Biogenic and anthropogenic contributions to urban terpenoid fluxes

Erin F. Katz[1,2], Caleb M. Arata[2], Eva Y. Pfannerstill[3,4], Robert J. Weber[2], Darian Ng[5], Michael J. Milazzo[2,6], Haley Byrne[6], Hui Wang[7], Alex B. Guenther[7], Camilo Rey-Sanchez[5], Joshua Apte[6,8], Dennis D. Baldocchi[2], Allen H. Goldstein[2,6]

[1]Department of Chemistry, University of California, Berkeley, California
[2]Department of Environmental Science, Policy, and Management, University of California, Berkeley, California
[3]Institute of Climate and Energy Systems (ICE-3): Troposphere, Forschungszentrum Jülich, Jülich, Germany
[4]Institute of Geophysics and Meteorology, University of Cologne, Cologne, Germany
[5]Department of Marine, Earth and Atmospheric Sciences, North Carolina State University
[6]Department of Civil and Environmental Engineering, University of California, Berkeley, California
[7]Department of Earth System Science, University of California, Irvine, California
[8]School of Public Health, University of California, Berkeley, California

Table S1: Summary of calibration results. VOCs in calibration gas mixtures were calibrated on the proton-transfer product unless otherwise indicated. The average sensitivity in counts per second per parts per billion (cps/ppb) is reported.

VOC	*Formula*	*Average Sensitivity (cps/ppb)*
Monoterpenes	$C_{10}H_{17}^+$	1145
D5 Siloxane	$C_{10}H_{31}O_5Si_5^+$	2777
Acetonitrile	$C_2H_4N^+$	4378
Acetaldehyde	$C_2H_5O^+$	2131
Ethanol	$C_2H_7O^+$	22
Dimethylsulfide	$C_2H_7S^+$	5941
Acrolein	$C_3H_5O^+$	2416
Propanol (dehydration product)	$C_3H_7^+$	211
Acetone	$C_3H_7O^+$	7031
Furan	$C_4H_5O^+$	3757
Methacrolein	$C_4H_7O^+$	1338
Butanol (dehydration product)	$C_4H_9^+$	1173
Isoprene	$C_5H_9^+$	760
D3 Siloxane	$C_6H_{19}O_3Si_3^+$	4622
Benzene (charge transfer product)	$C_6H_6^+$	416
Toluene	$C_7H_9^+$	3354
p-Cresol	$C_7H_9O^+$	6200
p-Xylene	$C_8H_{11}^+$	5009
D4 Siloxane	$C_8H_{25}O_4Si_4^+$	2251
1,3,5-Trimethylbenzene	$C_9H_{13}^+$	6924
Methanol	CH_5O^+	84

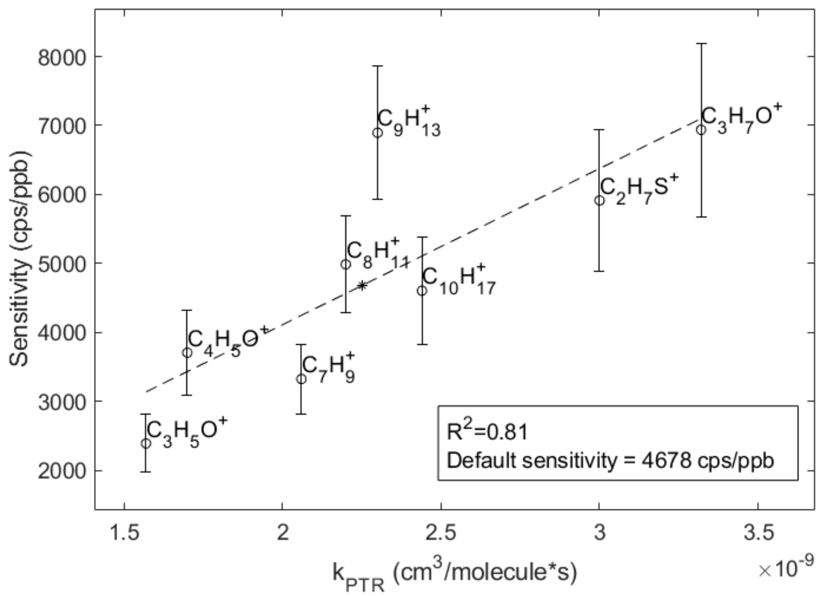

Figure S1: Average sensitivity versus proton transfer reaction rate constant (k_{PTR}). Sensitivities are presented in counts per second (cps) per ppb. The averages and standard deviations are shown. The default sensitivity, which is applied to non-calibrant VOCs, is denoted by the asterisk at a k_{PTR} of $2.25*10^{-9}$ cm^3/molecule*s. $C_{10}H_{17}^+$ represents the sum of the monoterpene parent ion ($C_{10}H_{17}^+$) and major fragment ($C_6H_9^+$).

