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

K. Jardine[1], **L. Abrell**[2], **S. A. Kurc**[3], **T. Huxman**[4], **J. Ortega**[5], **and A. Guenther**[5]

[1]University of Arizona-Biosphere 2, 32540 S. Biosphere Road, Oracle, AZ 85623, USA
[2]University of Arizona, Departments of Chemistry & Biochemistry and Soil, Water & Environmental Science, P. O. Box 210038, Tucson, AZ 85721-0038, USA
[3]University of Arizona, School of Natural Resources and the Environment, Biological Sciences East Tucson, AZ 85721, USA
[4]University of Arizona, Department of Ecology and Evolutionary Biology, P. O. Box 210088, Tucson, AZ 85721, USA
[5]National Center for Atmospheric Research, Atmospheric Chemistry Division, 3450 Mitchell Lane, Boulder, CO 80301, USA

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Abstract. We present results from the CREosote ATmosphere Interactions through Volatile Emissions (CREATIVE 2009) field study in southern Arizona aimed at quantifying emission rates of VOCs from creosotebush (*Larrea tridentata*) during the summer 2009 monsoon season. This species was chosen because of its vast distribution in North and South American deserts and because its resins have been reported to contain a rich set of volatile organic compounds (VOC). While a variety of ecosystems have been investigated for VOC emissions, deserts remain essentially unstudied, partially because of their low biomass densities and water limitations. However, during the North American monsoon, a pronounced increase in rainfall from an extremely dry June (<5 mm precipitation) to a rainy July (>80 mm) occurs over large areas of the Sonoran desert in the southwestern United States and northwestern Mexico. We observed a strong diurnal pattern of branch emissions and ambient concentrations of an extensive suite of VOCs with maxima in early afternoon. These include VOCs typically observed in forest sites (oxygenated VOCs and volatile isoprenoids) as well as a large number of other compounds, some of which have not been previously described from any plant including 1-chloro-2-methoxy-benzene and isobutyronitrile. Although generally considered to be derived from anthropogenic sources, we observed emissions of aromatic compounds including benzene, and a broad range of phenolics. Dimethyl sulfide emissions from creosotebush were higher than reported from any previously studied plant suggesting that terrestrial ecosystems should be reconsidered as an important source of this climatically important gas. We also present direct, primary emission measurements of isoprene and its apparent oxidation products methyl vinyl ketone, methacrolein, and 3-methyl furan (the later three compounds are typically assumed to form from secondary reactions within the atmosphere), as well as a group of compounds considered to be fatty acid oxidation products. These results suggest that one important function of some VOCs in creosotebush is as an antioxidant. We also find that emissions of nitriles from creosotebush could represent a significant but previously unaccounted nitrogen loss from this arid ecosystem. Our results demonstrate the richness of creosotebush volatile emissions and highlight the need for further research into their atmospheric and ecological impacts.

Correspondence to: K. Jardine
(jardine@email.arizona.edu)

1 Introduction

Surface emissions of volatile organic compounds (VOCs) profoundly influence the composition of the atmosphere by providing reactive species for tropospheric chemistry (Atkinson and Arey, 2003) and providing condensable oxidation products for the formation of organic aerosols (Sakulyanontvittaya et al., 2008; Saathoff et al., 2009). The atmospheric impact of biogenic VOC emissions by terrestrial vegetation is enhanced relative to the impact from anthropogenic VOC sources by biogenic VOCs having greater reactivity to oxidants, and larger global emission rates (Guenther et al., 1995). However, the southwestern US has recently become one of the fastest growing population regions in the country, resulting in increased anthropogenic emissions

of atmospheric pollutants like VOCs and nitrogen oxides. Together with natural biogenic VOC emissions from native desert vegetation, anthropogenic emissions may contribute to the exceedence of US air quality standards for hazardous air pollutants such as ground level ozone (Kleinman et al., 2003; Wise and Comrie, 2005; Diem, 2000). While ecosystems around the world have been studied for VOC emissions, most attention has been given to forests with a high leaf area index (LAI) such as Tropical (Kesselmeier, 2009), Boreal (Rinne, 2009), and Pine (Schade and Goldstein, 2001) forests where volatile isoprenoids and oxygenated VOCs have been consistently observed as the predominate compounds released. In contrast, very little is known about biogenic VOC emissions from native desert plants and the associated effects on air quality and climate. Higher air temperatures and solar insolation of desert ecosystems may drive high VOC emission rates from these regions.

