

# SUPPLEMENTARY INFORMATION: Does Green mean Clean? Volatile Organic Emissions from Regular versus Green Cleaning Products

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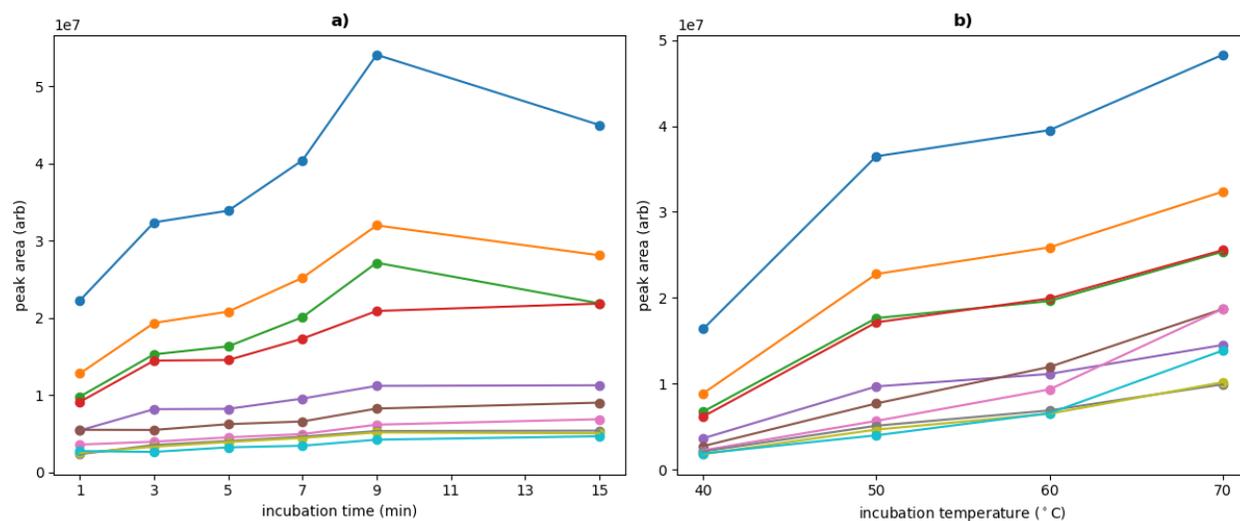
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# 1 Equilibrium headspace GC-TOF-MS

