Supplement of

Calibrating adsorptive and reactive losses of monoterpenes and sesquiterpenes in dynamic chambers using deuterated surrogates

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Text S1

As shown in Fig. S1, the dry air was divided to two paths, one with flow rate of F_1 (L min^{-1}) passed through an ultraviolet lamp (SOG-2, Analttik Jena, USA) to generate O_3 with targeted mixing ratio, and another with flow rate of F_2 (L min^{-1}) passed through a humidifier, then they were mixed and the total flow rate of F_1 and F_2 was maintained at 9 L min^{-1}, the final humidity of the mixed main airflow was adjusted by the ratio of F_1 and F_2. After that, the standard gas mixtures with flow rate of F_3 ($\leq$ 100 mL min^{-1}) were released into the main airflow and mixed again through a FEP Teflon tube with length of 3 m, then the mixed airflow was introduced into the chamber. All flow rates were controlled by calibrated mass flow controllers and all tubes were FEP Teflon materials in Fig. S1. The outer chamber body was intertwined by rubber hose with water circulating in it, the temperature of the circulating water was controlled by a water bath; this way, the temperature in the chamber can be controlled at nearly constant value with deviation of smaller than 0.5 °C. The concentrations of MTs and SQTs were measured continuously by a PTR-ToF-MS (PTR-ToF-MS 2000, Ionicon Analytik GmbH, Innsbruck, Austria; Wang et al., 2014), and the mixing ratio of O_3 was monitored by an ozone analyzer (Mode 49i, Thermo Fisher Scientific, USA). Temperature and humidity inside the chamber were monitored by sensors (HC2A-S, Rotronic, Switzerland). After the concentrations of MTs and SQTs in the chamber reached steady state, offline samples were collected simultaneously from inlet (C_0) and outlet (C_1) by commercial adsorbent cartridges (Tenax TA/Carbograph 5TD, Markes International Ltd, UK) connected onto a portable dual-channel sampler (ZC-QL, Zhejiang Hengda Instrumentation Ltd., China) at a rate of 200 mL min^{-1} for 5 min. Therefore, the recovery was expressed as C_1 / C_0 (%). Ozone scrubbers (Zeng et al., 2022a) were used only during the experiment of ozone effect (Fig. S1). Additionally, we tested whether the ozone scrubber will adsorb MTs and SQTs, the results showed that most MTs and SQTs had good recoveries of 92±2% to 103±1%. Linalool, for an exception, had obvious loss with recovery of only 40% (Fig. S2). Therefore, linalool did not include in the subsection of ozone effect.

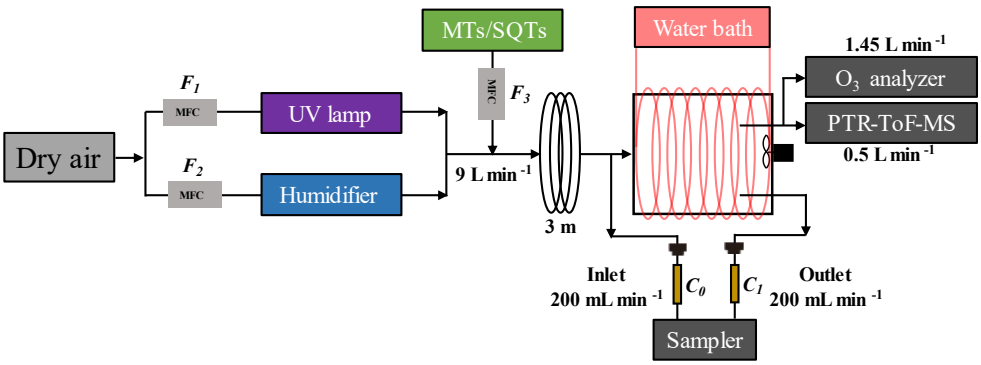

Figure S1. Schematic diagram of chamber evaluation experiments.