Several species of desert plants are well known for their strong odor. For example, creosotebush (*Larrea tridentata*) is often referred to in Sonora, Mexico as hediondilla, the "little stinker". By the Last Glacial Maximum, creosotebush already inhabited the southwestern United States (Duran et al., 2005). Over the last century, the area dominated by creosotebush in North America has increased, and is associated with coincident land degradation during that time (Grover and Musick, 1990). Creosotebush is pervasive in all three North American warm deserts: the Mojave, the Sonoran, and the Chihuahuan; suggesting that its contributions to regional biogenic VOC emissions could be significant.

Creosotebush leaves are opposite, with two asymmetrical oblong leaflets joined at the base, measuring about 10 mm long and 3 to 4 mm wide. The phenolic resin that coats these leaves has been shown to promote water use efficiency, deter herbivores, and screen ultra-violet radiation (Meinzer et al., 1990; Rhoades, 1977). This resinous coating is exuded from glandular trichomes; specialized epidermal cells containing volatile oils and other plant-produced secretions that can comprise as much as 20% of the dry leaf weight (Sakakibara et al., 1976). Previous work has identified nearly one hundred volatile constituents in these resins consisting mostly of monoterpenes, sesquiterpenes, aromatics, and unsaturated ketones (Mabry, 1981). The nonvolatile components of creosotebush resin such as waxes (Seigler et al., 1974), flavanoids (Sakakibara et al., 1976), and lignins (Konno et al., 1990) including the potent antioxidant nordihydroguaiaretic acid (Arteaga et al., 2005) have been studied.

To our knowledge, only three studies have attempted to measure VOC emissions from creosotebush (emission rates normalized to leaf dry weight, gdw). In the first study, significant emissions of the oxygenated VOCs formic and acetic acids (0.6 and 0.7 $\mu g\,C\,gdw^{-1}\,h^{-1}$ respectively) and formaldehyde (3.1 $\mu g\,C\,gdw^{-1}\,h^{-1}$) were observed (Knowlton et al., 1999). In a second study, 13 plants including creosotebush were surveyed for VOC emissions in the Mojave and Sonoran deserts for VOC emissions (Geron et al., 2006). The authors found that while creosotebush emissions were dominated by methanol (100 $\mu g\,C\,gdw^{-1}\,h^{-1}$), significant emissions of monoterpenes (2.0 $\mu g\,C\,gdw^{-1}\,h^{-1}$), sesquiterpenes (0.5 to 2 $\mu g\,C\,gdw^{-1}\,h^{-1}$, and acetaldehyde (1.0 $\mu g\,C\,gdw^{-1}\,h^{-1}$) also occurred. In the third study on creosotebush VOC emissions (Papiez et al., 2009), only monoterpenes were observed, but at emission rates that were a factor of six lower than those of Geron et al. which was attributed to differences in phenology or environmental conditions. While Geron et al. detected small isoprene emissions from several other desert plants, they found negligible isoprene emissions from creosotebush as did Papiez et al. (2009) Modeling results from Geron et al. (2006) suggested that isoprene emissions from the Mojave are 10–30 times less than from Eastern US forests while monoterpene emissions are 3–8 times less (normalized to land area). While these results suggest that desert ecosystems may represent a relatively small source of reactive hydrocarbons in the atmosphere, this conclusion was primarily based on a limited set of measurements from a large number of species, and on the assumption that like other forests studied, volatile isoprenoids are the dominant compounds released by desert vegetation.

Indirect evidence for substantial VOC emissions from desert vegetation was obtained from ambient ozone concentration monitoring at five stations around Tucson, Arizona between April and September of 1995–1998 (Diem, 2000). The results showed a dramatic change from a weekend effect in June (wherein ground-level ozone is greater on weekends than on weekdays) to a weekday effect in July (wherein the opposite is observed: ground-level ozone is greater on weekdays than on weekends) associated with the onset of the North American Monsoon. It was hypothesized that biogenic VOC emissions from the Sonoran desert increase dramatically with increased atmospheric moisture in July and August in the Tucson area thereby changing the limiting ozone precursor from VOCs to nitrogen oxides (NO_x). As a starting point towards testing this hypothesis, the objective of the current study was to identify potential VOCs emitted by creosotebush, quantify branch emission rates, and determine if significant ambient concentrations of VOCs could be measured during the summer monsoon season. We find substantial branch emissions and ambient concentrations of all compounds previously reported from creosotebush. In addition to volatile isoprenoids (isoprene, monoterpenes, oxygenated monoterpenes, sesquiterpenes, oxygenated sesquiterpenes), a large array of VOCs not typically observed from forest sites are reported here including sulfides, nitriles, and an extensive list of oxygenated VOCs, aromatics, and fatty acid oxidation products.

