Volatile organic compound emissions from *Larrea tridentata* (creosotebush)

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Supplementary Material Content

1 Identification of VOCs by GC-PTR-MS and GC-MS

The PTR-MS uses a chemical ionization technique (proton transfer from H_3O^+) which leads to the "soft ionization" of VOCs. Although some fragmentation is possible, this leads to a large fraction of the molecules being detected at an m/z value of the molecular weight+1. Therefore,

identification of the compound of interest is straightforward if some prior knowledge of the chemical composition of the air sample is known (eg. from GC-MS). However, given the relatively low mass resolution of the quadrupole PTR-MS (1 m/z), signals at a given m/z are not necessarily unique to a given compound; compounds with similar molecular weights and parent ion fragmentation can lead to overlapping signals. In general, as long as calibrations are performed, this has not been considered a problem for many compounds observed from plants including volatile isoprenoids (m/z 69:isoprene, m/z 137:monoterpenes, m/z 205:sesquiterpenes) and several oxygenated VOCs (m/z 33:methanol, m/z 59:acetone, m/z 45:acetaldehyde, m/z 47:ethanol, m/z 61:acetic acid) (Karl et al., 2004; Harley et al., 2007; Jardine et al., 2008; Bouvier-Brown et al., 2009; Inomata et al., 2008; Rottenberger et al., 2008). However, in this study we observed branch emissions and ambient concentrations of a large number of other compounds not typically detected from vegetation. Previous work has characterized the volatile components of creosotebush resin (Mabry, 1979), however there is limited data regarding gas-phase emissions of these compounds. We successfully detected PTR-MS MW+1 signals from creosotebush branch enclosure and ambient air measurements for many of these compounds (see Table 1, main manuscript). However, in order to verify the identities of these and other compounds, branch enclosure air was also analyzed for VOCs using thermal desorption gas chromatography-proton transfer reaction-mass spectrometry (GC-PTR-MS) in the field and thermal desorption gas chromatography-mass spectrometry (GC-MS) at Biosphere 2 and at the National Center for Atmospheric Research (NCAR) laboratory in Boulder, Colorado.

GC-PTR-MS was used to qualitatively determine if the dominant PTR-MS signals measured during the CREATIVE field campaign are due to one or more compounds. The technical details of GC-PTR-MS have been described in detail elsewhere (Warneke et al., 2003). A Varian CP-3800 GC with sample preconcentration trap (Varian, Inc.) was used for this study. Air samples were drawn into a hydrocarbon trap (carbopack C, carbopack B, carboxen 1000, carboxen 1001) held at 30 ^{o}C to avoid excessive water collection. Branch enclosure samples were drawn into the trap at 40 sccm for 5 min using a mass flow controller and a pump downstream of the trap. The collected sample was then injected directly onto the analytical column (Restek Rtx-Volatiles, 30m, 0.25 mm ID, 1 micron film thickness) by rapidly heating the trap to 200 ^{o}C for 5 min with 1.5 sccm of UHP helium carrier gas. After sample injection, the GC oven was held at 40 ^{o}C for 5 minutes and then heated 10 ^{o}C min^{-1} to 200 ^{o}C. The end of the column was connected to a 1/16 in O.D. Silcosteel® tube which extended out of the GC oven. Gas exiting the tubing was mixed with UHP nitrogen through a tee which was connected to the PTR-MS inlet. Upstream of this tee was a second tee which was overblown by 100 sccm UHP nitrogen. This allowed all of the analytes eluting from the column to be swept into the nitrogen air stream and carried into the PTR-MS which requires ~50 sccm. In order to target a few specific compounds, a reduced ion set (m/z 33, 45, 59, 61, 63, 69, 75, 81, 83, 137) was scanned by the quadrupole mass analyzer with reduced dwell times of 100 ms each.