Table S2: Parent ion fraction of nonanal, and the sesquiterpenes (SQT) caryophyllene and cedrene, for three voltage settings. *

					Parent ion fraction			
E/N (Td)	*Skimmer (V)*	*Skimmer Back (V)*	*BSQ Front (V)*	*BSQ Back (V)*	*Nonanal*	*Caryo-phyllene*	*Cedrene*	*SQT average*
125.7	-12.4	-24.8	-23.5	-23.5	0.03	0.19	0.13	0.16
121.7	-17.2	-23.5	-23.0	-23.1	n/a	0.51	0.32	0.41
125.7	-11.9	-22.9	-22.2	-22.7	n/a	0.24	0.16	0.20

* The first voltage setting was used in this study. These results emphasize how different voltage settings in the ion molecular reactor can change fragmentation despite similar E/N.

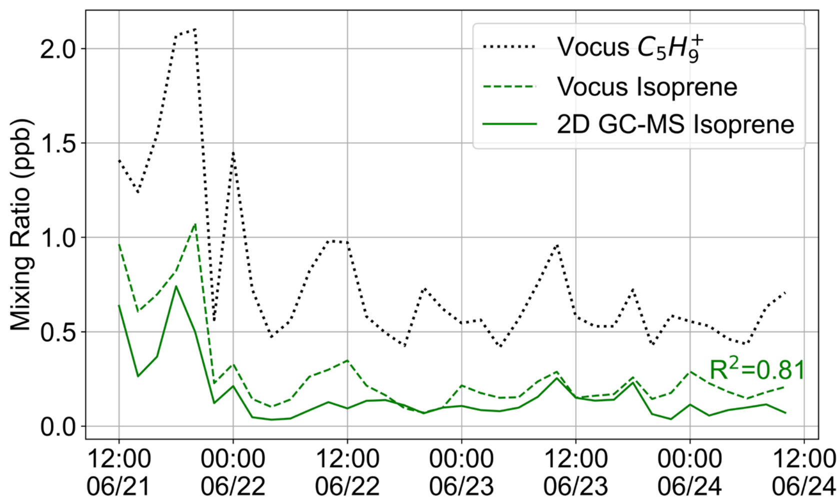

Figure S2: Comparison of corrected Vocus isoprene mixing ratio to isoprene measured by 2-dimensional gas chromatography mass spectrometry (2D GC-MS). Vocus $C_5H_9^+$ is the uncorrected signal including isoprene and interferences, and Vocus Isoprene is the corrected isoprene mixing ratio. Vocus isoprene and 2D GC-MS isoprene time series have an R^2 value of 0.81.