2 Material and methods

2.1 Site description

The CREATIVE (CREosote ATmosphere Interactions through Volatile Emissions) field experiment occurred between 10 June and 1 October 2009 at the Santa Rita Experimental Range (SRER), approximately 64 km north of the US/Mexico border in southern Arizona. Creosotebush (*Larrea tridentata*) is the dominant vegetation species at the SRER study site (Morton and Melgoza, 1991) within a reserve wherein vegetation measurements began in 1902. The specific location for this study was selected as a creosotebush (*Larrea tridentata*) dominated ecosystem at the northern central boundary of the SRER (31°54′44.26″ N, 110°50′12.92″ W, 994 m a.s.l.), where average annual rainfall totals 330 mm (http://ag.arizona.edu/SRER/data.html), split evenly between summer and winter seasons (McClaran, 2003). At this location, total canopy cover is about 24%:14% creosotebush and the other 10% a combination of annual grasses, annual herbaceous species, and cacti. (Kurc and Benton, 2010). Here, the creosotebush has an average height just under 2 m with about 24 stems per shrub, averaging about 10 mm in diameter, and soil in the area is a sandy loam with no caliche layer down to at least 1 m (Kurc and Benton, 2010).

2.2 Meteorological and VOC measurements

A 5.0 m aluminum tower was installed 36 m south of the laboratory and instrumented with a 3-D 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 s. In order to prevent condensation and the loss of VOCs to the tubing walls, the tubing was heated to 50 °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 °C (15 m, 1/4 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 (05:00 a.m.–02:59 a.m.; a total of almost 22 h), permeation tube standards (03:00 a.m.–03:59 a.m.), and zero air (04:00 a.m.–04:59 a.m.). During branch enclosure measurements, the valve continuously cycled between enclosure air (first 45 min of each hour) and ambient air entering the enclosure (last 15 min of each hour).

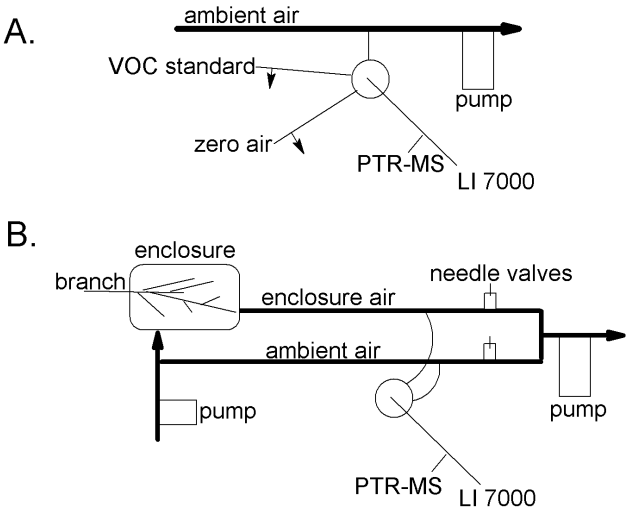

Fig. 1. Gas inlets for **(A)** ambient air VOC concentration and **(B)** branch VOC flux measurements. Excess calibration air not drawn into the PTR-MS or LI 7000 instruments was vented to an exhaust via a tee (small arrows). A six port valve was used (circle) to select one of the five gas samples for trace gas analysis (ambient air, zero air, VOC standard, enclosure air, or ambient air entering into enclosure).

2.3 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*)

Table 1. Summary of branch flux and ambient concentrations of creosotebush VOCs identified by GC-PTR-MS and GC-MS and quantified by PTR-MS. Compounds are grouped according to structural class as follows: (from top to bottom) volatile isoprenoids, oxygenated VOCs, nitriles, sulfides, aromatics, and isoprenoid and fatty acid oxidation products. Compounds identities were determined from branch enclosure samples analyzed in the field by GC-PTR-MS, by GC-MS at Biosphere 2 (B2), and the National Center for Atmospheric Research (NCAR) as designated in the fourth column. Averages branch VOC emission rates from seven branches are reported in the fifth column ±one standard deviation.

