SUPPLEMENTARY INFORMATION

Ethene, propene, butene and isoprene emissions from a ponderosa pine forest measured by Relaxed Eddy Accumulation

1. REA measurement quality control

To test the integrity of air samples collected by REA, several experiments were performed involving variations of sample storage followed by analysis by GC. First, an isoprene standard was measured from the REA bags and from the standard bypassing the REA system; the bag air had a relative error of 2% compared to the standard bypass. Second, carry-over experiments from one bag to the next were performed. Both sets of bags (2 flux periods) were filled with the isoprene standard, followed by GC measurement, sample evacuation and then filling with either (1) zero air (hydrocarbon-free air) or (2) a 50% diluted isoprene standard. For the zero air experiment, a relative isoprene carry-over of 1.4% was detected. For the second experiment, the isoprene measured in the dilution was within 2% of expected.

The transport of air from the sampling inlet to the segregator valves involves a lag time, which needed to be accounted for during conditional sampling. Lag times were experimentally determined in the laboratory using an automated 3-way solenoid pulse valve (MP12-62, Bio-Chem Fluidics Inc., Boonton, NJ, USA) switching between laboratory and CO_2-free air and a closed path infrared gas analyzer (Li-6262, LI-COR Biosciences, Lincoln, NE, USA), which was placed downstream of the sampling line. The sampling line lag equals the time between a switch in the valve and an increase/decrease in the CO_2 signal. The IRGA response time was measured independently and subtracted from the sampling line lag, to yield a lag of 1.2 seconds at a flow of 315 cc min^{-1} with an inlet line length of 75 cm. The segregator pumping speed (flow rate) was monitored downstream of the neutral line to verify that the flow rate did not change over time; small weekly adjustments of the segregator needle valve were made, as necessary.

For post processing, each hourly REA flux underwent the following quality control (QC): fluxes were flagged if (1) more than 5% of the ultrasonic high frequency data were impaired (e.g., due to rain), (2) less than 1.5 L of air was collected in either bag, (3) the Businger-Oncley parameter (b) was ± 2.5 standard deviations of median b, (4) there was a small gradient in the proxy scalar ($(\overline{T^+} - \overline{T^-}) < 0.1$ ºC), leading to a questionable b-value, and/or (5) asynchrony in up- and down-bag sample volume (>15%). Additionally (6) integral turbulence statistics and (7) stationarity tests as well as (8) footprint analysis (see section 3.7) were used to flag suspicious REA data. In total, 13% of REA data failed QC (flagged in at least 4/7 tests of QC 1-7), and a further 18% were marked as "medium quality". Including a footprint test (8), 47% of REA data were flagged. QC was most sensitive for fluxes close to zero and for apparent uptake (negative fluxes) **(Fig. S1)**. Most of the faulted and flagged fluxes originated from nighttime measurements within a stable boundary layer.
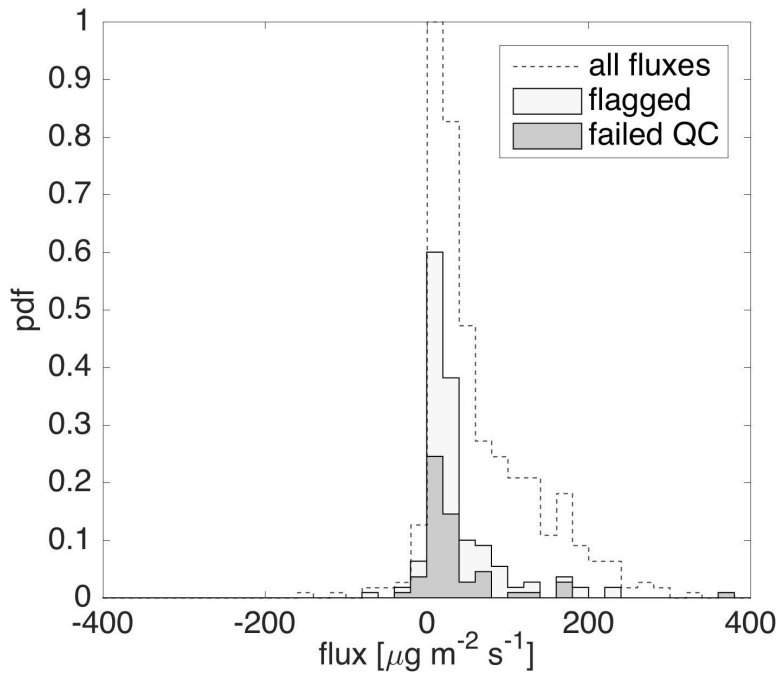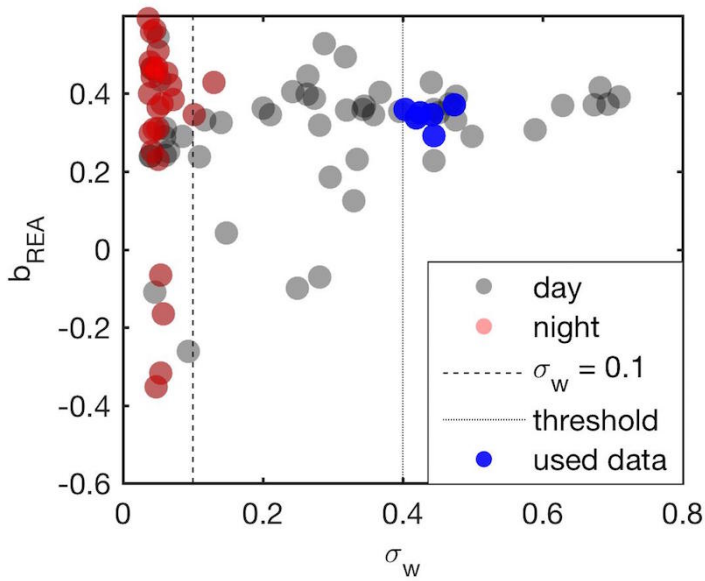
Fig S1. Probability density function of ethene fluxes failing QC (dark grey), failing QC or flagged (light gray) and all fluxes (hollow).