Two nearly identical thermal desorption GC-MS systems were used for VOC identification of branch enclosure samples. For the first system, a branch was detached, placed in distilled water, and transported from the field site to the Biosphere 2 laboratory near Oracle, Arizona. Identification of creosotebush VOC emissions was made with a Series 2 air server connected to a Unity 2 thermal desorption system (MARKES International) interfaced with a 5975C series Gas Chromatograph/electron impact ionization mass spectrometer with a triple-axis detector (GC-

MS, Agilent Technologies). The branch was enclosed in a 5.0 L Teflon enclosure with 2 slpm of UHP zero air flowing through. Enclosure air samples (1.5 L) were preconcentrated on an internal sorbent tube (water management cold trap, MARKES International) held at 30 ^{o}C (to avoid excess water collection) and dried by purging with dry carrier gas at 20 sscm for 20 min. During injection, the trap was heated to 300 ^{o}C for three minutes while backflushing with carrier gas at a flow of 6.5 sccm. In order to improve peak shape and further reduce the amount of water introduced into the GC-MS, 5 sccm of this flow was vented through the split vent while the remaining 1.5 sccm was directed to the column (Agilent DB624 60 m x 0.32 mm x 1.8 μm) temperature programmed with an initial hold of 2 min at 40 ^{o}C followed by an increase to 230 ^{o}C at 5 ^{o}C min^{-1}. The mass spectrometer (Agilent 5975C) was configured for scan mode (m/z 45-300) with a 4 min delay. Zero air and enclosure air samples were alternately analyzed. Identification of VOCs was made by comparison of mass spectra with the National Institute of Standards and Technologies (NIST) database and by comparison of retention times and mass spectra collected from injection of authentic commercial standard compounds if available to us. An assessment of the zero air results demonstrated that VOC blanks were negligible.

In the field, ambient air was pumped into an enclosure containing an intact branch at 5.0 slpm and VOC samples were collected on thermal desorption cartridges. Enclosure samples were collected by drawing 100 sccm of enclosure air through a cartridge for 30 minutes (3.0 L) by connecting a mass flow controller and a pump downstream of the cartridge. Two samples (without and with branch) were collected on thermal desorption cartridges that were purchased commercially filled with Carbopack C, Carbopack B, and Carbosieve SIII adsorbents (MARKES International, UK) and analyzed at Biosphere 2. After loading a sample cartridge in the Unity 2 thermal desorption system, cartridge samples were dried for 5 minutes with 30 sccm UHP helium before being transferred to the Unity 2 cold trap (held at 30 ^{o}C) by heating to 300 ^{o}C for 5 min with 50 sccm of UHP helium. Analysis of VOCs was then carried out using GC-MS operating under the identical conditions described above for online air samples.

Two field samples (without and with branch) were also collected on thermal desorption cartridges that were purchased commercially filled with Tenax GR and Carbograph 5TD adsorbents (MARKES International, UK) and analyzed at the NCAR laboratory in Boulder, Colorado. Adsorbed VOCs were measured using a Series 2 Ultra™ TD autosampler coupled to a Unity 1 thermal desorption system (MARKES International, Llantrisant, UK) interfaced with a 7890A series Gas Chromatograph/5975C Electron Impact Mass Spectrometer (GCMS) with a triple-axis detector (Agilent Technologies, Santa Clara, CA, USA). The GC was fitted with a DB5 column and was temperature programmed with an initial hold of 1 min at 35 ^{o}C and a subsequent temperature rampings of 6 °C/min to 80 °C, 3 °C/min to 155 °C, 10 °C/min to 190 °C, 25 °C/min to 260 °C with a final hold of 5.2 min. to a final temperature of 300 ^{o}C. The MS was simultaneously operated both in scan and SIM modes, with SIM ions selected to be representative of terpenoid compounds as well as two internal standards added to each sample. Identification of VOCs was made by comparison of mass spectra with the National Institute of Standards and Technologies (NIST) libraries.

2 Evaluation of the interference of dimethyl sulfide PTR-MS concentration measurements by the hydrated acetaldehyde ion

To investigate the possibility that some of the dominant PTR-MS signals may have arisen from protonated VOC-water clusters, we studied the effect of humidity and acetaldehyde concentrations on the PTR-MS signal at m/z 63 which could be due to an acetaldehyde-water cluster instead of dimethyl sulfide (DMS). Zero air humidified with a dew point generator (LI 610, Licor) was introduced into the PTR-MS while signals at m/z 45 and m/z 63 were measured. Each of the following air samples were measured for at least 30 minutes: (1) zero air saturated at 0 ^{o}C, (2) zero air saturated at 20 ^{o}C, (3) zero air saturated at 20 ^{o}C with 19 ppbv acetaldehyde, and (4) zero air saturated at 0 ^{o}C with 19 ppbv acetaldehyde.