VOCs detected in this study	PTR-MS PTR-MS *m/z*	Detected in resins? Mabry 1979	Branch GC-MS	Average noontime branch emission rates $\mu g\,C\,gdw^{-1}\,h^{-1}$	Range of noontime ambient concentrations pptv or ppbv
isoprene*	69	no	NCAR, B2	7.5 ± 7.8	300 pptv
monoterpenes*	137	yes	NCAR, B2	10.4 ± 9.6	0.3–1.5 ppbv
camphor, methyl salicylate*	153	yes	NCAR, B2	0.9 ± 0.7	100 pptv
borneol, limonene oxide	155	yes	NCAR, B2	0.04 ± 0.04	30 pptv
sesquiterpenes*	205	yes	NCAR, B2	0.8 ± 0.8	600 pptv
methanol	33	no	GC-PTR-MS	4.5 ± 4.1	2.0–7.0 ppbv
acetaldehyde	45	no	GC-PTR-MS	3.7 ± 3.2	1.5–2.0 ppbv
ethanol	47	no		11.1 ± 7.9	40–100 ppbv
acetone*	59	no	GC-PTR-MS, B2	2.5 ± 2.1	2.0–3.5 ppbv
acetic acid*	61	no	NCAR, B2	1.7 ± 0.9	1.0–5.5 ppbv
methyl acetate*	75	no	B2	0.3 ± 0.2	300–400 pptv
pyruvic acid	89	no		0.2 ± 0.2	100 pptv
Isobutyronitrile*	70	no	NCAR, B2	0.7 ± 1.1	
2-methyl butanenitrile	84	no	NCAR, B2	0.2 ± 0.3	
dimethyl sulfide	63	no		0.2 ± 0.2	150–500 pptv
2,4-dithiapentane	109	no	NCAR	1.2 ± 0.6	
benzene*	79	no	NCAR, B2	0.2 ± 0.2	120–150 pptv
phenol*	95	no	B2	0.5 ± 0.2	80 pptv
xylene, benzaldehyde*	107	yes	NCAR, B2	0.4 ± 0.2	200 pptv
acetophenone*	121	yes	NCAR, B2	0.4 ± 0.2	300 pptv
1-methoxy-2-methyl-benzene	123	no	B2	0.2 ± 0.0	
guaiacol	125	no		0.1 ± 0.1	200–400 pptv
octanal, 3-methyl-2-buten-1-ol acetate	129	no	NCAR, B2	0.1 ± 0.1	100–200 pptv
homosalate	139	no	NCAR, B2	3.5 ± 3.1	0.6–2 ppbv
methyl vinyl ketone*, methacrolein	71	no	GC-PTR-MS, B2	0.4 ± 0.3	140–300 pptv
methyl ethyl ketone*, 2-methyl-propanal	73	no	GC-PTR-MS, B2	0.9 ± 0.8	200–1500 pptv
hexanal*, 3-hexen-1-ol acetate, 3-methyl furan	83	no	NCAR, B2	1.0 ± 1.0	100–150 pptv
3-methyl-2-butenal, 2-methyl-1-pentene	85	no	NCAR, B2	1.5 ± 1.1	140 pptv
2-methyl-3-buten-2-ol, 2-pentanone, pentanal	87	no	NCAR, B2	0.7 ± 0.4	400 pptv
1-hexen-3-one, 1-heptene	99	no	NCAR, B2	2.0 ± 1.8	500–600 pptv
hexanal*	101	yes	NCAR, B2	0.5 ± 0.3	300–400 pptv
2-heptanone, 2-methyl cyclohexanol, heptanal	115	yes	NCAR, B2	0.2 ± 0.0	200-300 pptv
1-octen-3-one, 1-nonene, 1-nonanol, 6-methyl-5-hepten-2-one	127	no	NCAR, B2	1.5 ± 1.0	0.7–2.0 ppbv
2,6-dimethyl-1,3,5,7-octatetraene, cymene*	135	no	NCAR, B2	0.1 ± 0.1	
1-decene	141	no	NCAR, B2	0.3 ± 0.2	20 pptv
nonanal*, 3-hexen-1-ol acetate, 1-chloro-2-methoxy-benzene	143	no	NCAR, B2	3.0 ± 2.5	0.6–1.0 ppbv
hexyl acetate	145	no	NCAR, B2	0.2 ± 0.2	10–12 pptv
2-(2-butenyl)-3-methyl-cyclopenten-1-one	151	no	NCAR	0.5 ± 1.1	150 pptv
decanal*	157	no	NCAR, B2	0.8 ± 1.1	300 pptv
2-undecanone	171	yes	NCAR, B2	0.9 ± 1.2	300 pptv

* Compounds identities verified using GC-MS with authentic standards.

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 at *m/z* 19 ($H_3^{16}O^+$) was estimated by measuring the signal at *m/z* 21 ($H_3^{18}O^+$) 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 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 VOC signal intensities (counts per second, cps_{VOC}) were normalized by the primary ion signal (cps_{21}) and thirty minute averages were calculated. Background signals from the zero air measurements were also normalized by the primary ion single and subtracted from the ambient air measurements to obtain normalized counts per second (ncps) according to Eq. (1).

$$ncps=(cps_{VOC}/cps_{21})_{sample}-(cps_{VOC}/cps_{21})_{zeroair} \quad (1)$$

VOC concentrations were calculated by multiplying a calibration factor (as discussed in Sect. 2.5) by the ncps. Because the signals at *m/z* 32 (O_2^+) and *m/z* 37 (H_2O-H_3O^+) remained below 5% and 2% of the primary ion signal respectively, reactions between VOCs and water clusters (H_2O-H_3O^+) and oxygen (O_2^+) were not considered.