5

Figure S2. Businger-Oncley parameter (*b*) versus turbulence parameter, calculated for September 1-2, 2014, including the time period of the measured understory fluxes (blue). Nighttime hourly averages (red) mostly fall below the mixing criteria thresholds. 6 of 8 understory flux measurements exceeded the 0.4 threshold which was determined for this site, while the two that did not were early morning fluxes that were near zero.

2. GC-FID analyses

GC analyses began on the hour (e.g., 2:00, 3:00, etc), following each hour-long sampling period. Air was drawn sequentially from the "up" and "down" sample reservoirs in 20-minute sample preparation periods each, with the order of analysis alternating each hour ("up" bag then "down" bag, or "down" bag then "up" bag). First, a vacuum was pulled on the tower sample Teflon line for 2 minutes; then the chosen bag valve was opened, and ~750 cm^3 of sample gas was used to flush the sample line, including 300 cm^3 to flush the GC-FID inlet system.

A 300 cm^3 air sample was then drawn at 60 ml min^{-1} for 5 minutes through a series of traps: a cold zone at -50 °C to remove water, an Ascarite II trap (replaced daily) at room temperature to remove CO_2 and residual ozone, and then a sample cold trap (section of aluminum oxide coated fused silica capillary tubing) at -150°C (Goldan et al., 2000). Both water and sample traps traversed through the top part of a copper block, which was resting atop a dewar, with a vertical cold finger extending from the base of the cold block where it entered the dewar and was immersed in liquid nitrogen. The liquid nitrogen level was maintained with an autofill system.