## Incubation optimisation

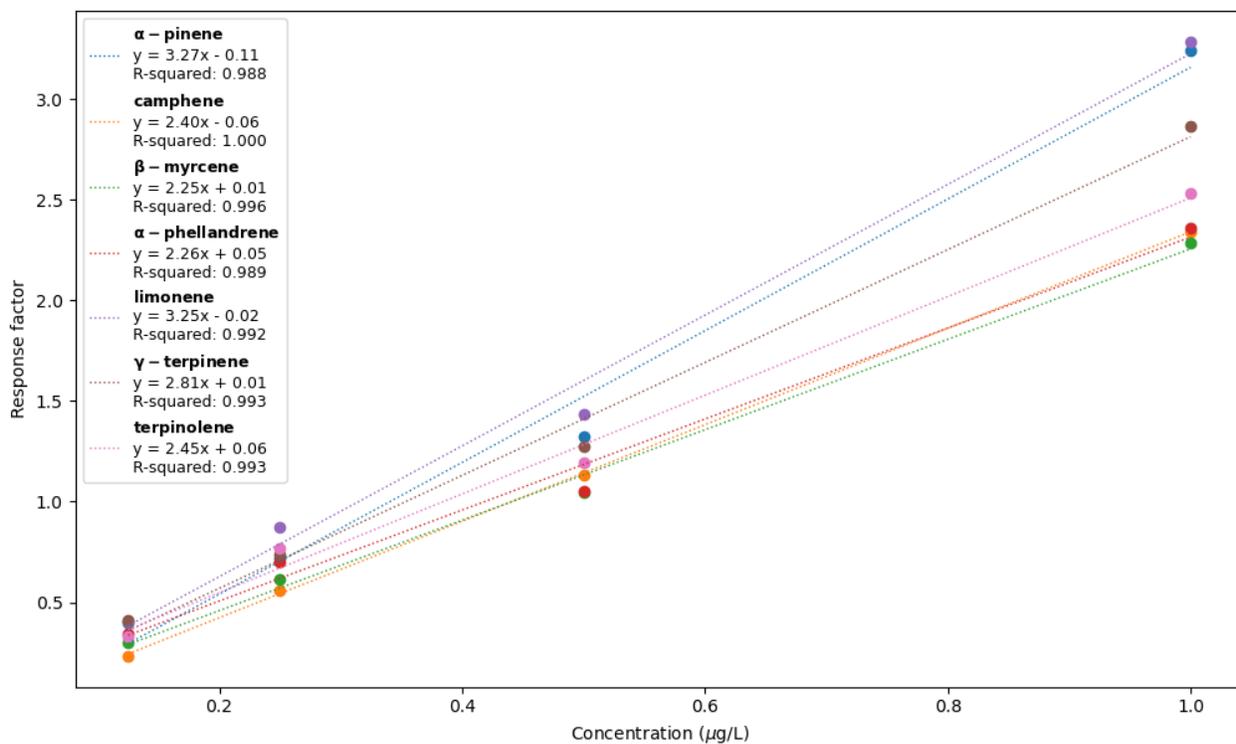
A range of incubation times and temperatures were tested to optimise sensitivity of the equilibrium headspace GC-TOF-MS analytical method for qualitative VOC characterisation. The peak areas of the top 10 chromatogram peaks obtained from analysis of SR1 at varying incubation times and temperatures are shown in Fig. S1A and S1B, respectively. While increasing the incubation time and temperature across the test range generally increased the peak areas, it also increased the method duration and background noise levels. Therefore, an incubation time of 5 minutes and temperature of 50 °C was selected to achieve an efficient and sensitive method for the identification of VOCs in the sample headspace. A lower incubation temperature of 35 °C (the lowest temperature possible using the Gerstel MPS autosampler) was selected for the quantitative analysis of monoterpene species to emulate the liquid-gas partitioning of monoterpenes at ambient room temperature more closely.



**Figure S1:** Peak areas of the top 10 peaks identified in the chromatogram of SR1 when analysed by equilibrium headspace GC-TOF-MS with varying headspace sample incubation conditions. a) incubation times varying from 1-15 minutes (incubation temperature 50 °C), b) incubation temperature varying from 40-70 °C (incubation time 5 minutes).

### Monoterpene calibration

A range of monoterpene compounds were calibrated by analysing solutions of known concentrations of monoterpene analytical standards. The resulting calibration curves are shown in Fig. S2. For monoterpenes which were not calibrated, an average of the calibration curves was used for quantification, except for  $\beta$ -pinene and  $\alpha$ -terpinene, for which the calibration curve of their isomers,  $\alpha$ -pinene and  $\gamma$ -terpinene was used.



**Figure S2:** Calibration curve obtained from equilibrium headspace GC-TOF-MS of monoterpene standards in 50:50 H<sub>2</sub>O:methanol with internal standard, concentration range 0.125 - 1.00  $\mu\text{g/L}$ .

## 2 SIFT-MS

The VOCs measured using each reagent ion in the SIFT-MS method are shown in Table S1, along with the species molecular weights, product ions, rate coefficients and branching ratios. Whether or not detection of a species on that particular reagent ion was used for quantification is also shown in the ‘Included in Analysis’ column. Table S2 shows the species that were measured by SIFT-MS, their limits of detection (LOD), and whether or not the species are calibrated against a gas standard.

**Table S1:** The compounds measured by SIFT-MS and their corresponding reagent ions, molecular masses (MM) and product ion chemical formulae