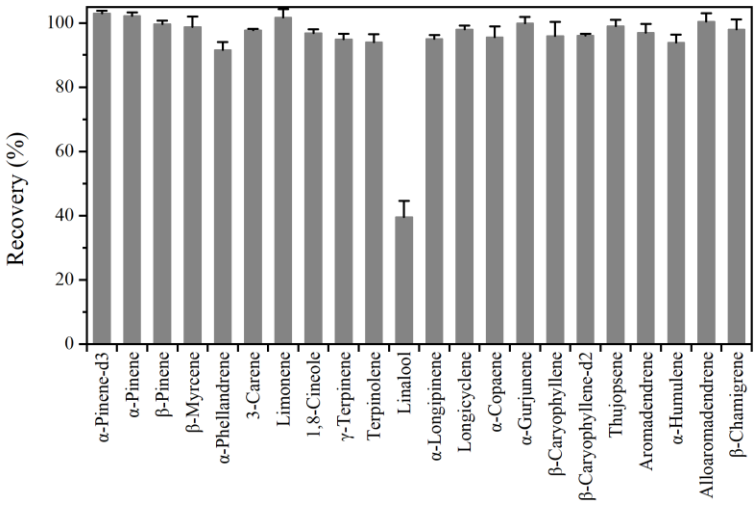

Figure S2. The effect of O_3 scrubber on the recoveries of MTs and SQTs.

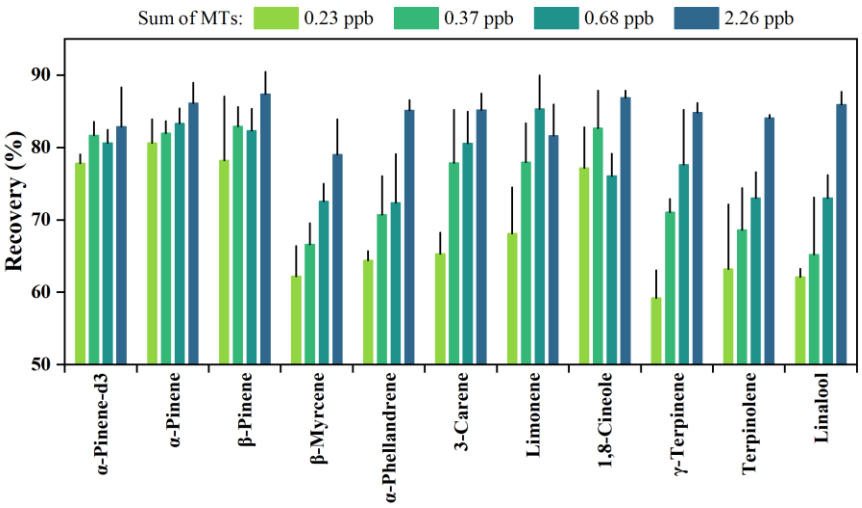

Figure S3. Recoveries of MT monomers under different concentration levels.

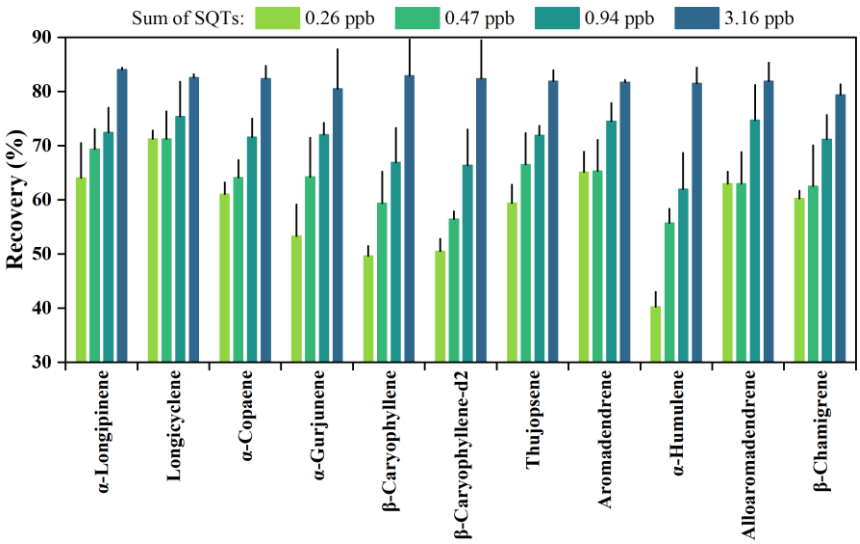

Figure S4. Recoveries of SQT monomers under different concentration levels.

