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

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1 Meteorological and VOC measurements

A 5.0 m aluminum tower was installed 36 m south of the laboratory and instrumented with a 3D sonic anemometer (4.0 m above ground) and data logger which recorded wind speed and air temperature data at 10 Hz (CSAT3 and CR3000 respectively, Campbell Scientific, Inc., Logan, Utah). Above canopy air (~0.1 m from the sonic anemometer) was drawn through a 30 m (1/4 in O.D.) Teflon® PFA tube using an oil free diaphragm pump (KNF Neuberger) with a sample point to detector delay time of ~6 seconds. In order to prevent condensation and the loss of VOCs to the tubing walls, the tubing was heated to 50 ^{o}C by placing it in a 2 in neoprene insulating jacket with a Teflon® coated self-regulating heating tape (Omega Engineering). During branch enclosure studies, the ambient air sampling line was disconnected from the pump and replaced with two additional tubes also heated to 50 ^{o}C (15 m, ¼ in O.D.). These tubes were pumped in parallel and the flow rate was reduced to 1 slpm, each using needle valves upstream of the pump. For each sample tube, a tee was installed just upstream of the pump which diverted

a small portion of the flow to the PTR-MS and a LI7000 (Licor, Lincoln Nebraska USA) for trace gas analysis (see Fig. 1 for plumbing diagram). The PTR-MS and the LI7000 drew sample air at 50 sccm and 400 sccm, respectively (flows were measured with a Definer 220 Primary Flowmeter, Bios International). For calibration purposes, two additional sample lines were used. One line had ~1.0 slpm UHP zero air flowing through it (controlled by a needle valve) and a second line had 100 sccm UHP nitrogen passing over temperature controlled VOC permeation tube standards diluted with 1.0 slpm UHP zero air. Flows through the permeation oven and zero air dilution were controlled by mass flow controllers (Cole-Parmer). All five of the sample inlet lines were connected to a six port Teflon (PTFE) solenoid valve (Cole-Parmer). During ambient air measurements, the valve cycled through the ambient air, zero air, and the permeation tube VOC standard lines according to the following schedule; ambient air (5:00 AM-2:59 AM; a total of almost 22 hr), permeation tube standards (3:00 AM-3:59 AM), and zero air (4:00 AM-4:59 AM). During branch enclosure measurements, the valve continuously cycled between enclosure air (first 45 minutes of each hour) and ambient air entering the enclosure (last 15 minutes of each hour).

1,1 Ambient air VOC concentration measurements

PTR-MS has been used extensively to measure the concentrations of atmospheric volatile organic compounds with proton affinities higher than water. The technical details of the PTR-MS have been previously described (Lindinger and Hansel, 1997; de Gouw and Warneke, 2007). A commercial high sensitivity PTR-MS instrument (IONICON, Austria, with a QMZ 422 quadrupole mass spectrometer, Balzers, Switzerland) was used for this study. For ambient air VOC concentration measurements, the PTR-MS was operated with a drift tube voltage of 600 V and drift tube pressure of 2.1 mb. The following mass to charge ratios (m/z) were sequentially monitored during each PTR-MS measurement cycle; m/z 21 ($H_3{}^{18}O^+$), m/z 32 ($O_2{}^+$), and m/z 37 (H_2O-H_3O^+) with a dwell time of 20 ms. The primary ion signal ($H_3{}^{16}O^+$) was calculated by measuring the $H_3{}^{18}O^+$ signal at m/z 21 and multiplying it by the oxygen isotopic ratio of a representative natural abundance water sample ($^{16}O/^{18}O$ = 500). Most of the creosotebush compounds identified by GC-MS were also measured by PTR-MS as protonated parent ions produced in the drift tube with a 1 s dwell time (Table 1). However, a fragment at m/z 83 was used to monitor 3-hexenol, 2-hexenol, hexanal, and hexenyl acetate (Fall et al., 1999) and at m/z 139 for homosalate (determined from mass scans of a homosalate standard). Continuous ambient concentration measurements were carried out ten times, each lasting 2-3 days. The raw ion intensities were normalized by the primary ion signal and thirty minute averages were calculated. Background signals from the zero air measurements were averaged and subtracted from the ambient air measurements. VOC concentrations were calculated by multiplying a calibration factor (as discussed in section 2.5) by the normalized and background-subtracted signals.

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.