2.4 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, $\mu mol\, m^{-2}\, s^{-1}$) at branch height (outside of the enclosure) and enclosure air temperature (°C) 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 min averages were calculated. Compound identities were made using thermal desorption gas chromatography (GC-MS and GC-PTR-MS) as described in the supporting material.

2.5 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 zero air (each measured for 1 h). 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 °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 °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 a 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 ($ppbv\, ncps^{-1}$) 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, see Eq. 1).

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. The third method used a calibration factor of $80346\, ppbv\, ncps^{-1}$ to estimate the concentrations of compounds where standards were unavailable. This factor was chosen because it is the mean of the calibration factors determined for compounds calibrated using methods 1 and 2.

Calibration of the PTR-MS with permeation tube standards (methanol, ethanol, acetone, acetic acid, and isoprene) during ambient air monitoring revealed normalized VOC sensitivities ($ppbv\, ncps^{-1}$) that remained relatively constant over the course of the experiment (<30% relative standard deviation from 9 calibrations). Using the second calibration technique described above (cyclohexane solutions), the normalized sensitivity for methyl vinyl ketone measured during the field experiment was within 3% of that determined after the experiment using the same technique. Normalized sensitivities for α-pinene determined using a permeation tube

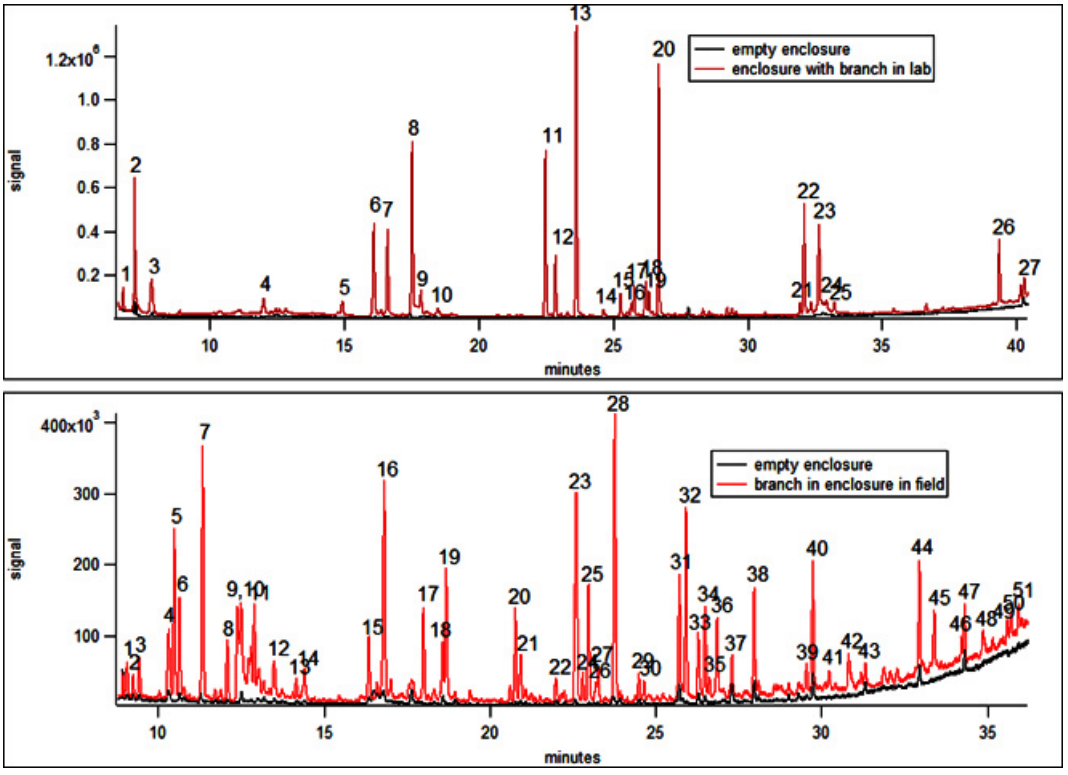

Fig. 2. Total ion chromatograms of creosotebush VOCs from GC-MS air samples taken in the lab (top graph) and in the field (bottom graph). Compounds present in the lab sample (top) include (1) isoprene, (2) unknown, (3) methyl acetate, (4) isobutyronitrile, (5) acetic acid, (6) 2-methyl-butanitrile, (7) unknown, (8) 1-hexen-3-one, (9) unknown, (10) hexanal, (11) tricyclene, (12) alpha-pinene, (13) camphene, (14) beta-pinene, (15) 1-octen-3-one, (16) limonene oxide, (17) 3-hexen-1-ol acetate, (18) 1-methoxy-2-methyl-benzene, (19) limonene, (20) ocimene, (21) unidentified monoterpene, (22) camphor, (23) isoborneol, (24) unknown, (25) methyl salicylate, (26) beta-caryophyllene, (27) 1,5,9,9-tetramethyl-1,4,7-cycloundecatriene (a sesquiterpene). Compounds present in the field sample (bottom) include isoprene