

Supplementary information for “Airborne flux measurements of biogenic isoprene over California”

**P. K. Misztal^{1,2}, T. Karl^{2,3}, R. Weber¹, H. H. Jonsson⁴, A. B. Guenther^{2,5}, and A. H.
Goldstein¹**

[1]{University of California at Berkeley, Berkeley, California, USA}

[2]{National Center for Atmospheric Research, Boulder, Colorado, USA}

[3]{now at: Institute for Meteorology and Geophysics, University of Innsbruck, Innsbruck,
Austria}

[4]{Center for Interdisciplinary Remotely-Piloted Aircraft Studies, Monterey, CA, USA}

[5]{now at: Atmospheric Sciences and Global Change Division, Pacific Northwest National
Laboratory, Richland, WA, USA}

Correspondence to: P. K. Misztal (pkm@berkeley.edu)

Oak ecosystem



Figure S1. A typical oak savannah ecosystem seen from the twin-otter. Note spatial variability in oak densities. The photo is showing the Tonzi Ranch tower, where REA flux measurements took place (see Sect. 3.2.2).

Flight description

RF 1 – June 8

Research flight 1 occurred on the coolest (but still clear) day of the field study and passed to the WSW across the Central Valley, then above the most southern segment of the oak band of the Sierra Nevada foothills and further towards the shrublands of the Mojave Desert. The returning leg diagonally cut through some of the more polluted regions of the Central Valley, passing over oil fields, dairies and other anthropogenic VOC sources. It may be relevant that the preceding period prior to June 8 was particularly cold so the biogenic emission capacity was expected to be increasing on this flight and the flight the next day. The VOCs measured included some anthropogenic VOC mass-to-charge ratios (m/z) not measured in other flights, comprised of isoprene (m/z 69), methanol (m/z 33), benzene (m/z 79), toluene (m/z 93) and C-8 aromatics (C2-benzenes, benzaldehyde) (m/z 107).

RF 2 – June 9

Research flight 2 occurred during cool-weather and measured fluxes to the north east passing near the Walnut Grove tower (WGC), Tonzi Ranch Tower (TRT) and the Blodgett Forest site (BF). This flight continued up to 40 °N latitude of the northern Sierra Nevada foothill oak band and returned on the same path providing data near the WGC, TRT and BF sites located approximately half way and seen by the aircraft twice over a 2 hour period. The region covered by this RF overlapped about 50% with RF 3 and 4. The compounds measured included: isoprene (m/z 69), methyl vinyl ketone and methacrolein (MVK + MACR) (m/z 71), methanol (m/z 33), monoterpenes (m/z 81, 137), and methyl butenol (MBO) (m/z 87).

RF 3 – June 10

Half of research flight 3 was spent doing the first stacked “racetrack” profile flight, and the rest was devoted to segments overlapping spatially with the ground-based towers (WGC and TRT) and with RF 2 and 4. The racetrack legs were relatively long in order to oversample and then determine the optimal track lengths for wavelet flux determination with this particular aircraft.

1 Targeted compounds were isoprene (m/z 69), MVK+MACR (m/z 71), hydroxyacetone (m/z 75),
2 and methanol (m/z 33).

3 RF 4 – June 14

4 Research flight 4 was a survey that shared the same initial route to the San Joaquin Delta as the
5 two previous flights and after reaching the Sierra foothills it continued South right over the oak
6 woodlands until intersection with the route used in RF1. This provided extensive coverage of a
7 portion of the oaks on the eastern edge of the Central Valley. The return flight followed the same
8 path until reaching Bakersfield to the left and then proceeded straight across the Central Valley
9 above some of the many dairies in the region. Isoprene (m/z 69), MVK+MACR (m/z 71),
10 methanol (m/z 33), monoterpenes (m/z 81, 137), and MBO (m/z 87) were the measured
11 compounds.