Reagent Ion	Compound	MM (g mol <sup>-1</sup> )	Product Ion	Reaction Rate (cm <sup>3</sup> molecules <sup>-1</sup> s <sup>-1</sup> )	Branching ratio (%)	Included in Analysis
H <sub>3</sub> O <sup>+</sup>	1,2,4-trimethylbenzene	121	C <sub>9</sub> H <sub>12</sub> .H <sup>+</sup>	2.40 × 10 <sup>-9</sup>	100	
	2-phenethyl acetate	105	C <sub>8</sub> H <sub>9</sub> <sup>+</sup>	3.50 × 10 <sup>-9</sup>	80	
	acetaldehyde	45	C <sub>2</sub> H <sub>4</sub> O.H <sup>+</sup>	3.70 10 <sup>-9</sup>	100	✓
	total sesquiterpenes	205	C <sub>15</sub> H <sub>25</sub> <sup>+</sup>	2.50 × 10 <sup>-9</sup>	64	✓
	benzyl benzoate	151	C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> <sup>+</sup>	3.70 × 10 <sup>-9</sup>	60	
		169	C <sub>8</sub> H <sub>7</sub> O <sub>3</sub> <sup>+</sup> .H <sub>2</sub> O	3.70 × 10 <sup>-9</sup>		
	cinnamaldehyde	133	C <sub>9</sub> H <sub>8</sub> OH <sup>+</sup>	2.00 × 10 <sup>-9</sup>	100	
	citral	153	C <sub>10</sub> H <sub>17</sub> O <sup>+</sup>	3.00 × 10 <sup>-9</sup>	60	✓
		171	C <sub>10</sub> H <sub>17</sub> O <sup>+</sup> .H <sub>2</sub> O	3.00 × 10 <sup>-9</sup>		
	ethanol	47	C <sub>2</sub> H <sub>7</sub> O <sup>+</sup>	2.70 × 10 <sup>-9</sup>	100	✓
	formaldehyde	31	CH <sub>3</sub> O <sup>+</sup>	3.40 × 10 <sup>-9</sup>	100	✓
	total monoterpenes	137	C <sub>10</sub> H <sub>17</sub> <sup>+</sup>	2.60 × 10 <sup>-9</sup>	30	
	m-xylene	107	C <sub>8</sub> H <sub>10</sub> .H <sup>+</sup>	2.30 × 10 <sup>-9</sup>	100	
	methanol	33	CH <sub>5</sub> O <sup>+</sup>	2.70 × 10 <sup>-9</sup>	100	✓
NO <sup>+</sup>	2-phenethyl acetate	104	C <sub>8</sub> H <sub>8</sub> <sup>+</sup>	2.90 × 10 <sup>-9</sup>	85	✓
	2-tert-butylcyclohexyl acetate	138	C <sub>10</sub> H <sub>18</sub> <sup>+</sup>	2.80 × 10 <sup>-9</sup>	40	✓
	acetaldehyde	43	CH <sub>3</sub> CO <sup>+</sup>	6.90 × 10 <sup>-10</sup>	80	
		61	CH <sub>3</sub> CO <sup>+</sup> .H <sub>2</sub> O	6.90 × 10 <sup>-10</sup>		
	total sesquiterpenes	204	C <sub>15</sub> H <sub>24</sub> <sup>+</sup>	2.00 × 10 <sup>-9</sup>	38	
	benzene	78	C <sub>6</sub> H <sub>6</sub> <sup>+</sup>	1.50 × 10 <sup>-9</sup>	55	✓
		108	NO.C <sub>6</sub> H <sub>6</sub> <sup>+</sup>	1.50 × 10 <sup>-9</sup>	45	
	benzyl benzoate	180	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub> NO <sup>+</sup>	2.50 × 10 <sup>-9</sup>	45	✓
	cinnamaldehyde	132	C <sub>9</sub> H <sub>8</sub> O <sup>+</sup>	2.00 × 10 <sup>-9</sup>	100	
	citral	151	C <sub>10</sub> H <sub>15</sub> O <sup>+</sup>	2.50 × 10 <sup>-9</sup>	35	
	ethanol	45	C <sub>2</sub> H <sub>5</sub> O <sup>+</sup>	1.20 × 10 <sup>-9</sup>	100	
		63	C <sub>2</sub> H <sub>5</sub> O <sup>+</sup> .H <sub>2</sub> O	1.20 × 10 <sup>-9</sup>		
	eugenol	164	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub> <sup>+</sup>	2.40 × 10 <sup>-9</sup>	100	✓
	lactic acid	73	CH <sub>3</sub> CH(OH)CO <sup>+</sup>	2.50 × 10 <sup>-9</sup>	50	✓
	total monoterpenes	88	?	2.20 × 10 <sup>-9</sup>	25	
		136	C <sub>10</sub> H <sub>16</sub> <sup>+</sup>	2.20 × 10 <sup>-9</sup>	75	✓
m-xylene	106	C <sub>8</sub> H <sub>10</sub> <sup>+</sup>	1.90 × 10 <sup>-9</sup>	100	✓	
O <sub>2</sub> <sup>+</sup>	1,2,4-trimethylbenzene	120	C <sub>9</sub> H <sub>12</sub> <sup>+</sup>	2.00 × 10 <sup>-9</sup>	85	✓
	2-tert-butylcyclohexyl acetate	57	C <sub>4</sub> H <sub>9</sub> <sup>+</sup>	4.50 × 10 <sup>-9</sup>	45	
	benzene	78	C <sub>6</sub> H <sub>6</sub> <sup>+</sup>	1.10 × 10 <sup>-9</sup>	100	
	cinnamaldehyde	132	C <sub>9</sub> H <sub>8</sub> O <sup>+</sup>	2.00 × 10 <sup>-9</sup>	100	✓