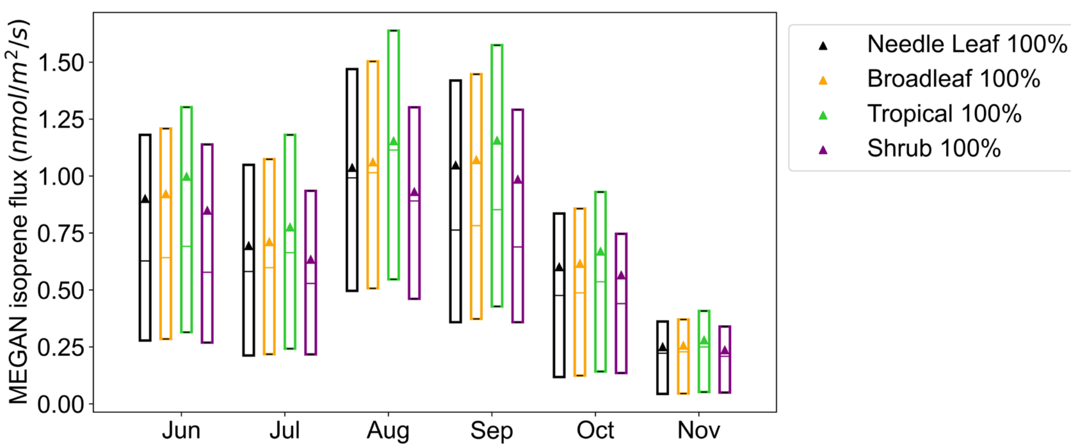

Figure S3: Modeled isoprene fluxes (MEGAN) using different plant functional types: needle leaf, temperate broadleaf, tropical, and shrub. The default emission factor of 10 nmol/m^2/s was used here.

Table S3: Updated isoprene emission factors for use in the single-point MEGAN model. The mean is presented with the 95% confidence interval (CI). The number of observations indicates the number of hour-average data points for each category. The entire study includes a few days of data from May and November in addition to the months listed.

Month	*Emission Factor Median (nmol/m²/s)*	*Emission Factor Mean (95% CI) (nmol/m²/s)*	*Number of Observations*
June	4.11	5.79 (4.19-7.39)	61
July	4.12	4.60 (4.02-5.19)	103
August	3.48	3.79 (3.38-4.21)	127
September	4.15	5.27 (4.13-6.42)	84
October	2.78	3.56 (2.67-4.46)	44
Entire Study	3.79	4.56 (4.18-4.95)	426

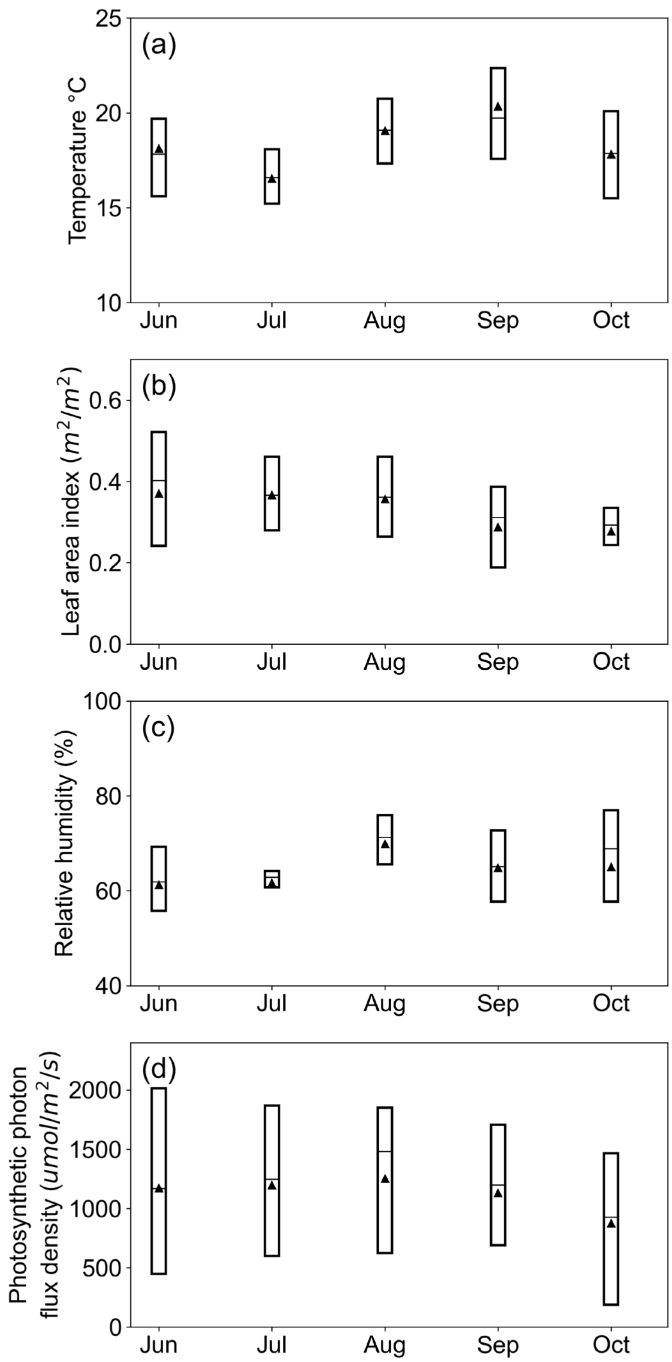

Figure S4: Summary of meteorological data for each full month of analysis: (a) temperature, (b) leaf area index, (c) relative humidity, and (d) photosynthetic photon flux density.