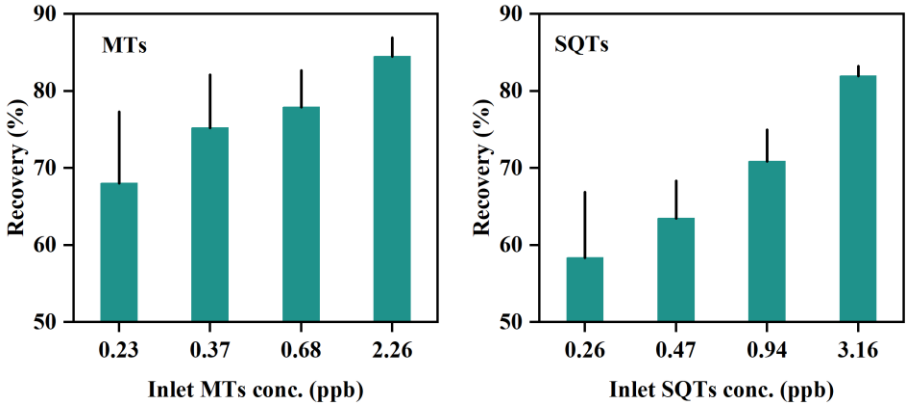

Figure S5. The average recoveries of MTs and SQTs under different concentration levels.

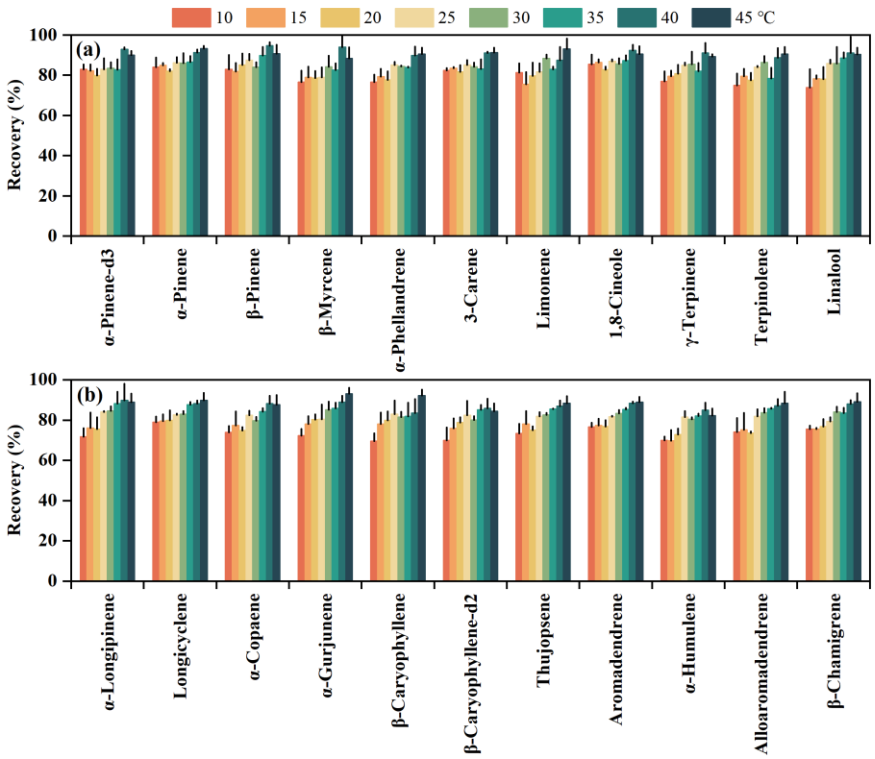

Figure S6. Recoveries of different MT (a) and SQT (b) monomers under different temperatures among high concentration regime.