and acetone (not shown), (1) 2-methyl propanal, (2) hexane, (3) methacrolein, (4) methyl vinyl ketone, (5) 3-methyl furan, (6) methyl ethyl ketone, (7) 2-methyl-3-buten-2-ol, (8) carbon tetrachloride, (9) isobutyronitrile, (10) benzene, (11) 1-heptene, (12) 2-methyl-1-pentene, (13) 2-pentanone, (14) pentanal, (15) 2-methyl-butanenitrile, (16) unknown, (17) unknown, (18) hexanal, (19) 3-methyl-2-butenal, (20) 1-nonene, (21) xylene, (22) unknown, (23) tricyclene, (24) 1-nonanol, (25) α-pinene, (26) 1-(2-chloroethoxy) butane, (27) unknown, (28) camphene, (29) 1-decene, (30) unknown, (31) benzaldehyde, (32) 3-hexen-1-ol acetate, (33) octanal, (34) limonene, (35) cymene, (36) ocimene, (37) 2-ethyl-1-hexanol, (38) phenol, (39) acetophenone, (40) nonanal, (41) 2,6-dimethyl-1,3,5,7-octatetraene, (42) 1-chloro-2-methoxy-benzene, (43) dodecane, (44) decanal, (45) methyl salicylate, (46) 1-tridecene, (47) tridecane, (48) benzothiazole, (49) 2-undecanone, (50) Acetic acid, 1,7,7-trimethyl-bicyclo[2.2.1]hept-2-yl ester, (51) octadecanal.

during the experiment was within 6% of that determined after the experiment using the cyclohexane technique. These results suggest that cyclohexane solutions offer a repeatable and accurate method for calibration of the PTR-MS to VOCs not easily obtained in permeation tubes or compressed gas cylinders. However, compounds with a low solubility in cyclohexane should be avoided (e.g., organic acids).

3 Results and discussion

Unlike many broad leaf and conifer forests where VOC emissions are dominated by volatile isoprenoids (isoprene, monoterpenes, sesquiterpenes), creosotebush emissions include a rich set of non-isoprenoid compounds. GC-MS results from branch enclosure samples collected from a detached branch transported to Biosphere 2 (Fig. 2, Top) and in-situ in the field (Fig. 2, Bottom) demonstrates the richness of creosotebush VOC emissions (Table 1). We have classified these VOCs into six structural groups: (1) volatile isoprenoids, (2) oxygenated VOCs, (3) fatty acid oxidation products, (4) aromatics, (5) sulfides, and (6) nitriles.

Except for a variety of alkanes which cannot be detected by PTR-MS (hexane, dodecane, tridecane, etc.), the PTR-MS was used to quantify the majority of the compounds identified by GC-MS from creosotebush branch enclosures. PTR-MS was also used to quantify several additional VOCs that the GC-MS did not detect well, including the highly volatile compounds methanol, acetaldehyde, ethanol, and dimethyl sulfide. These compounds are not quantitatively retained on sorbent tubes under field conditions and/or are lost during dry purging.