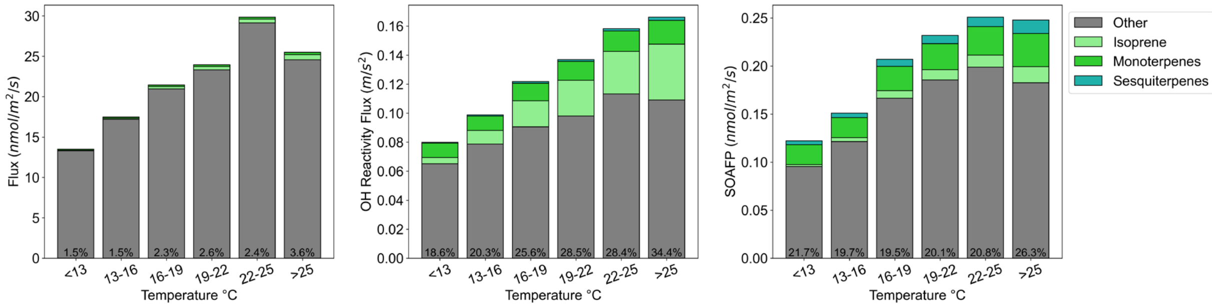

Figure S5: Measured flux, calculated OH reactivity flux, and calculated secondary organic aerosol formation potential (SOAFP) in discrete temperature bins.