dihydromyrcenol	59	$C_3H_7O^+$	$2.90 \times 10^{-9}$	50	✓
	77	$C_3H_7O.H_2O^+$	$2.90 \times 10^{-9}$		
eugenol	139	$C_{10}H_{19}^+$	$2.90 \times 10^{-9}$	15	
	164	$C_{10}H_{12}O_2^+$	$1.90 \times 10^{-9}$	100	

**Table S2:** Species identified by SIFT-MS, their limits of detection (average  $\pm$  standard deviation of 23 samples), and whether or not their concentrations were calibrated against a gas standard

Species	LOD ( $\mu\text{g m}^{-3}$ )	Calibrated
Formaldehyde	$13.35 \pm 2.58$	
Acetaldehyde	$5.25 \pm 1.01$	✓
Methanol	$10.18 \pm 1.62$	✓
Ethanol	$20.00 \pm 7.70$	✓
Total monoterpenes	$9.67 \pm 5.72$	✓
Total sesquiterpenes	$22.22 \pm 6.49$	
Dihydromyrcenol	$30.41 \pm 9.43$	
Eugenol	$2.47 \pm 0.45$	
Citral	$15.91 \pm 3.39$	
Cinnamaldehyde	$7.20 \pm 2.02$	
2-tert-butylcyclohexyl acetate	$20.72 \pm 9.24$	
2-phenethyl acetate	$3.53 \pm 0.76$	
1,2,4-trimethyl benzene	$3.60 \pm 0.85$	
Benzyl benzoate	$8.81 \pm 2.52$	
benzene	$5.12 \pm 2.70$	✓
m-xylene	$3.46 \pm 0.68$	
Lactic acid	$10.36 \pm 10.07$	

### 3 Measurement uncertainty

Sources of uncertainty in the experimental method for the quantification of VOCs in cleaning product formulations were identified as: 1  $\mu\text{L}$  sample volume measurement ( $\pm 5\%$ ), headspace sample gas flow rate ( $\pm 1\%$ ) and SIFT-MS measurements (see Table S3).