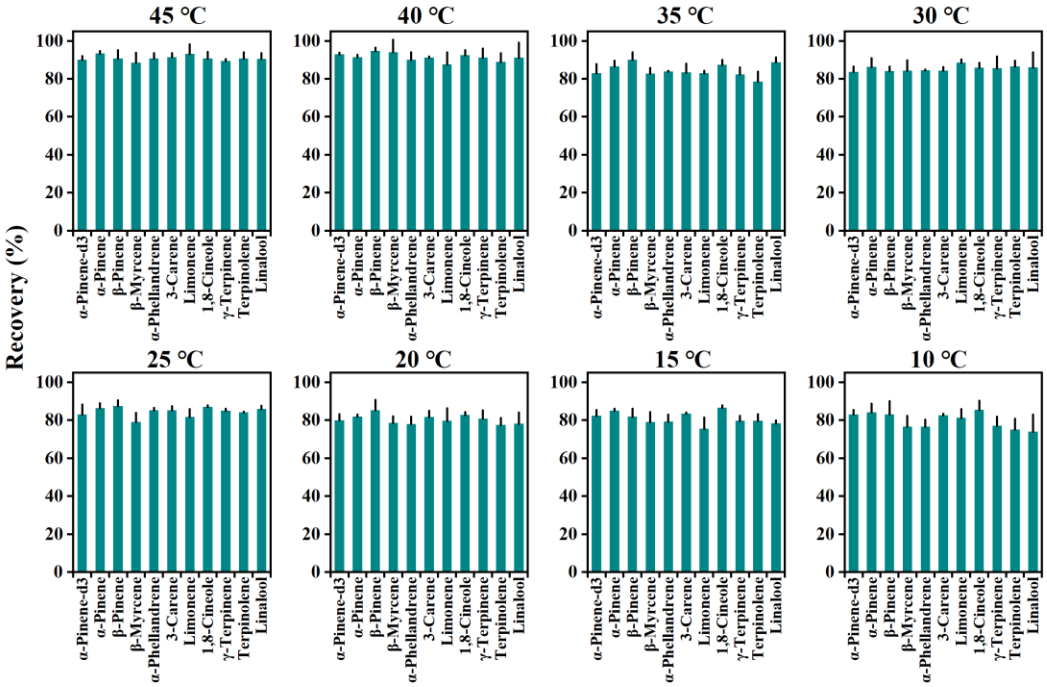

Figure S7. Recoveries of different MT monomers under different temperatures among high concentration regime.