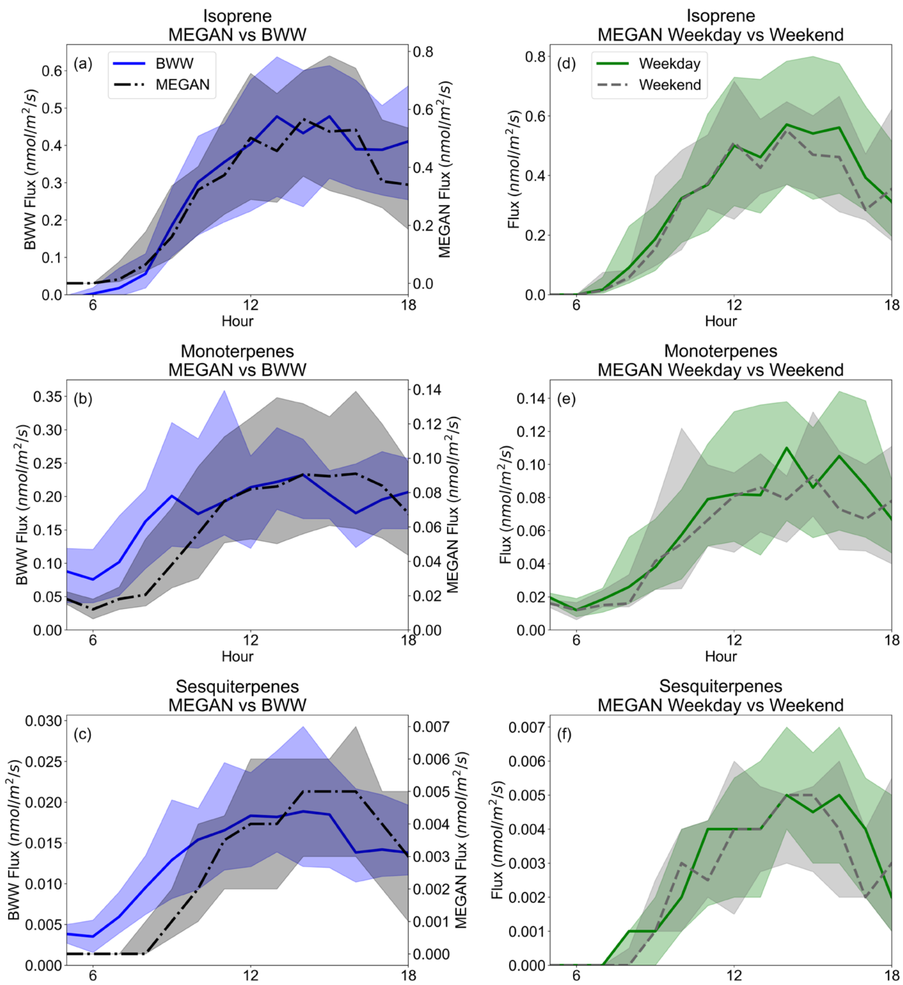

Figure S6: Measured (BWW) diurnal fluxes of (a) isoprene, (b) monoterpenes, and (c) sesquiterpenes with comparison to modeled (MEGAN) fluxes. (d), (e), and (f) compares MEGAN fluxes by weekdays and weekends. Lines represent the medians and the shaded area represents the interquartile range for each hour.

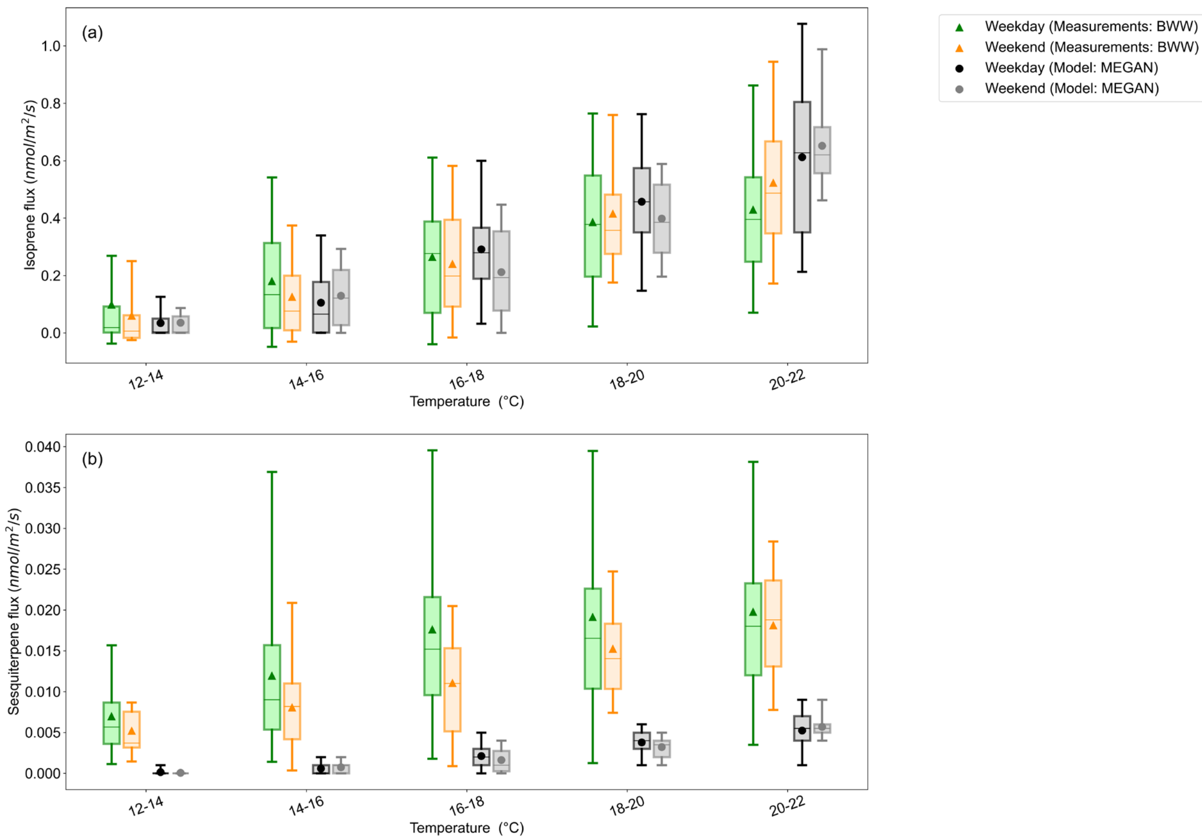

Figure S7: (a) Isoprene and (b) sesquiterpene fluxes binned by temperature. Data is split by weekday and weekend. Measurements (BWW) and modeled data (MEGAN) are shown.