12 RF 5 – June 15

13 Research flight 5 went to the North through the San Francisco Bay Area and near Santa Rosa to
14 measure emissions from oak woodlands in the coastal regions. After reaching the most northern
15 point the plane flew towards the San Joaquin Delta region near rice paddies. A biomass burning
16 episode from one rice field was explored with the aircraft to observe methanol, acetaldehyde, and
17 possibly furan (see supplementary video). Measured compounds were isoprene (m/z 69),
18 MVK+MACR (m/z 71), methanol (m/z 33), monoterpenes (m/z 81, 137), and acetaldehyde (m/z
19 45).

20 RF 6 – June 16

21 Research flight 6 was focused on flying a stack of racetracks over relatively homogeneous oak
22 terrain in the Sierra foothills near Madera. The racetrack consisted of 5 sequential segment
23 lengths of 15 km at evenly distributed altitudes within the PBL. The racetrack started at the top
24 level directly following a saw-tooth sounding. The plane performed one lap at each height on the
25 decent and again on the ascent. When the top level was reached another saw-tooth sounding was
26 performed and the whole racetrack sequence was repeated. Since this paper is focused on the
27 results from survey transects, the reader is referred for details of vertical profile racetrack results

1 to Karl et al. (2013). Just three masses were measured: isoprene (m/z 69), MVK+MACR (m/z
2 71), and MBO (m/z 87).

3 RF 7 – June 20

4 Research flight 7 was also focused on racetrack profiles and was situated in a similar location to
5 the racetrack in RF 6, but was rotated for the predicted wind direction to be perpendicular to the
6 straight side of the track. One main difference was that this racetrack saw higher temperatures
7 than RF6 four days earlier which was reflected in observed higher concentrations. However, the
8 flux divergence terms obtained from both racetracks 6 and 7 were very similar. The measured
9 masses corresponded to the following targeted compounds: isoprene (m/z 69), MVK+MACR
10 (m/z 71), and hydroxyacetone (m/z 75).

11 RF 8 – June 21

12 Research flight 8 was a survey towards the south of Monterey covering the coastal oak
13 savannahs during the hottest day of all RFs. While in previous flights concentrations of a few
14 ppb of isoprene were observed, the instantaneous maximal concentrations in this RF reached 8
15 ppb. The following compounds were targeted on this flight: isoprene (m/z 69), MVK+MACR
16 (m/z 71), methanol (m/z 33), monoterpenes (m/z 137), and MBO (m/z 87).

1 **Sensitivities and settings**

2 Table S1. PTR-MS sensitivities and settings during CABERNET

	6/8/2011	6/9/2011	6/10/2011	6/14/2011	6/15/2011	6/16/2011	6/20/2011	6/21/2011
	RF1	RF2	RF3	RF4	RF5	RF6	RF7	RF8
Normalized sensitivities (ncps ppbv⁻¹)								
M79	19.816	22.124	19.622	21.913	20.788	18.842	24.852	23.559
M93	18.000	20.097	17.824	19.905	18.883	17.115	22.575	21.401
M105	14.108	13.588	10.719	14.059	13.779	11.146	17.496	15.551
M107	10.155	14.142	11.899	13.096	12.917	11.023	15.783	14.964
M113	10.570	15.216	12.546	13.665	13.224	11.669	16.476	15.435
M121			8.4953	11.468	12.061	9.5474	15.166	14.011
M147	2.4690	3.0201	2.5351	4.4609	4.5862	2.8743	7.4852	6.5489
M181	0.0533	0.1434	0.0836	0.0944	0.1333	0.0783	0.1722	0.1793
M41	1.5316	2.1000	1.5369	2.3115	2.4218	1.9551	2.4882	2.4709
M69	12.303	14.838	12.040	14.309	15.182	12.922	15.322	16.566
M81*	7.0856	7.5255	7.0029	7.8044	8.4026	7.4407	8.6862	9.1489
M137*	7.2781	7.0122	7.2037	6.9632	7.2211	6.9476	7.5266	8.0743
Isoprene	13.835	10.800	13.577	16.6202	17.603	14.877	17.810	19.037
MVK+MACR*	22.014	24.578	21.798	24.343	23.093	20.932	27.609	26.172
Monoterpenes*	14.364	14.538	14.207	14.768	15.624	14.388	16.213	17.223
M33*	15.916	15.916	15.916	15.916	15.916	15.916	15.916	15.916
M45*	25.017	25.017	25.017	25.017	25.017	25.017	25.017	25.017
M87 (MBO)*	3.6625	4.4172	3.5844	4.2596	4.5195	3.8467	4.5613	4.9316
Settings								
p _d (mb)	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
U _d	560	540	560	560	560	560	560	560
T (°C)	50	50	50	50	50	50	50	50
H ₂ O flow (sccm)	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4
M21 (cps)	19,123,000	24,000,000	20,900,000	20,000,000	18,000,000	19,200,000	19,100,000	19,100,000
SEM (V)	2335	2404	2435	2496	2510	2518	2626	2626