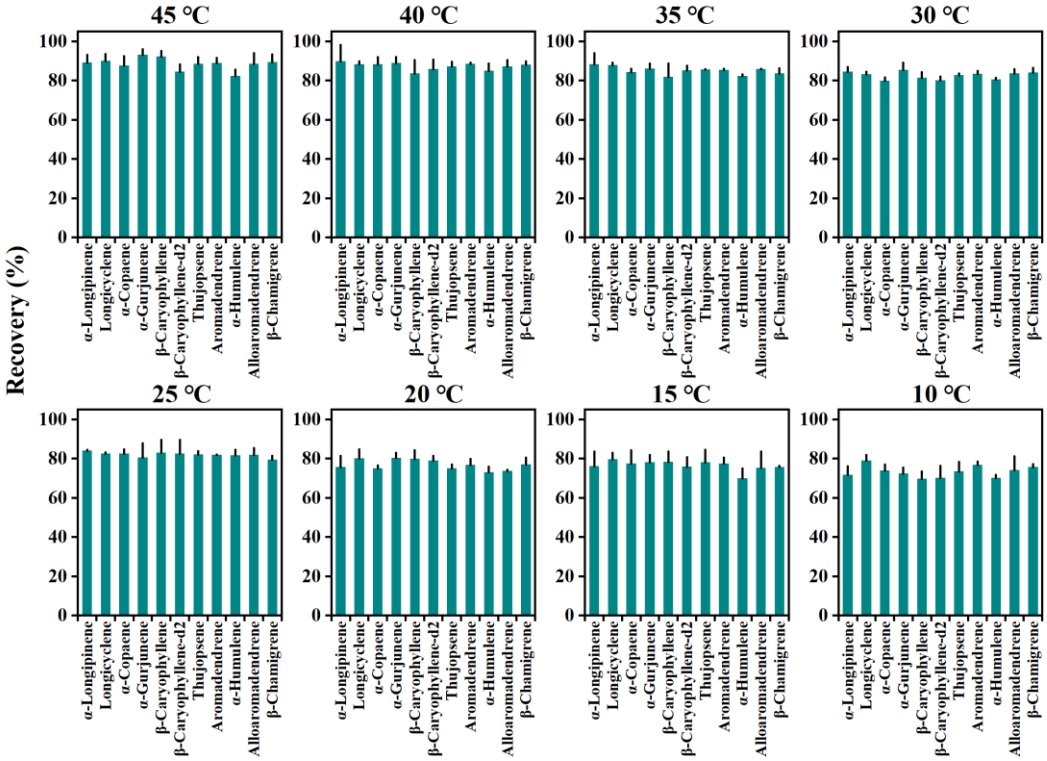

Figure S8. Recoveries of different SQT monomers under different temperatures among high concentration regime.

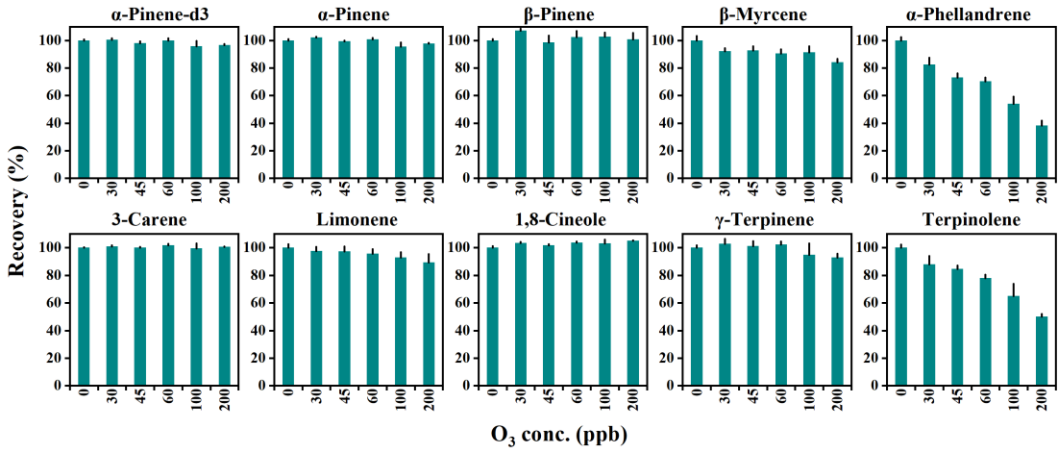

Figure S9. Reactive losses of different MT monomers under different O_3 mixing ratios.