Table S4: Details for each temperature (T) bin: median temperature, mean temperature, standard deviation (Std) of temperature, and median hour of the data included.

T Range (K)	Median T Weekday (K)	Median T Weekend (K)	Mean T Weekday (K)	Mean T Weekend (K)	Std T Weekday (K)	Std T Weekend (K)	Median Hour Weekday	Median Hour Weekend
(285 - 287)	286.2	286.0	286.1	286.0	0.6	0.6	6	6
(287 - 289)	288.0	288.1	288.0	288.1	0.6	0.5	8	11
(289 - 291)	289.9	289.7	289.9	289.8	0.6	0.6	12	12
(291 - 293)	291.9	291.9	292.0	291.9	0.6	0.5	13	14
(293 - 295)	293.8	293.7	293.9	293.8	0.6	0.6	15	14

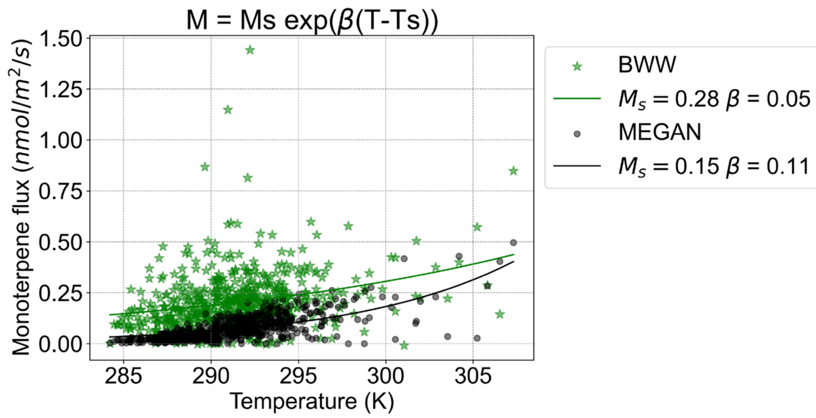

Figure S8: Measured (BWW) and modeled (MEGAN) monoterpene flux versus temperature with exponential trendlines.

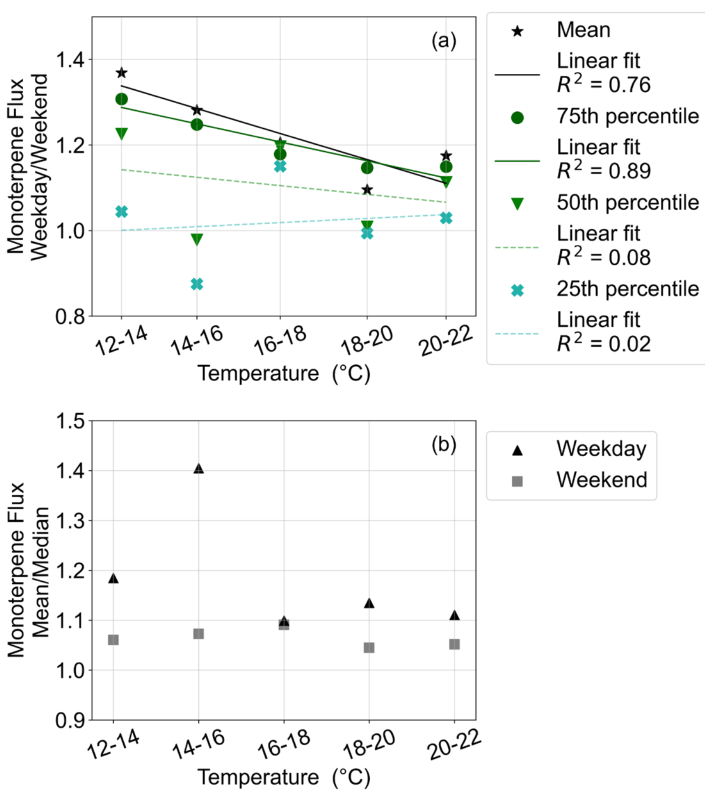

Figure S9: (a) Monoterpene weekday flux divided by weekend flux for the means, 75th percentiles, 50th percentiles, and 25th percentiles of each distribution for each temperature bin. Linear fits with R^2>0.7 are shown in solid lines, and linear fits with R^2<0.7 are shown in dashed lines. (b) Monoterpene mean/median flux ratio in each temperature bin separated by weekday and weekend. Mean/median greater than 1 indicates episodic emission sources. The data presented is measured flux data for all hours of the day (30-minute time resolution).