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*derived from daily sensitivity curves and post-campaign calibrations

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Ground measurements

Walnut Grove Tower

A PTR-MS was measuring vertical profiles of VOC concentrations at WGC as part of a separate study and we flew by the tower on RF 2 and RF 4 to take advantage of the opportunity to intercompare measurements. The vertical profile data from WGC also provides a broader perspective on the diurnal cycle and vertical distribution of BVOCs over California's Central Valley than can be obtained from the aircraft data which focused almost exclusively on midday and a specific altitude.

Briefly, the setup at WGC featured a PTR-MS analyzing air from 5 different heights (10, 131, 262, 394 and 525 m) for 2 min at each level per 10 min measurement cycle. There were 24 m/z monitored at 0.1 s dwell time each. The concentration measurement footprint of the Tower increases with height and the top levels can pick up VOCs from the Central Valley's extensive agricultural, industrial, wetland, dairy, biomass burning and other activities from as far as the San Francisco Bay area hundreds of km away. The immediate vicinity of several km is mostly farmlands and wetlands with patchy biogenic sources constituted by mixed deciduous trees and broadleaf trees such as California Laurel (*Umbellularia californica*) therefore being only a small relative portion of the footprint at lower levels. The Twin Otter flew close to the tower on RF2 and more closely on RF4 (13:18) at 513 m (during an initial climb before the saw-tooth sounding) coinciding with the sampling of the tower at the top level (525 m) for which the intercomparison is shown in Sect. 3.1.5 and Supplementary Fig. S2a.

Tonzi Ranch Tower

Tonzi Ranch tower is part of the long-term flux measurement network known as FLUXNET (Baldocchi and Ma, 2013; Baldocchi et al., 2006). During CABERNET, BVOC fluxes were measured for the first time at this site using a compact relaxed eddy accumulation (REA) system custom built by NCAR and deployed at 23 m height to measure half-hourly flux data. The aircraft flew near the tower during RF2 and RF3. The closest flights which were compared passed right above the tower on June 9 at 11:41:15 at 280 m a.g.l., and on the returning leg on the same day at 13:33:19 at 410 m a.g.l.

1 *Relaxed Eddy Accumulation (REA) measurements*

2 The REA technique segregates air into different storage containers based on the direction
3 of the instantaneous vertical wind velocities thus replacing the need for fast concentration
4 measurement required for the eddy covariance technique. The REA used for this study consisted
5 of a datalogger (Campbell Scientific, CR1000), a 3-D sonic anemometer (RM Young, Model
6 81000V) and a sampling segregator. The datalogger received the wind velocity data from the
7 anemometer at a sampling rate of 10 Hz and then controlled the valves within the sampling
8 segregator, selecting the proper cartridge based on the direction of the instantaneous vertical
9 wind velocity at the time of sample capture. Air samples were accumulated over a 30 minute
10 period onto two solid adsorbent cartridges – one for upward moving air and one for downward
11 moving air. After the end of the sampling period, the cartridges were shipped to the NCAR
12 Boulder CO laboratory and analyzed using GC-MS to identify and GC-FID to quantify isoprene.
13 The area-averaged flux was calculated according to Businger and Oncley (1990) as the
14 concentration difference between the “up” and “down” reservoirs as:

$$15 \quad F_i = \sigma_w b (C_{up} - C_{down}) \quad (1)$$

16
17 where σ_w is the standard deviation of the vertical wind velocity, b is an empirical coefficient
18 (described below) and C_{up} and C_{down} are the concentrations of isoprene in the up and down
19 reservoirs, respectively. The b -coefficient was determined from the heat flux (the covariance of
20 w and T or $w'T'$) and by conditionally sampling the sonic-derived temperature to obtain average
21 temperatures in the up and down reservoirs, T_{up} and T_{down} , then re-arranging equation (1):

$$22 \quad b = \frac{w'T'}{\sigma_w (T_{up} - T_{down})} \quad (2)$$

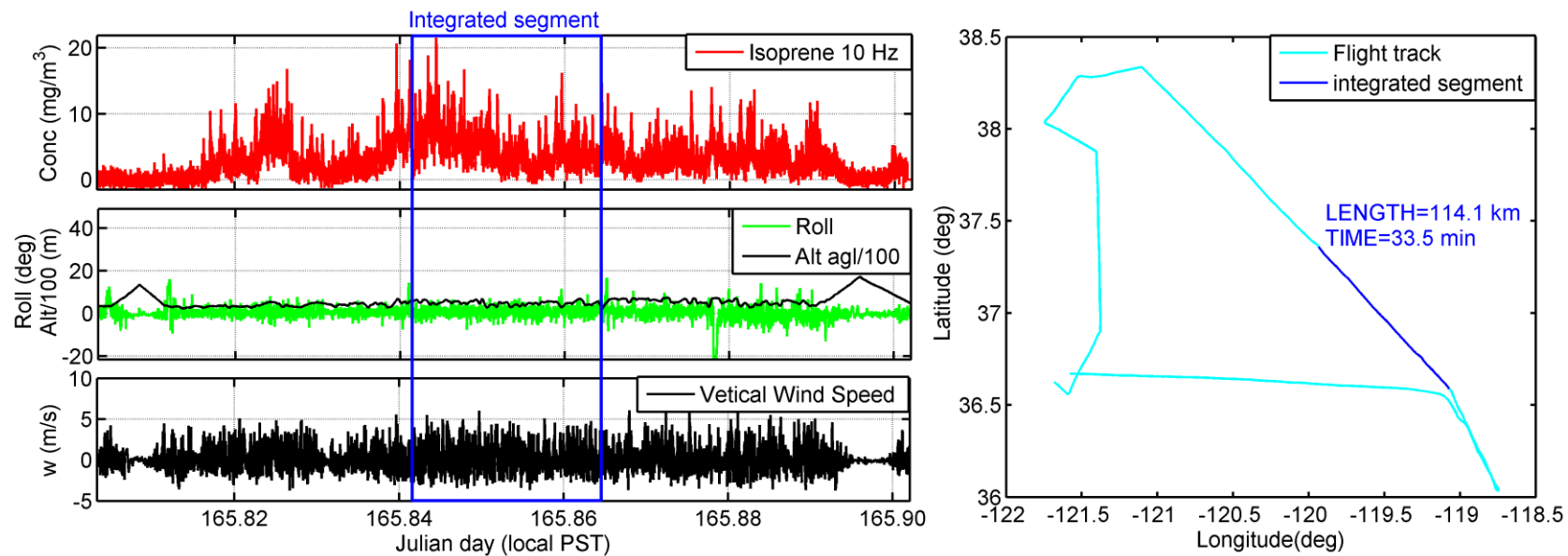
23
24 A threshold (or sampling deadband) of $0.5 \sigma_w$ was used to enhance the concentration difference
25 between the up and down reservoirs.

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Flux segment selection

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Figure S2. Example of segment selection for flux calculation based on roll to exclude turns and altitude to exclude large changes in altitude such as sawtooth soundings.

Inter-comparison with Walnut Grove tower

The ground-airborne comparison was focused on methanol, isoprene, and MVK+MAC. Overall, the comparison for methanol suggested agreement within 30%. However, looking at simultaneous fine resolution data from the two PTR-MS instruments (Supplementary Fig. S3a), a dip in methanol concentration was seen consistently by both the aircraft and the tower when the plane was closest to the tower's top level, with excellent measurement agreement (11.6 ± 1.16 ppbv seen by the tower at 525 m vs 11.9 ± 1.19 ppbv measured by the aircraft at 513 m). The variability of the methanol concentration over a five minute segment adjacent to the tower was within several ppbv, giving insight into spatial variability of methanol at that time and altitude. The measurement during the aircraft pass at 13:18 showed very little isoprene (below 50 ppt) in excellent agreement with simultaneous observations at the top level (525 m) of the tower, even though concentrations around 1 ppb were observed at the 10 m level. The agreement for MVK+MAC (0.18 ± 0.02 ppbv aircraft vs 0.20 ± 0.02 ppbv 525 m tower) was also good.