Air flow was regulated with a small pump (KNF Neuberger Inc., Trenton, NJ) on the front end of the inlet system and a mass flow controller (SEC4400, Horiba Stec Inc., Santa Clara, USA) at the back end, after which the remainder sample gas was vented to the atmosphere. After 300 cm^3 STP sample volume was collected, the sample trap was flash-heated by resistive heating of wiring (California Fine Wire, Grover Beach, CA) surrounding the trap, and held at 100 °C while the sample was transferred onto the GC column. During sample transfer, the water trap was heated to 50 °C and the water trap and CO_2 trap were back-flushed with clean zero air to prepare for the next sampling cycle. Temperatures were regulated with Watlow (St. Louis, MO) temperature controllers.

Gas chromatographic separation **(Fig. S3)** occurred on two 25 m sections of a 0.53 mm ID KCl passivated Al_2O_3 capillary column (Chrompack) separated by a 6-port Valco valve, used for backflushing purposes. Hydrogen was used as the carrier gas flowing at 8 cm^3 min^{-1}. The oven temperature was held at 85°C for 100 seconds, with ramping at 0.24 °C sec^{-1} for 500 seconds to reach and hold at 205 °C. At that point, the valve was switched to backflush the first column while the sample continued its elution on the second column and into the FID.

The FID fuel gas (16 sccm H_2) and oxidant gas (200 sccm zero air) combined with the carrier gas flow (8 sccm H_2). The FID was enclosed in a box held at sub-ambient pressure (500 mb) using a small vacuum pump in-line with a pressure controller (Bronkhorst USA Inc., Bethlehem, PA), eliminating the need for a makeup gas (Bernier and Yost, 1993).
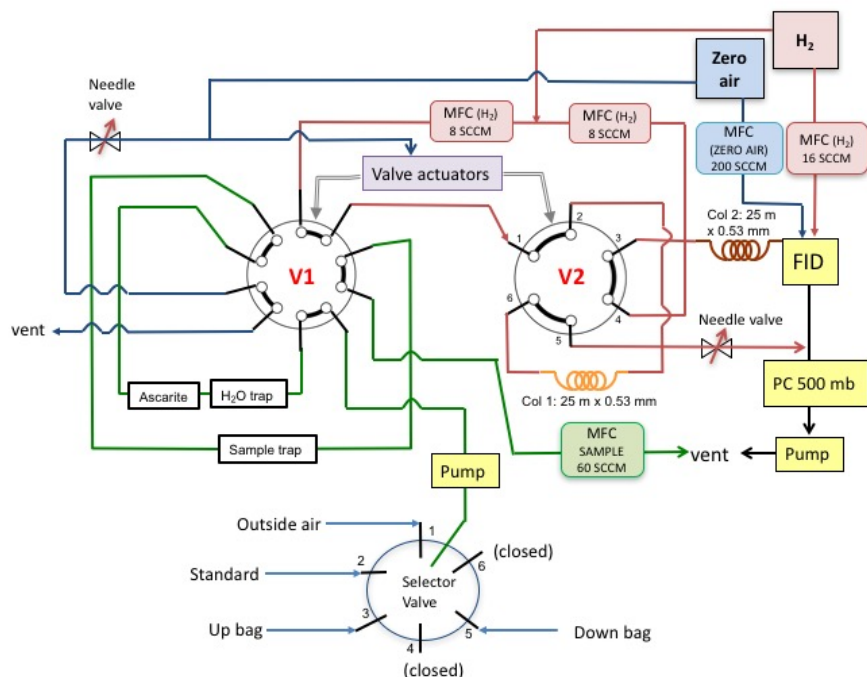
3

Figure S3. GC-FID inlet system, with mass flow controllers (MFC); flame ionization detector (FID); pressure controller (PC); and air actuated valves 1 (V1) and 2 (V2). Configuration shows valve 1 in 'load' mode and valve 2 in 'backflush' mode.