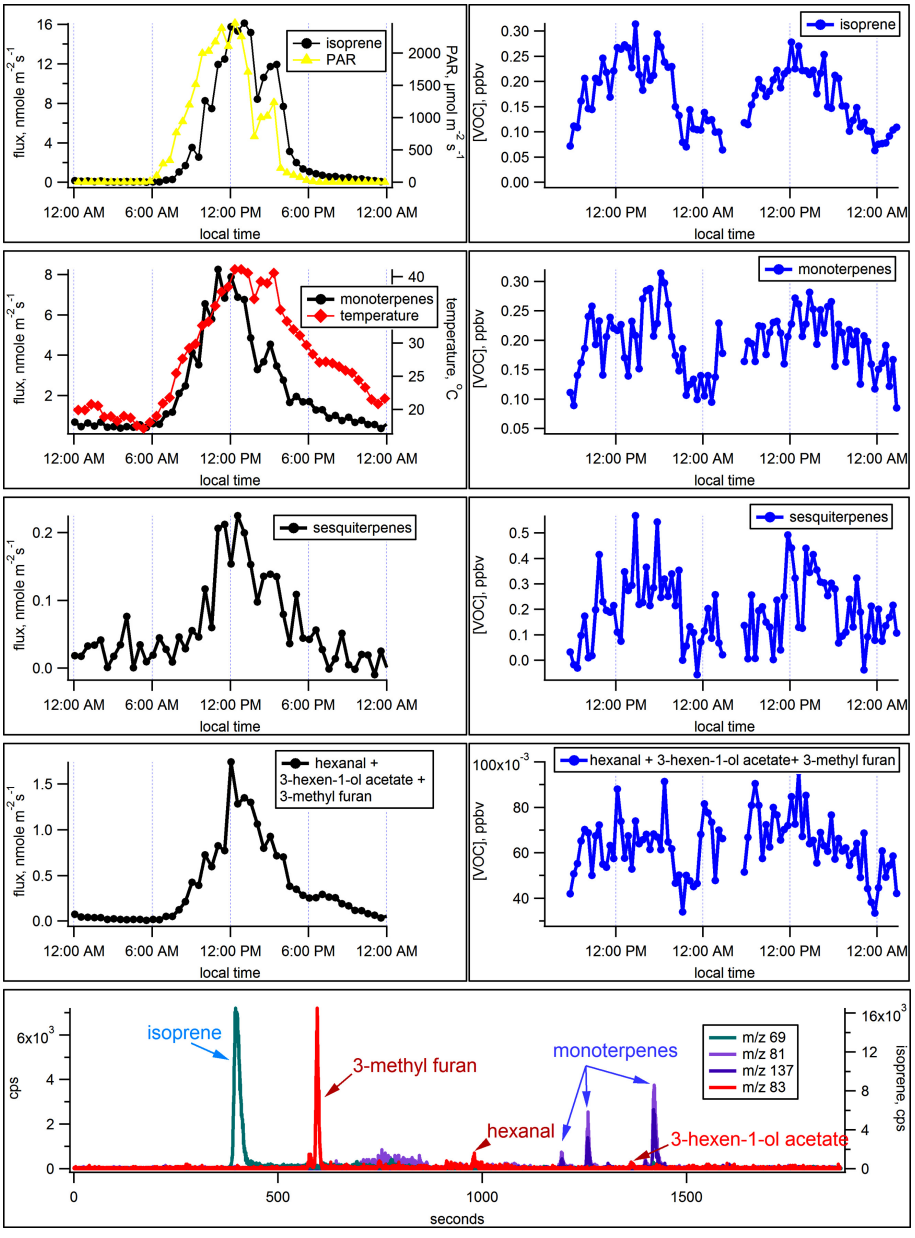

Fig. 3. Branch enclosure flux (left column) and ambient concentration (right column) of volatile isoprenoids and the potential isoprene oxidation product 3-methyl furan. PAR at branch height (triangles) and enclosure air temperature (diamonds) are also plotted. GC-PTR-MS chromatogram (bottom).

GC-PTR-MS chromatograms obtained in the field from branch enclosure samples revealed distinct peaks for methanol (*m/z* 33), acetaldehyde (*m/z* 45), acetone (*m/z* 59), isoprene (*m/z* 69), methacrolein and methyl vinyl ketone (*m/z* 71), methyl ethyl ketone and 2-methyl propanal (*m/z* 73), methyl acetate (*m/z* 75), 3-methyl furan, hexanal, and 3-hexen-1-ol acetate (*m/z* 83), and five different monoterpenes (*m/z* 137,81) (Figs. 3–5). At least five monoterpenes were identified from creosotebush branch samples by GC-MS including α-pinene, camphene, carene, limonene, and ocimene. These results demonstrate that for some mass to charge ratios (*m/z*), single creosotebush compounds can be measured by PTR-MS. However, other *m/z* values have two or more compounds that contribute to the measured signal. Although the use of PTR-MS to quantify biosphere-atmosphere exchange rates of VOCs is becoming more common, validation of mass assignments to specific compounds is less common. Our results demonstrate that the use of thermal desorption GC-PTR-MS and GC-MS is a useful method for this validation. While the oxygenated VOCs,

volatile isoprenoids, and nitriles were present in every intact branch enclosure sample collected in the field and analyzed by GC-MS (four replicate samples were collected with two analyzed at Biosphere 2 and two analyzed at the National Center for Atmospheric Research, NCAR), the presence of individual aromatics and fatty acid oxidation products was more variable, with some compounds only appearing in one sample. All but four compounds (1-hexen-3-one, 1-octen-3-one, limonene oxide, 1-methoxy-2-methylbenzene) detected from the detached branch were also found to be emitted from intact branches in the field. However, intact branches in the field emitted many additional compounds (>24) not detected from the detached branch under laboratory conditions. Therefore, we recommend that GC-PTR-MS and GC-MS work be routinely performed on complex VOC samples such as creosotebush emissions to validate PTR-MS measurements.