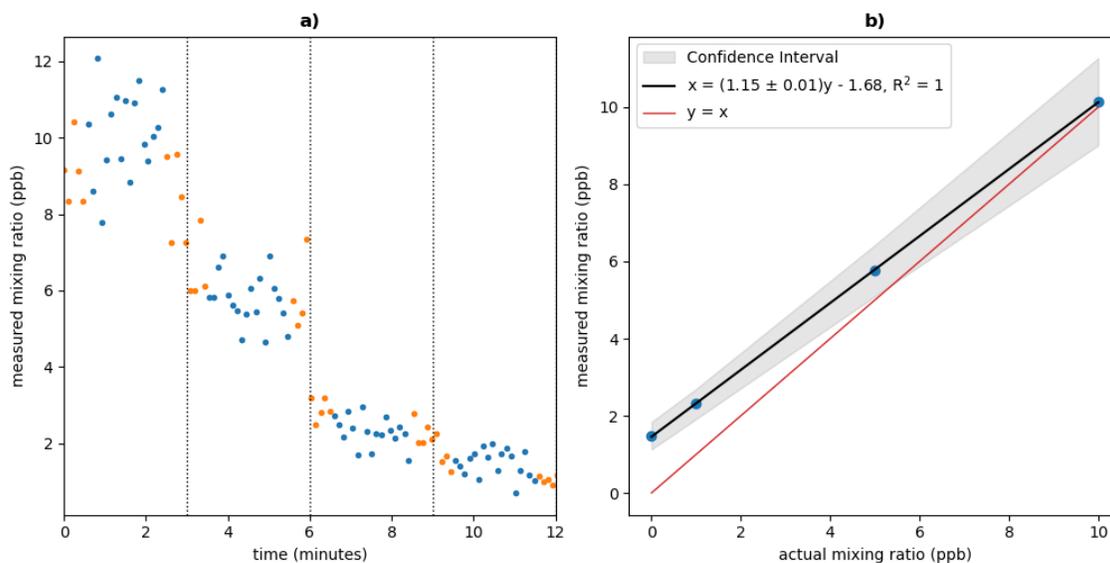
For uncalibrated species, the SIFT-MS measurements are calculated using the ion-molecule reaction rate coefficients and branching ratios given in Table S1 (taken from Syft Technologies kinetic database). The uncertainty in these uncalibrated measurements is assumed to be  $\pm 35\%$ , as recommended in Syft training resources<sup>1,2</sup>. For species which were quantified using reference calibration, the calibration factors were calculated as the average of the calibration curve slopes from multiple instrument calibrations, and the associated uncertainties calculated as the average of the standard errors (Table S3).

**Table S3:** The calibration factors and associated uncertainties used in this study, determined from multiple instrument calibrations using gas standards

Species	Calibration factor	Relative uncertainty (%)
acetaldehyde	$0.52 \pm 0.045$	8.69
ethanol	$1.02 \pm 0.109$	10.72
benzene	$0.81 \pm 0.035$	4.44
Total monoterpenes <sup>a</sup>	$0.78 \pm 0.059$	7.61
methanol	$1.17 \pm 0.024$	2.09

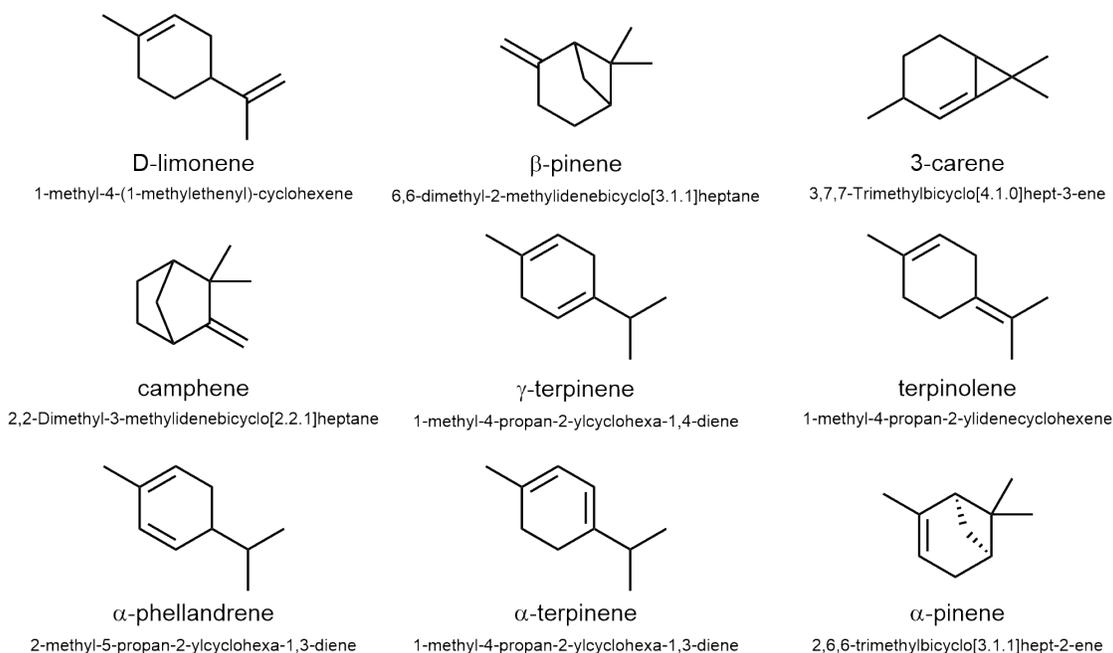
<sup>a</sup>Limonene used as calibration gas.