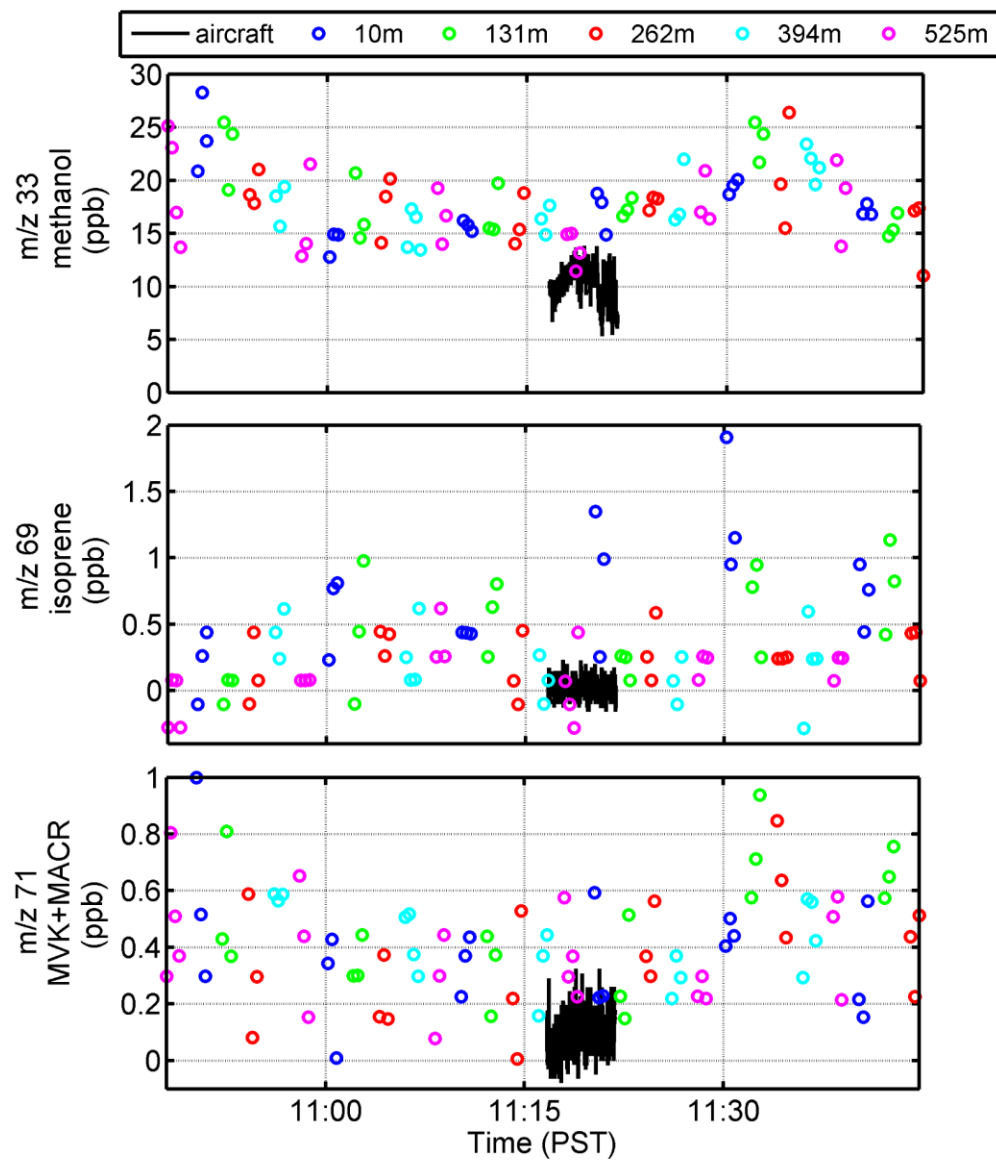