3. Calibration standards

Fifteen C_2-C_6 hydrocarbons were quantified in the 12 minute sample chromatogram recorded from 80 to 720 seconds into the run (**Table S1**): ethane, ethene, propane, propene, acetylene, i-butane, n-butane, trans-2-butene, 1-butene, cis-2-butene, i-pentane, n-pentane, n-hexane, isoprene, and benzene. The synthetic standard mixture (AAL073352) used to identify peaks was developed at the National Oceanographic and Atmospheric Administration, Chemical Sciences Division (NOAA CSD) laboratory using a 56-component hydrocarbon mixture (PAMS standard, Scott Specialty Gases, Plumsteadville, PA) diluted in UHP nitrogen in a passivated aluminum cylinder at ~1.1 ppb each, based on an intercomparison with primary gravimetric standards.

Following each pair of up/down REA samples, either a blank sample or hydrocarbon gas standard was analyzed using the same analytical procedures described above. Two hydrocarbon gas standards were utilized during routine operations: a low (23-549 ppt) and a high (~1.1 ppb) concentration standard. The low concentration hydrocarbon standard was a dilution of a 16-component hydrocarbon mixture created at the National Center for Atmospheric Research (NCAR) and calibrated against NIST standards, and this was used daily to determine instrument sensitivities in the field; twelve components were present in the chromatography (**Table S1**). The high concentration

standard (CAL018200b) was similar to AAL073352; it was developed at NOAA CSD as a dilution of a hydrocarbon mixture that included the butenes (trans-2-butene, 1-butene and cis-2-butene), although apparent partial degradation of these compounds meant that this standard was used for peak identification rather than for quantification (**Table S1**). For the first 5 days of the field campaign (June 25 to 29), the low concentration standard

5   was analyzed ~6 times per day. On July 17th, a 6-port stainless steel selector valve (EUTB-3SD6MWE, VICI, Houston TX) was installed to facilitate sampling automation; gas standards were then analyzed every third sample, following every up/down bag sequence (July 17 to August 9). The low standard was utilized to calculate the daily averaged FID response for each compound, and this was then applied to each standard run to determine the instrument precision and minimum flux detection limit for each day of the campaign (**Table S1**). The high standard identified the three

10   butene isomer peaks, but for concentration determination in air samples, the butene isomers utilized the FID response factor for ethylene in the low standard, scaled to carbon content (Goldstein et al., 1995;Dietz, 1967). The resulting FID response factors for all of the alkenes were consistent with multiple prior field campaigns using this same gas chromatograph (A. Koss, *pers. comm.*).

      To test for potential interferences with isoprene caused by high concentrations of methyl-3-buten-2-ol

15   (MBO) expected at this site (0-3 ppb, (Kaser et al., 2013)), a high concentration MBO standard was analyzed on July 17th at 2 and 3 p.m. at 55 ppb and 27 ppb respectively. These results yielded 110 ppt and 63 ppt isoprene, or a potential isoprene interference of 0.2% from MBO. If we assume a 10% difference in concentration for MBO in the up and down bags, this would amount to roughly a maximum of 0.6 ppt of isoprene, well below the instrumental precision (**Table S1**).

20   The impact of ambient ozone on measurements was considered. Atmospheric daytime ozone concentrations at the site are typically 50-60 ppb. On the GC system, if any residual ozone made it past the stainless steel tubing sections and Ascarite trap and onto the cryogenic trap, it should not significantly affect the measurement of light hydrocarbons (Koppmann et al., 1995). Production or consumption of VOCs via reaction with ozone would more likely occur while stored in the Tedlar bags in the REA system. If this were happening to a large extent, then the 2nd

25   bag analyzed each hour would be affected the most because the residence time in the bag is 20 minutes longer before sampling on the GC. That would lead to a readily detected systematic VOC increase or decrease in the second bag analyzed. Since the order of the "up" and "down" samples were switched each hour, a seesaw pattern should be readily apparent. The only observed pattern like this occurred during the sunrise and sunset transitions when both fluxes and ozone concentrations were expected to be low; even under these conditions, negative fluxes were

30   generally not observed.

      Another possibility is that the "down" samples descending from the boundary layer could have a slightly higher ozone concentration than the "up" samples rising from the canopy, leading to greater reduction of alkenes in the down bags and hence a small overestimation of calculated emissions. However, the difference in ozone

concentrations between up and down bags is likely to be a small percentage of ambient ozone concentrations and hence not likely to influence the overall flux.