When 19 ppbv acetaldehyde was introduced into zero air humidified to 20 ^{o}C (Fig. S7), a strong H^{+}-acetaldehyde signal was detected at m/z 45, but without an increase in the signal at m/z 63 (H^{+}-acetaldehyde-H_2O cluster). Given the high sensitivity of PTR-MS to m/z 63 when dimethyl sulfide in cyclohexane was used for calibration, we conclude that significant VOC-water cluster formation does not occur during ambient air and branch flux measurements. Given that we operated the PTR-MS in standard conditions with a high drift tube voltage of 600 V, we did not expect significant VOC-water cluster formation.

3 Supporting Figures

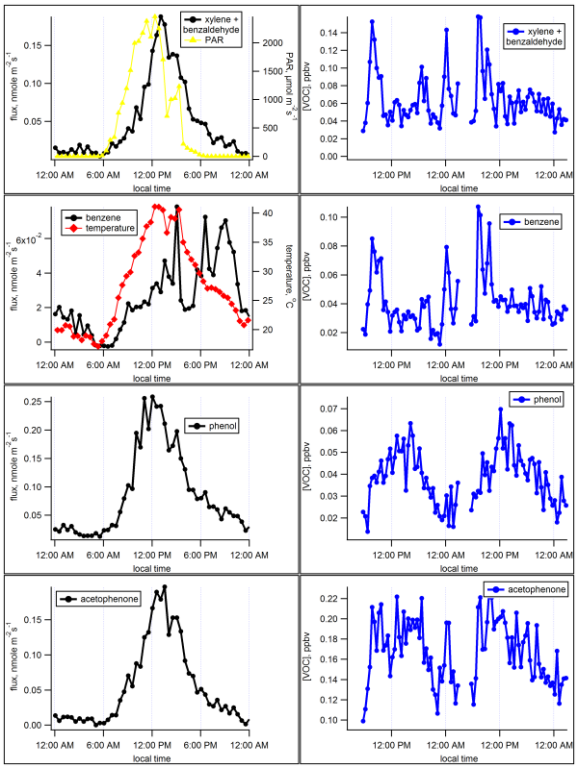

Figure S1: Branch enclosure flux (left column) and ambient concentration (right column) of several aromatic compounds. PAR at branch height (triangles) and enclosure air temperature (diamonds) are also plotted.

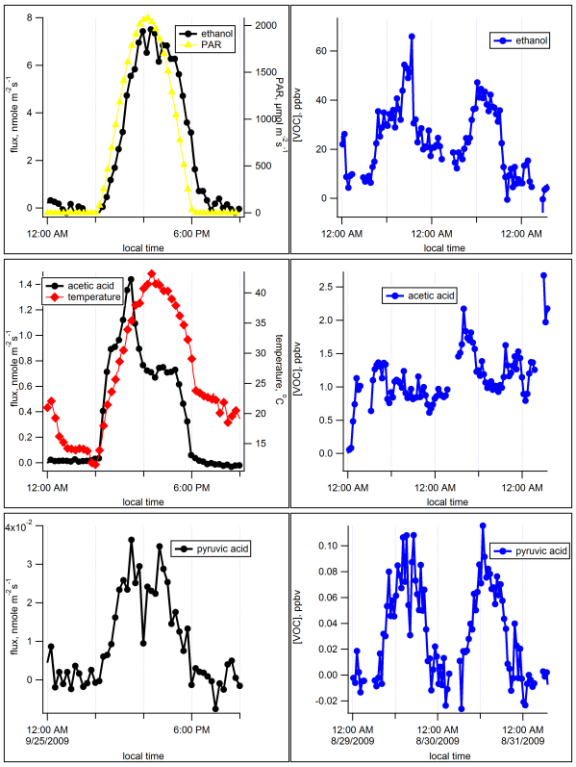

Figure S2: Branch enclosure flux (left column) and ambient concentration (right column) of the highly water soluble oxygenated VOCs. PAR at branch height (triangles) and enclosure air temperature (diamonds) are also plotted.