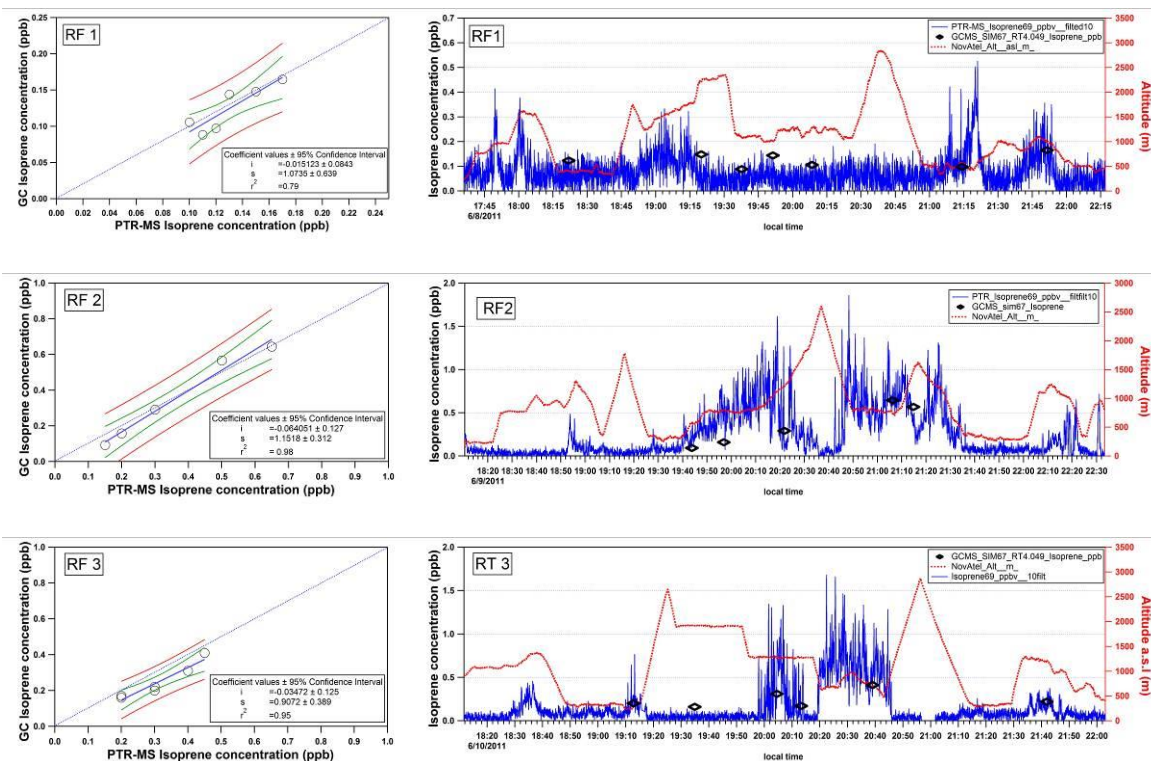