An example of the calibration process is shown in Fig. S3A. Calibration of the SIFT-MS was achieved by performing stepwise dilutions of reference calibration gases using a custom-built automated gas calibration unit. Two gas standards were used for SIFT-MS calibration: a 14-component gas standard (1 ppm certified National Physical Laboratory, UK) and a limonene only standard (1 ppm in  $\text{N}_2$ ). The limonene standard was prepared in-house by injecting a controlled amount of liquid standard (Sigma Aldrich, 99.8% purity) into an evacuated gas cylinder and subsequently pressurising the cylinder with research-grade  $\text{N}_2$  (N6, BOC). The resulting limonene concentration was determined via GC-FID (calibrated using 1 ppm limonene in  $\text{N}_2$  standard, NPL) after 7 days equilibration at room temperature. Each gas standard was diluted in the AGCU using zero air which was provided by a heated palladium alumina-based zero air generator. The 14-component gas standard was diluted to a concentration range of 1 to 10 ppb, while the limonene gas standard was diluted to a range of 1.8 to 18 ppb. Each concentration step was measured for 3 minutes, with the first and last 30 seconds of each step being discounted to minimise the error associated with instrument equilibration between concentration steps. The resulting data was used to generate a multi-point calibration curve, from which the calibration factor was derived by linear regression analysis (Fig. S3B).



**Figure S3:** An example of SIFT-MS reference calibration for methanol using a 14-component gas standard (1 ppm certified National Physical Laboratory, UK), diluted with N<sub>2</sub> to 0 - 10 ppb. a) The mixing ratio of methanol measured during the automated step-down calibration process. The middle 2 minutes of each step (blue) were averaged to produce the multi-point calibration curve. Orange datapoints were discounted to minimise the error associated with instrument equilibration between concentration steps. b) Calibration curve produced from the automated calibration process, with linear regression analysis to determine the calibration factor (1.15) and standard error (0.01).