1.2 Branch VOC emission measurements

For branch VOC emission measurements, a Teflon® branch enclosure (5 L) was placed around a creosotebush branch near the laboratory. During the first experiment, zero air was pumped into this enclosure at 5.0 slpm by pumping ambient air through a catalytic converter system rated to 10 slpm (Aadco Instruments). For subsequent experiments (seven additional branches), ambient air was pumped directly into the enclosure at flow rate of 5.0 slpm. Photosynthetically Active Radiation (PAR) at branch height (outside of the enclosure) and enclosure air temperature were measured using a quantum light sensor and a micro temperature sensor and stored every five minutes on a WatchDog data logger (Spectrum Technologies). Leaves on the branch were harvested at the end of the experiment and total dry weight was determined. For the first branch, leaf specific mass was also determined (158 gdw m^{-2}), the value of which was used to convert dry leaf weight (gdw) to leaf area for the other branches. Branch flux measurements of VOCs were calculated based on the concentration difference between the incoming and outgoing air, the flow rate through the enclosure, and the total leaf area. For each branch, continuous VOC emission rate measurements were made for 1-2 days with the PTR-MS in scan mode (m/z 21-213, 0.1 s dwell time). For each data set, 10 minute averages were calculated.

1.3 PTR-MS calibration

The sensitivity of the PTR-MS to the VOCs shown in Table 1 was determined by three different methods, depending on the compound. For the first method, VOC sensitivities were measured automatically during each ambient air measurement (a total of 10) using a two point calibration consisting of a background measurement of zero air and a VOC calibration standard diluted with hydrocarbon free air (each measured for 1 hour). 10 sccm of a 2.0 ppmv gravimetrically prepared gas standard (Apel Riemer Environmental Inc, USA) was used for acetaldehyde while NIST traceable permeation tubes (KIN-TEK Laboratories, Inc.) placed in a permeation chamber (VICI Valco Instruments Co. Inc.) held at 30 ^{o}C with 100 sccm of ultra high purity (UHP) nitrogen flowing through were used to generate known concentrations of methanol (518 ppbv), ethanol (579), acetone (456 ppbv), acetic acid (485 ppbv), and isoprene (329 ppbv). Upon dilution in 1.0 slpm UHP zero air, the resulting concentrations ranged between 20-53 ppbv. At the beginning of the experiment, a single calibration was performed with an α-pinene permeation tube in the chamber held at 100 ^{o}C. Dilution of the α-pinene standard (313 ppbv) in 1.0 slpm UHP zero air resulted in a concentration of 28 ppbv. A second calibration of α-pinene was also performed using the second method (see below).

Calibration solutions for VOCs not stable or difficult to acquire in permeation tubes/gas cylinders were generated by dissolving a small volume (5-10 μL) of an authentic liquid standard in 100 mL of cyclohexane. 5-10 μL of this solution was then injected into a Tedlar bag with known volume of UHP zero air (2-8 L). The resulting air mixture (VOC concentrations of 8-31 ppbv) was then introduced directly into the PTR-MS. Background samples of Tedlar bags containing only zero air with cyclohexane were also measured and used for background subtraction of the calibration samples. Background and sample signals for each m/z included in the PTR-MS scans (Table 1) were normalized to the primary ion signal and averaged. This method, is the same as that reported in previous work on biogenic sesquiterpenes (Bouvier-Brown et al., 2009), but extends this technique from sesquiterpenes to a much larger range of compounds. Calibration factors (ppbv/ncps) were calculated for both methods by dividing the mixing ratio of the compound in the calibration sample (ppbv) by the normalized background-subtracted calibration signals (ncps = cps VOC/cps H_3O^+, where cps is the signal intensity in

counts per second). VOC calibrations using the second method were performed once during the experiment with two different solutions containing different mixtures of compounds and once at the end of the experiment with four different solution mixtures. For comparison of results between calibrations, methyl vinyl ketone was present in a solution during and after the experiment. For a comparison between the two techniques, a calibration of α-pinene was performed during the experiment using a permeation tube and after the experiment by including α-pinene in one of the four cyclohexane solutions.

For the third method, a calibration factor of 80346 ppbv $ncps^{-1}$ was used to estimate the concentrations of compounds without standards; where ncps is the background subtracted normalized PTR-MS signals (ncps) at a given m/z. This value was chosen because it is the mean of the calibration factors determined for compounds calibrated using methods 1 and 2.

1.4 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., 2004a; 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 measured from other vegetation assemblies. A limited amount of work has been done on characterizing the volatile components of creosotebush resin (Mabry, 1979). We successfully detected PTR-MS MW+1 signals from creosotebush branch enclosure and ambient air measurements for many of these compounds (see Table 1). 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 the National Center for Atmospheric Research (NCAR) Boulder Laboratory.

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 ^oC 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 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 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 Boulder, Colorado Laboratory. 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.