Figure S3. Intercomparison of concentrations at Walnut Grove tower coinciding with top level of the tower.

Inter-comparison of concentrations from PTR-MS and GC-MS

Measured concentrations of isoprene by GC-MS from cartridge samples collected at constant flow rate for 8 minutes during the flights generally agreed well with PTR-MS measurements averaged for the same periods, but there were occasional outliers most probably caused by cartridge sampling or analysis issues. The comparisons for each flight are presented in Supplementary Fig. S4. Linear fits (excluding tubes which were found leaking or not sampled) ranged from R^2 0.79 for RF 1 (which was the flight with coldest weather and consequently lowest isoprene concentrations) to 0.98 for RF4, and was typically around R^2 0.9. The slope of the comparison ranged from 0.9 to 1.15 so within the combined measurement uncertainties (10+10%). The analysis of the cartridges helped also in the exclusion of potential interferences at measured m/z .



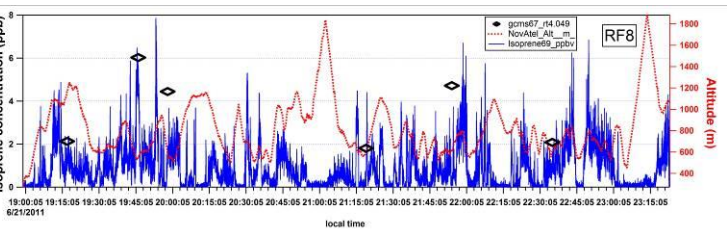
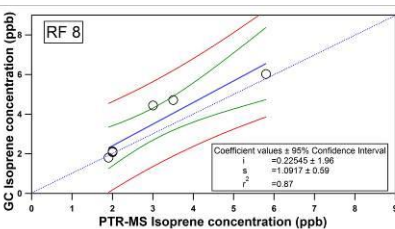
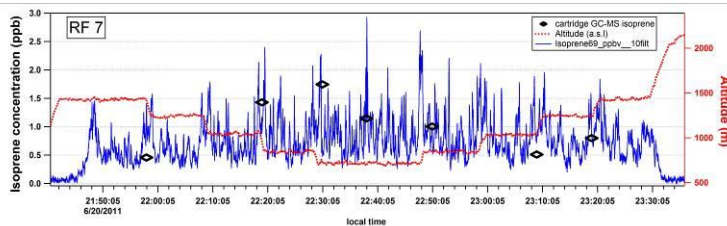
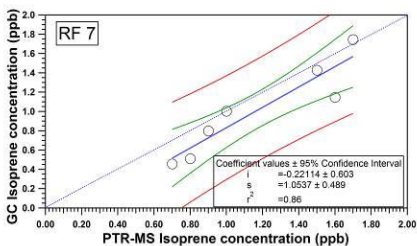
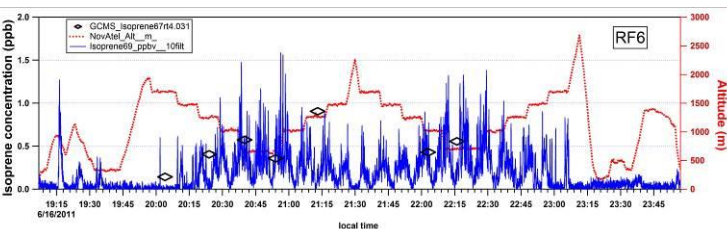
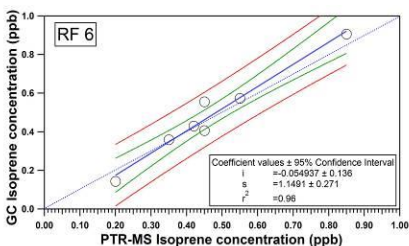
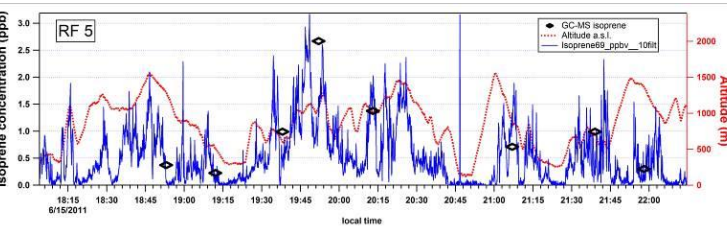
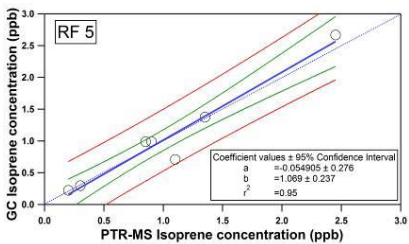
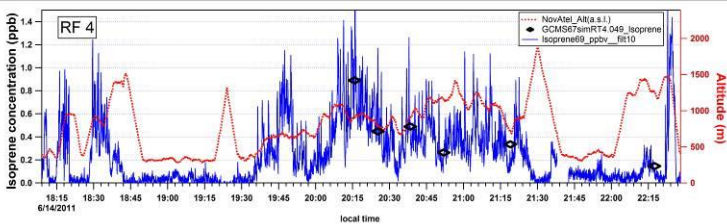
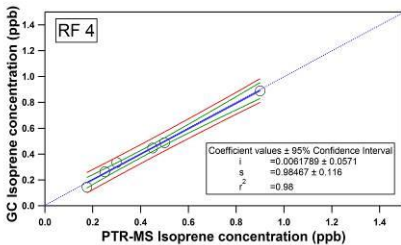


Figure S4. Comparison of isoprene concentrations between PTR-MS and GC cartridges.