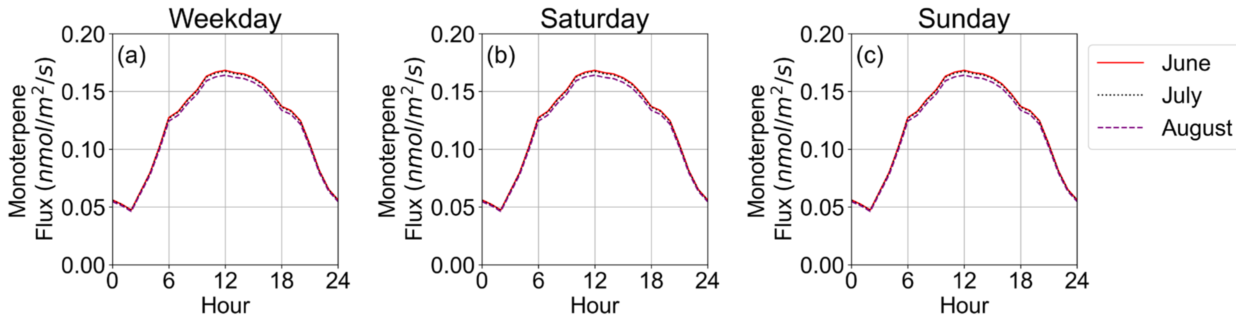

Figure S10: FIVE-VCP monoterpene emissions for each month available on (a) weekdays, (b) Saturdays, and (c) Sundays.

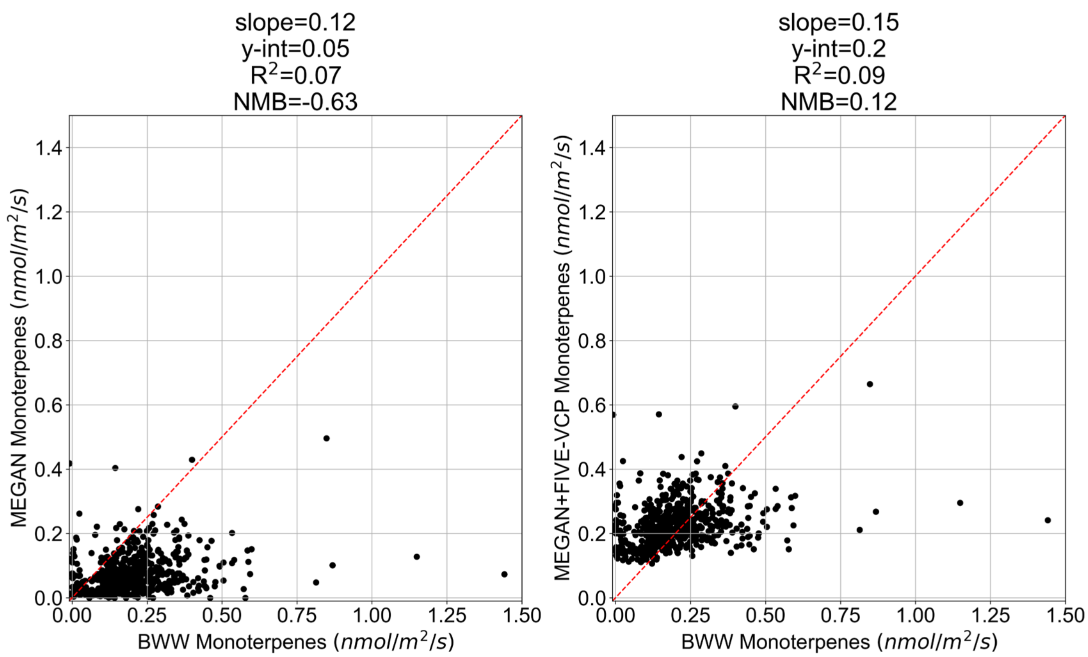

Figure S11: Scatter plots of modeled versus measured (BWW) monoterpene fluxes. Left: biogenic model (MEGAN). Right: biogenic model + anthropogenic emissions inventory (FIVE-VCP). Normalized mean bias (NMB) is the ratio of the average modeled flux to the average measured flux, minus one.