## 4 Monoterpene chemical structures

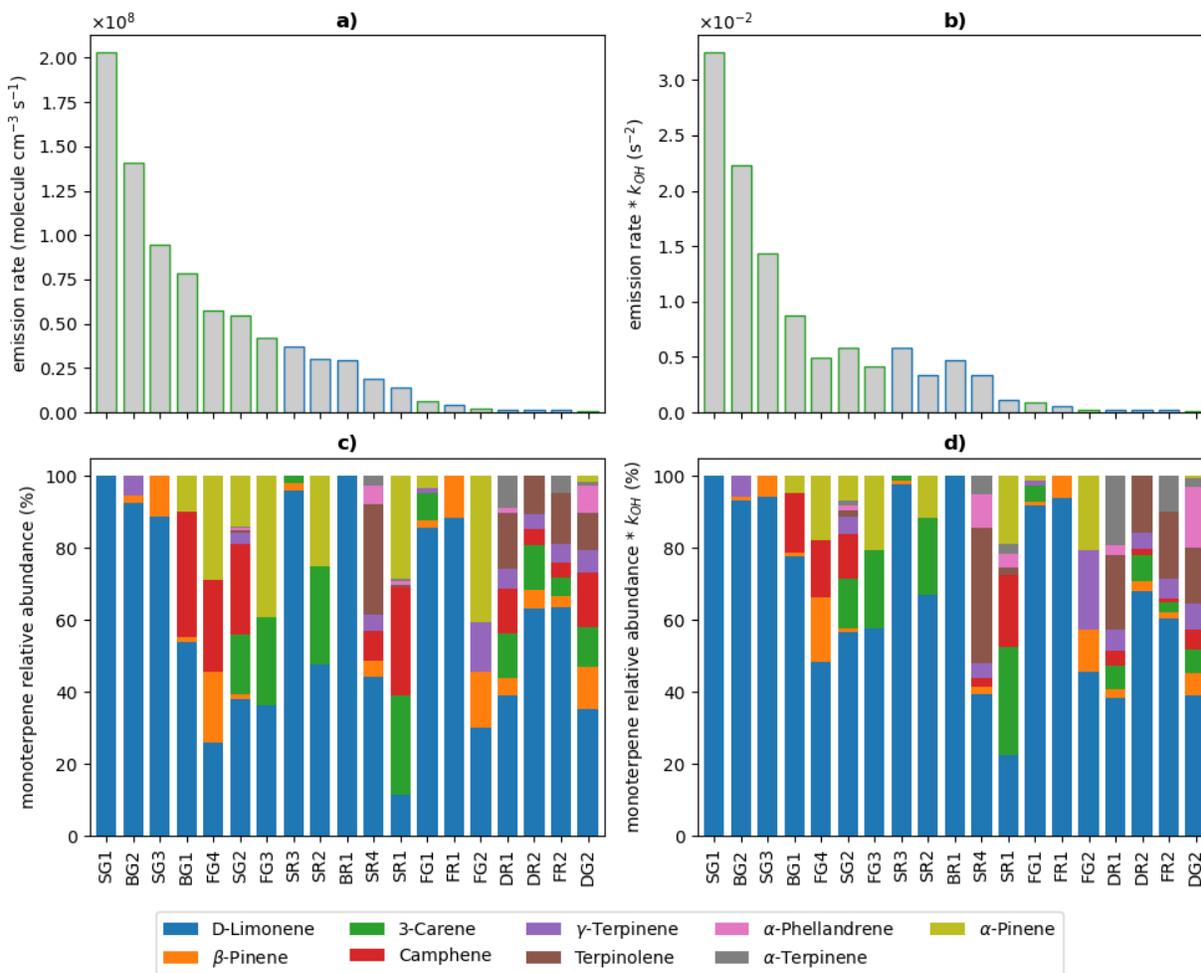


**Figure S4:** Chemical structures and corresponding IUPAC names of the monoterpenes discussed in this study.

## 5 Application of analytical approach to a previous study

The approach taken to calculate emission rates described in the methods section was applied to the data reported by Singer et al.<sup>3</sup> to estimate monoterpene emission rates for their reported conditions. We used the terpene composition of the pine oil-based general-purpose cleaner reported by Singer et al., along with their experimental protocol for a floor mopping experiment (experiment N) to determine individual monoterpene emission rates. The emission rates were then applied to the INCHEM-Py model to simulate the cleaning experiment, using the approach described in this study. The simulation resulted in a peak monoterpene concentration of 165 ppb, which was 32% of the 1-hour average total monoterpene concentration of 513 ppb reported by Singer et al.. However, the theoretical maximum monoterpene concentration in the Singer et al.<sup>3</sup> experiment was estimated to be 186 ppb, assuming all terpene emissions originated from the 105 mL dispensed cleaning solution only. The discrepancy between the two values is likely to be caused by additional emissions originating from the preparation of the cleaning solution in the room and from the bulk solution during the cleaning event. Consequently, the emission rates estimated by our method could be 2-3 times too low, depending on how the cleaning is carried out.

## 6 Monoterpene emissions scaled to OH rate coefficient



**Figure S5:** a) Estimated total monoterpene emission rates per product, as determined from SIFT-MS measurements (green edge bar = green cleaners, blue edge bar = regular cleaners). b) The sum of the monoterpene emission rates scaled to the monoterpene OH rate coefficient per product. c) The relative abundance (%) of monoterpenes applied to the total monoterpene emission rates to be input to the model, as determined from GC-MS chromatogram peak areas. d) the relative abundance (%) of monoterpenes scaled to their respective OH rate coefficients.

## 7 References

- [1] Syft Technologies. (2014). Quantitation: SIFT-MS Calibration Principles. Syft Technologies Training Materials.
- [2] Langford, V. S. and G. I. and M. M. J. (2014). Rapid monitoring of volatile organic compounds: a comparison between gas chromatography/mass spectrometry and selected ion flow tube mass spectrometry. *Rapid Communications in Mass Spectrometry*, 28(1), 10–18. <https://doi.org/10.1002/rcm.6747>
- [3] Singer, B. C., Destailats, H., Hodgson, A. T., & Nazaroff, W. W. (2006). Cleaning products and air fresheners: Emissions and resulting concentrations of glycol ethers and terpenoids. *Indoor Air*, 16(3), 179–191. <https://doi.org/10.1111/j.1600-0668.2005.00414.x>