Half-dome footprint representations

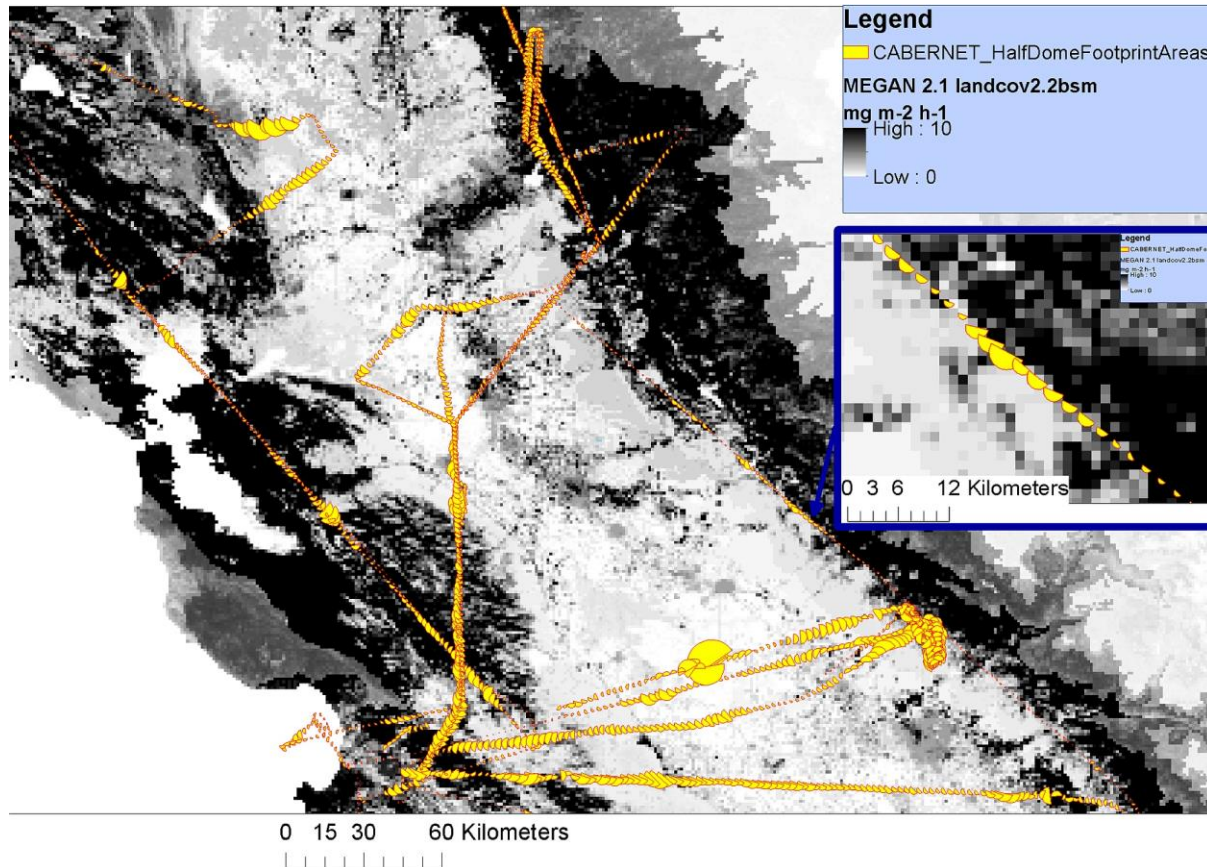


Figure S5. Half-dome footprint-approach representations shown over isoprene emission factors (MEGAN 2.1).

References

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