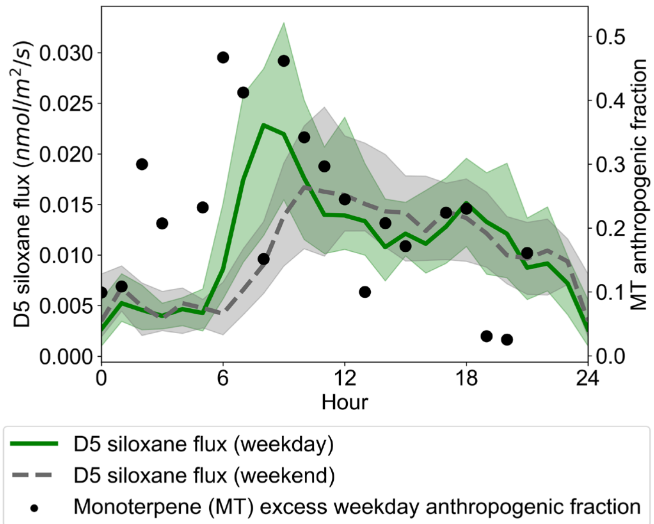

Figure S12: Left axis: diurnal trend of D5 siloxane flux for weekdays and weekends. The lines represent the median and the shaded regions represent the interquartile range. Right axis: monoterpene excess weekday anthropogenic fraction by hour of day.

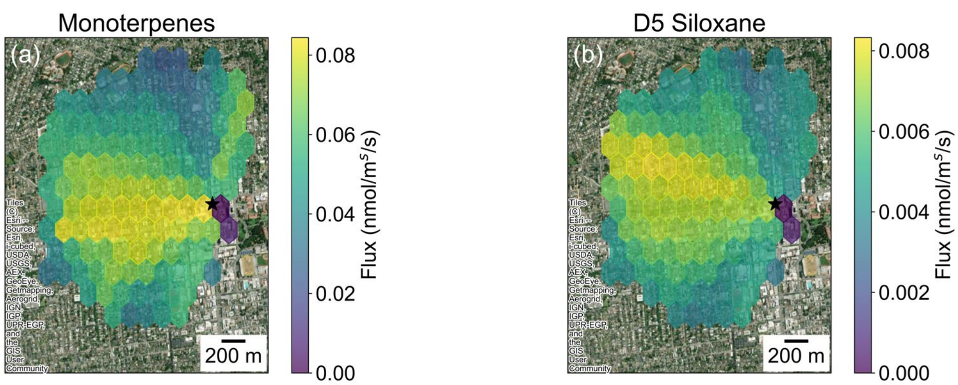

Figure S13: Average spatial distributions of fluxes for (a) monoterpenes and (b) D5 siloxane. The flux tower location is denoted by the black star.

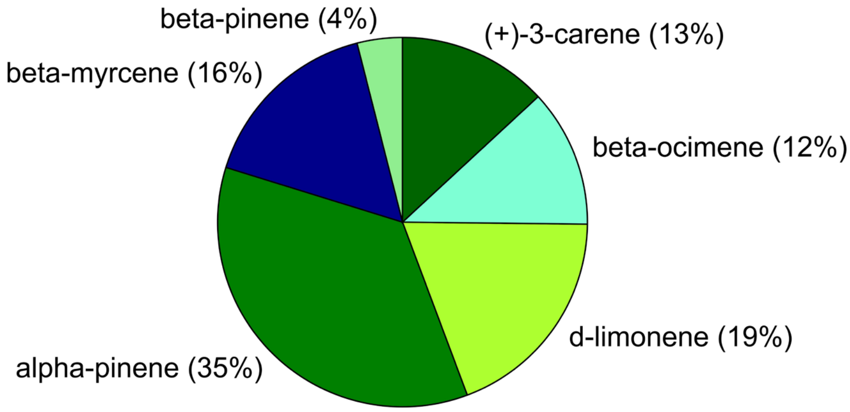

Figure S14: Monoterpene speciation measured by sorbent tubes with 2D GC-MS. The percentages represent the fraction of the average mixing ratio from three days of sorbent tubes. Percentages may not add up to 100 because of rounding.