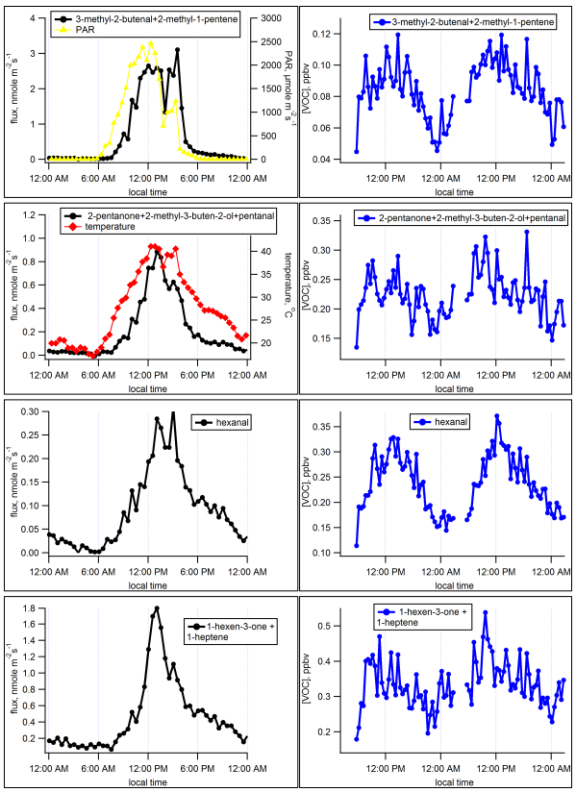

Figure S3: Branch enclosure flux (left column) and ambient concentration (right column) of potential fatty acid oxidation products. PAR at branch height (triangles) and enclosure air temperature (diamonds) are also plotted.

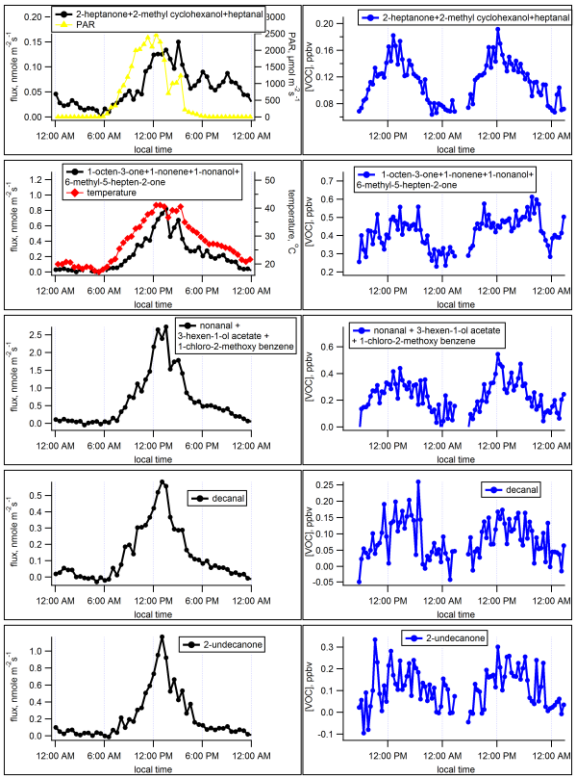

Figure S4: Branch enclosure flux (left column) and ambient concentration (right column) of possible fatty acid oxidation products. PAR at branch height (triangles) and enclosure air temperature (diamonds) are also plotted.

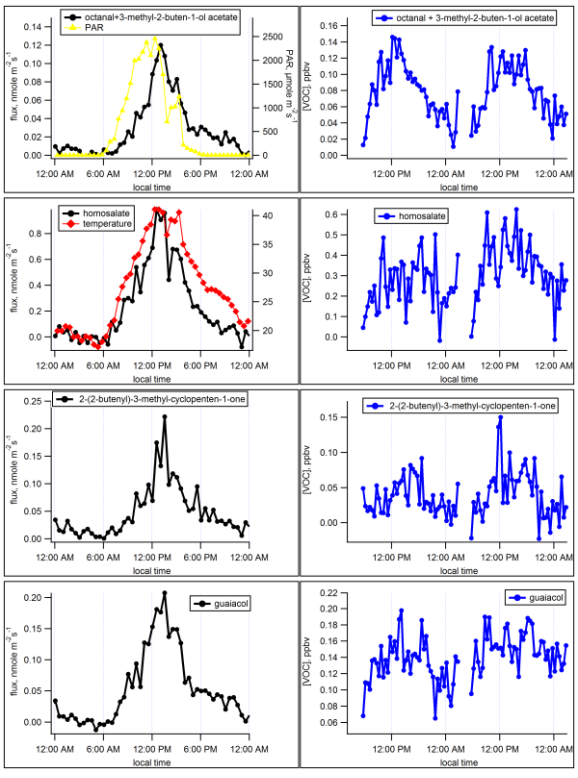

Figure S5: Branch enclosure flux (left column) and ambient concentration (right column) of various creosotebush VOCs. PAR at branch height (triangles) and enclosure air temperature (diamonds) are also plotted.