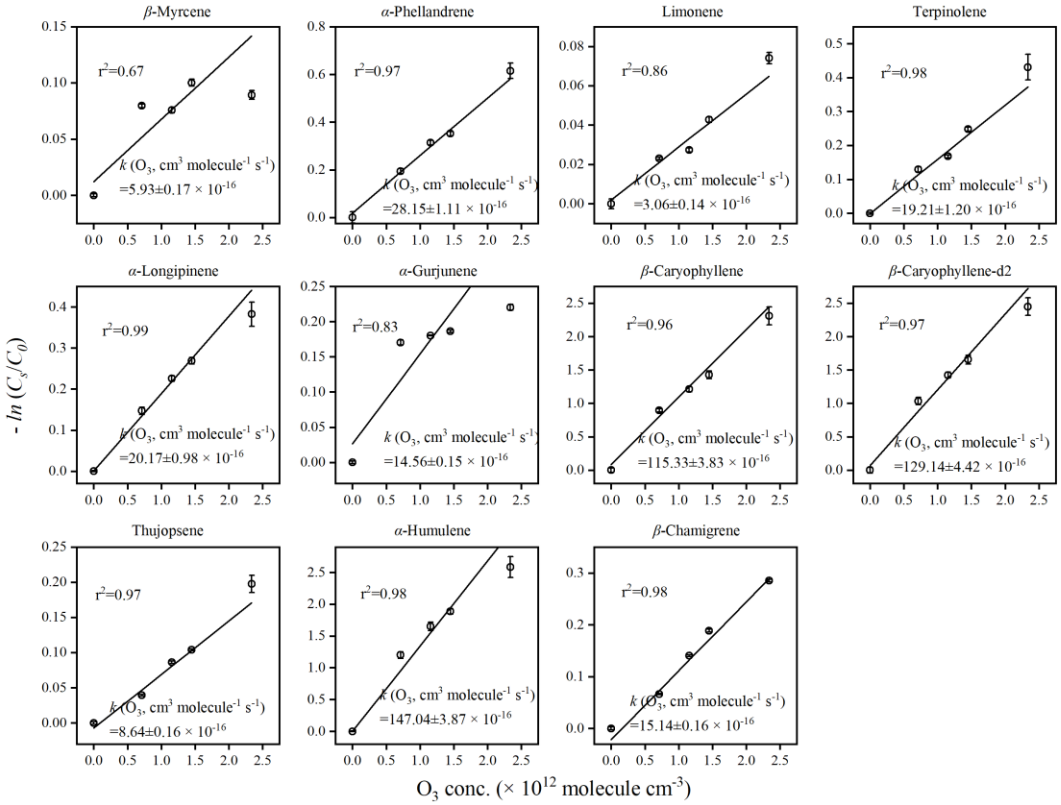

Figure S10. The rate constants of different MT and SQT monomers with ozone.

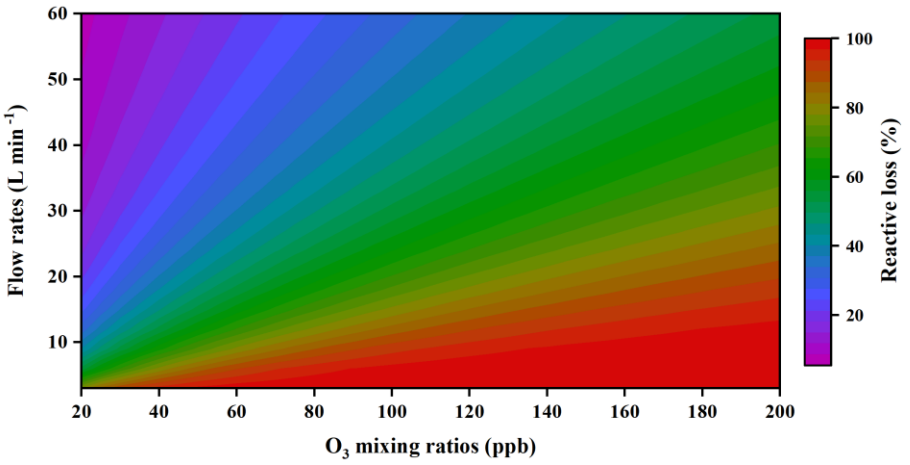

Figure S11. Reactive losses of β-caryophyllene under different ozone mixing ratios and flow rates.

Table S1. The information of monoterpene and sesquiterpene standards.