During the daytime, ozone photolysis might occur due to sunlight through the portion of Teflon transfer line from the tower that was not covered by foam insulation, which may create OH in the line. However, the relatively
5   high concentrations of MBO at the site (ppb level) should act as a built-in scavenger for OH and be its primary loss mechanism (Kim et al., 2010). The product of such a reaction, and for most oxidation reactions of other VOCs, should be oxygenated VOCs rather than ethene, propene or butenes.

Table S1. Hydrocarbon compounds measured by GC-FID, concentrations present in the low concentration standard, and instrumental
10   precision determined for the 2 sampling periods.

Compound	NCAR low concentration standard (ppt)	NOAA standard (CAL018200b) (ppt)	Precision (June 25-29, 2014)	Precision (July 17-August 9, 2014)	Average FID area/ppb response ratio
Ethane	549	1167	8.1%	10.8%	18.7
Ethylene	189	1156	3.3%	3.6%	27.1
Propane	23	1156	4.2%	3.4%	34.9
Propylene	59	1156	6.2%	7.2%	43.1
Acetylene	148	1167	10.2%	12.4%	18.3
i-butane	76	1156	8.1%	8.0%	42.3
n-butane	114	1156	5.5%	4.3%	48.6
t-2 butene	--	1156	--	--	--
1-butene	--	1112	--	--	--
c-2-butene	--	1200	--	--	--
i-pentane	200	1101	6.1%	4.7%	57.8
n-pentane	96	1134	5.9%	8.8%	57.7
n-hexane	47	1156	10.3%	6.3%	55.7
Isoprene	391	1069	7.8%	7.5%	51.1
Benzene	86	1123	6.1%	6.1%	69.2

4. REFERENCES

Bernier, U. R., and Yost, R. A.: Vacuum operation of the flame-ionization detector for gas chromatography, Journal of Chromatographic Science, 31, 358-362, 1993.

5 Dietz, W. A.: Response factors for gas chromatographic analyses, Journal of Gas Chromatography, 1, 68-71, 1967.

Goldan, P., Parrish, D., Kuster, W. C., Trainer, M., Mckeen, S., Holloway, J., Jobson, B. T., Sueper, D., and Fehsenfeld, F. C.: Airborne measurements of isoprene, CO, and anthropogenic hydrocarbons and their implications, J. Geophys. Res., 105, 9091-9105, 2000.

Goldstein, A. H., Daube, B. C., Munger, J. W., and Wofsy, S. C.: Automated in-situ monitoring of atmospheric non-

10 methane hydrocarbon concentrations and gradients, J. Atmos. Chem., 21, 43-59, 1995.

Kaser, L., Karl, T., Schnitzhofer, R., Graus, M., Herdlinger-Blatt, I. S., DiGangi, J. P., Sive, B., Turnipseed, A., Hornbrook, R. S., Zheng, W., Flocke, F. M., Guenther, A., Keutsch, F. N., Apel, E., and Hansel, A.: Comparison of different real time VOC measurement techniques in a ponderosa pine forest, Atmos. Chem. Phys., 13, 2893-2906, 10.5194/acp-13-2893-2013, 2013.

15 Kim, S., Karl, T., Guenther, A., Tyndall, G., Orlando, J., Harley, P., Rasmussen, R., and Apel, E.: Emissions and ambient distributions of Biogenic Volatile Organic Compounds (BVOC) in a ponderosa pine ecosystem: interpretation of PTR-MS mass spectra, Atmos. Chem. Phys., 10, 1759-1771, www.atmos-chem-phys.net/10/1759/2010/, 2010.

Koppmann, R., Johnen, F. J., Khedim, A., Rudolph, J., Wedel, A., and Wiards, B.: The influence of ozone on light nonmethane hydrocarbons during cryogenic preconcentration, J. Geophys. Res., 100, 11383-11391, 1995.

20