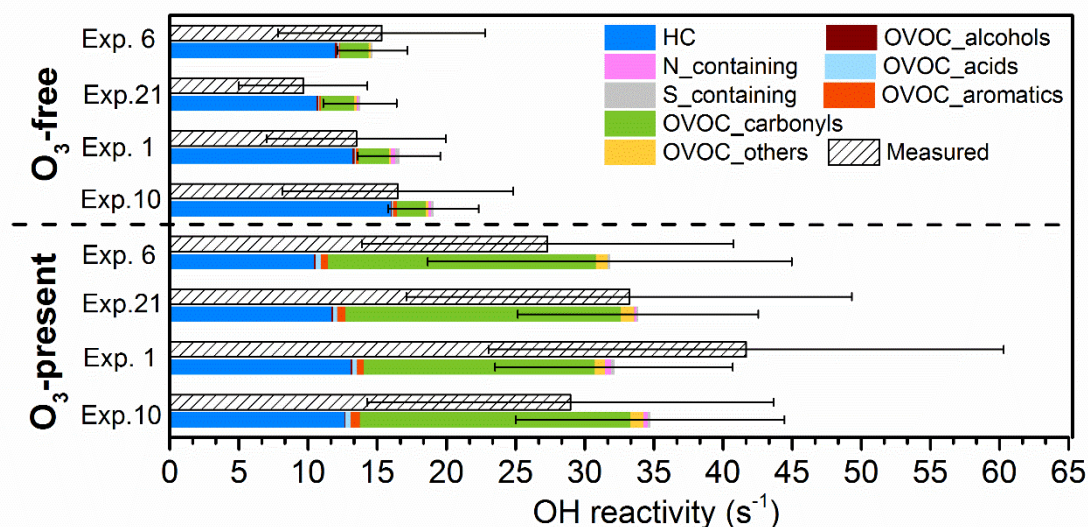


Figure S1. Calculated and measured OH reactivity during ozone-free and ozone-present steady-state conditions of the benchmark experiments with young adults. Error bars represent the total uncertainty of measured OH reactivity and calculated OH reactivity. Experiment 21 is a replicate of Experiment 6.

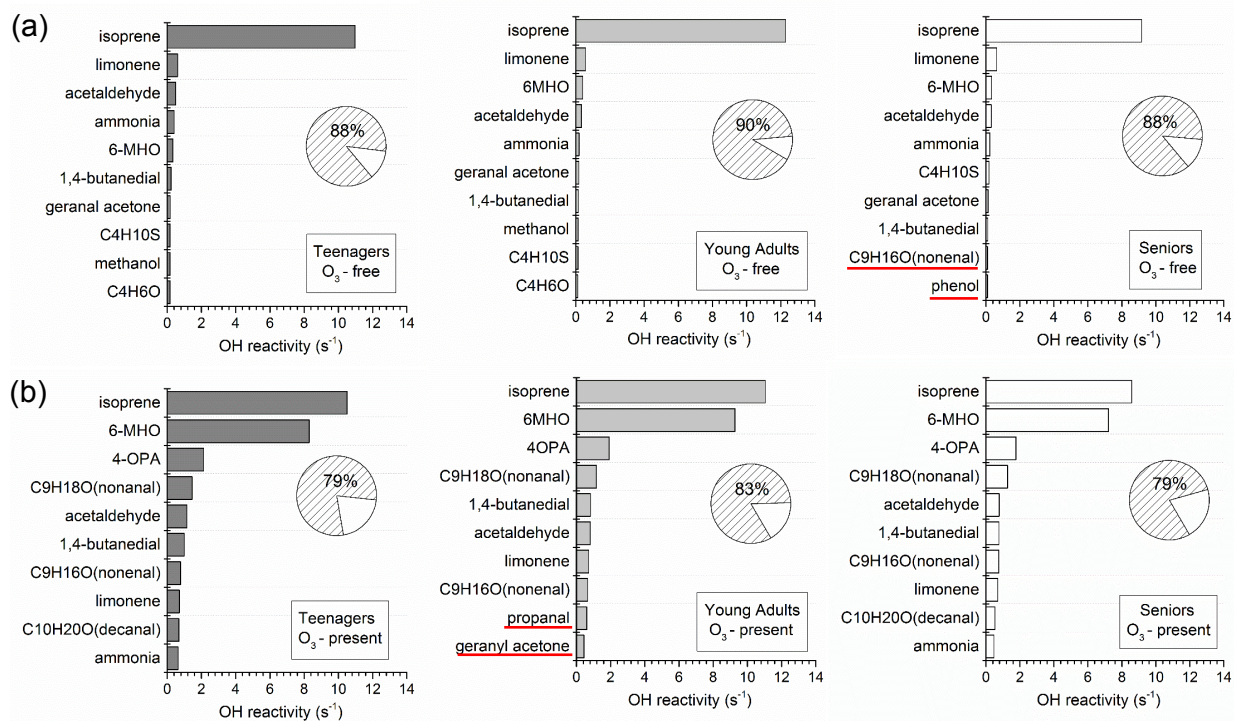


Figure S2. Top ten species contributing to the total OH reactivity for teenagers, young adults and seniors under (a) ozone-free condition and (b) ozone-present condition. The species marked with red underline represent unique species that do not appear among the top ten species of the other two groups. The pie chart in each plot represents the fractions of the total reactivity attributable to the top ten species (hatched) and remaining species (blank).

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