Compounds	CAS No.	Chemical formula	Molecular weight (g mol^{-1})	Purity	Supplier
α-Pinene-d3	75352-01-1	$C_{10}H_{13}D_3$	139.23	>95 %	TRC
α-Pinene	7785-26-4	$C_{10}H_{16}$	136.23	>95 %	Sigma-Aldrich
β-Pinene	18172-67-3	$C_{10}H_{16}$	136.23	>98.5 %	Sigma-Aldrich
β-Myrcene	123-35-3	$C_{10}H_{16}$	136.23	>90 %	TRC
α-Phellandrene	4221-98-1	$C_{10}H_{16}$	136.23	>95 %	Sigma-Aldrich
3-Carene	13466-78-9	$C_{10}H_{16}$	136.23	>95 %	Sigma-Aldrich
Limonene	5989-27-5	$C_{10}H_{16}$	136.23	>95 %	Sigma-Aldrich
1,8-Cineole	470-82-6	$C_{10}H_{18}O$	154.25	>99 %	Sigma-Aldrich
γ-Terpinene	97-85-4	$C_{10}H_{16}$	136.23	>95 %	Sigma-Aldrich
Terpinolene	586-62-9	$C_{10}H_{16}$	136.23	>97 %	Fluka
Linalool	78-70-6	$C_{10}H_{18}O$	154.25	>97 %	Sigma-Aldrich
α-Longipinene	5989-08-2	$C_{15}H_{24}$	204.35	>99 %	Sigma-Aldrich
Longicyclene	1137-12-8	$C_{15}H_{24}$	204.35	>95 %	Sigma-Aldrich
α-Copaene	3856-25-5	$C_{15}H_{24}$	204.35	>95 %	Fluka
α-Gurjunene	489-40-7	$C_{15}H_{24}$	204.35	>97 %	Sigma-Aldrich
β-Caryophyllene	87-44-5	$C_{15}H_{24}$	204.35	>98.5 %	Sigma-Aldrich
β-Caryophyllene-d2	2006272-96-2	$C_{15}H_{22}D_2$	206.37	>95 %	TLC
Thujopsene	470-40-6	$C_{15}H_{24}$	204.35	>97 %	Sigma-Aldrich
Aromadendrene	25246-27-9	$C_{15}H_{24}$	204.35	>98 %	Sigma-Aldrich
α-Humulene	6753-98-6	$C_{15}H_{24}$	204.35	>96 %	Sigma-Aldrich
Alloaromadendrene	489-39-4	$C_{15}H_{24}$	204.35	>97 %	Sigma-Aldrich
β-Chamigrene	18431-82-8	$C_{15}H_{24}$	204.35	>90 %	Sigma-Aldrich

Table S2. Method detection limits and measurement precisions of monoterpenes and sesquiterpenes.

Compounds	m/z	Chemical formula	MDL (ng m^{-3})	RSD (%)
α-Pinene-d3	96	$C_{10}H_{13}D_3$	6	4.5 %
α-Pinene	93	$C_{10}H_{16}$	8	4.5%
β-Pinene	93	$C_{10}H_{16}$	38	3.9%
β-Myrcene	93	$C_{10}H_{16}$	92	2.3%
α-Phellandrene	93	$C_{10}H_{16}$	20	3.0%
3-Carene	93	$C_{10}H_{16}$	10	2.8%
Limonene	93	$C_{10}H_{16}$	36	4.8%
1,8-Cineole	93	$C_{10}H_{18}O$	8	3.8%
γ-Terpinene	93	$C_{10}H_{16}$	38	3.8%
Terpinolene	93	$C_{10}H_{16}$	30	2.7%
Linalool	93	$C_{10}H_{18}O$	28	3.6%
α-Longipinene	93	$C_{15}H_{24}$	50	2.7%
Longicyclene	93	$C_{15}H_{24}$	10	1.5%
α-Copaene	93	$C_{15}H_{24}$	16	3.3%
α-Gurjunene	93	$C_{15}H_{24}$	2	3.4%
β-Caryophyllene	204	$C_{15}H_{24}$	92	2.0%
β-Caryophyllene-d2	206	$C_{15}H_{22}D_2$	28	2.0 %
Thujopsene	93	$C_{15}H_{24}$	20	1.1%
Aromadendrene	93	$C_{15}H_{24}$	6	2.6%
α-Humulene	93	$C_{15}H_{24}$	2	1.7%
Alloaromadendrene	93	$C_{15}H_{24}$	8	2.4%
β-Chamigrene	93	$C_{15}H_{24}$	4	1.8%

References

Wang, X., Liu, T., Bernard, F., Ding, X., Wen, S., Zhang, Y., Zhang, Z., He, Q., Lü, S., Chen, J., Saunders, S., and Yu, J.: Design and characterization of a smog chamber for studying gas-phase chemical mechanisms and aerosol formation, Atmos. Meas. Tech., 7, 301-313, https://doi.org/10.5194/amt-7-301-2014, 2014.

Zeng, J., Zhang, Y., Zhang, H., Song, W., Wu, Z., and Wang, X.: Design and characterization of a semi-open dynamic chamber for measuring biogenic volatile organic compound (BVOC) emissions from plants, Atmos. Meas. Tech., 15, 79-93, https://doi.org/10.5194/amt-15-79-2022, 2022a.