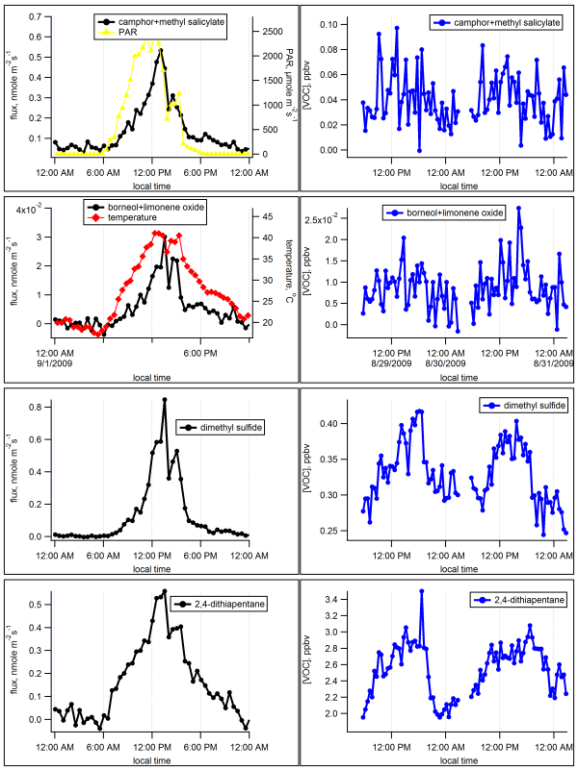

Figure S6: Branch enclosure flux (left column) and ambient concentration (right column) of various creosotebush VOCs. PAR at branch height (triangles) and enclosure air temperature (diamonds) are also plotted.

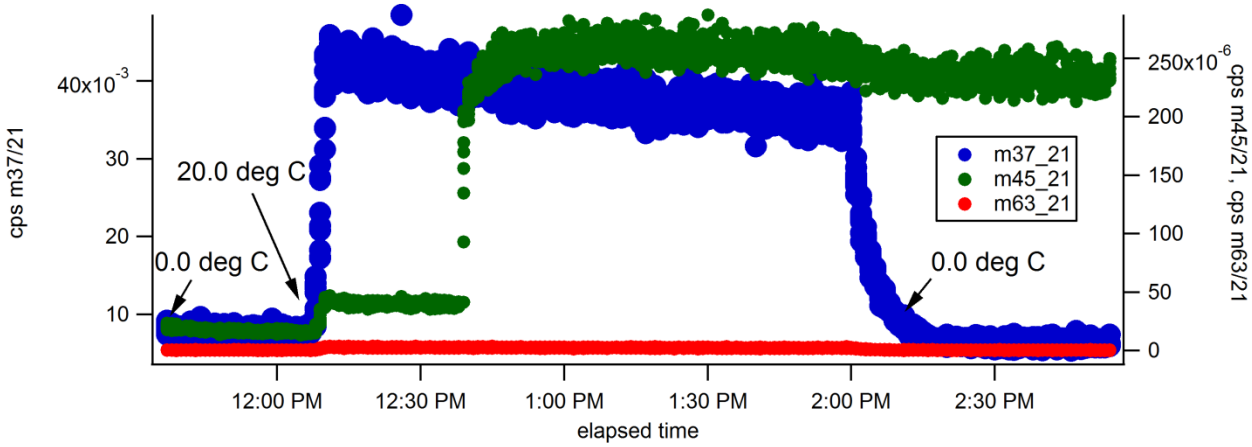

Figure S7: Analysis of potential interference of acetaldehyde water clusters on the PTR-MS signal (m/z 63) for dimethyl sulfide. Calibration of a PTR-MS to 19.0 ppbv acetaldehyde in air with a 20 °C dewpoint and 0 °C dewpoint. The lack of signal at m/z 63 upon addition of acetaldehyde to the humidified air demonstrates the lack of significant acetaldehyde-water cluster formation. Because calibration with dimethyl sulfide results in a strong signal at m/z 63 (data not shown), we conclude that dimethyl sulfide is present in ambient air and creosotebush branch emissions.