In the case where more than one compound contributes to a given *m/z* value measured by PTR-MS, we estimate that they possess similar calibration factors. By calibrating the PTR-MS to one of the compounds and applying the calibration factor to the measured signal (ncps), we then estimate total concentrations. For example, since the signal at *m/z* 73 is due to both methyl ethyl ketone and 2-methyl propanal, we calculate the total concentration of methyl ethyl ketone + 2-methyl propanal by calibrating the PTR-MS to methyl ethyl ketone.

3.1 PTR-MS branch enclosure and ambient concentration measurements

Figures 3–5 include representative time series plots of several VOCs made during CREATIVE 2009 with PTR-MS including one day of creosotebush branch emission rates (left column) followed by two days of ambient mixing ratios (right column). Similar time series plots for a wide variety of other VOCs emitted by creosotebush can be found in the Supplement, Figs. S1–S6. Branch emissions of all VOCs followed a strong diurnal pattern that generally tracked PAR and temperature with maxima during mid day to early afternoon. Because air temperatures in the enclosure decreased at a much lower rate than PAR following sunset, strictly light dependent VOC emissions can potentially be distinguished from temperature dependent VOC emissions. For example, emissions of isoprene (Fig. 3), acetaldehyde (Fig. 5), and acetone (Fig. 5) appear to be strictly light dependent while elevated emissions of methanol (Fig. 5), methyl ethyl ketone + 2-methyl propanal (Fig. 4), and methyl acetate (Fig. 4) at night suggest a temperature dependent evaporation from storage pools such as resins or continued production at night. Continued methanol production and emission from leaves at night has been observed by others (Harley et al., 2007) and may be related to cell wall expansion during growth (Fall, 2003) and decaying/drying plant matter (de Gouw et al., 1999).

Maximum noon time (12:00–14:00 local time) air temperatures inside the enclosure used for the eight branches studied for VOC emissions by PTR-MS ranged between 40–48 °C, and photosynthetically active radiation conditions at branch height (made outside the enclosure) ranged between 2000–2500 $\mu mol\ m^{-2}\ s^{-1}$. By comparison, maximum ambient temperatures during the same time period measured by the sonic anemometer (sonic temperature) ranged between 39–46 °C. Although an offset of a few degrees between the sonic temperature and the actual air temperature likely exists due to humidity effects on air density, these values fall into a normal ambient temperature range for low elevations of the southwest region during the summer, and suggest that extreme heating inside the branch enclosure did not occur. A summary of branch emission rates and ambient concentrations measured with PTR-MS is shown in Table 1. We estimate total noon time VOC emission rates of 14–118 $\mu g\ C\ gdw^{-1}\ h^{-1}$ (seven branches). The cause of the variation observed in noon time branch VOC emission rates may be due to variations in environmental conditions like light and temperature, natural variability between branches/plants, and variability influenced by physiological processes like flowering during the experiment. During the summer of 2009 monsoon, at least two distinct flowering events occurred. Unlike the observations by Geron et al., where creosotebush emissions which were dominated by methanol and ethanol (97% by carbon mass), a much wider variety of compounds were observed here including isoprenoids (32.7%), an extended suite of oxygenated VOCs (35.0%), fatty acid oxidation products (21.1%), aromatics (8.0%), sulfides (1.9%), and nitriles (1.3%). Figure 6 shows the noon-time averages of these compounds from seven branch enclosures.

Except for methanol, ambient concentrations of all VOCs observed also showed a strong diurnal pattern with maxima during mid day. In contrast with other VOCs whose concentrations peaked at midday, continued methanol emissions at night coupled with the decreased height of the atmospheric boundary layer may have contributed to the observed methanol concentration pattern with a maximum at night (Fig. 5). These observations demonstrate that the majority of compounds detected from branch emissions can be detected in ambient air above the canopy. However, in order to determine the atmospheric impacts of creosotebush VOC emissions, future research should attempt to quantify ecosystem scale VOC fluxes.

3.2 Oxygenated VOCs

We found creosotebush to be a strong source of oxygenated VOCs, with average noon time emissions of 24.0 $\mu g\ C\ gdw^{-1}\ h^{-1}$, 35.0% of the total VOC emissions by mass of carbon. Average noon time emission rates of methanol, acetone, and acetaldehyde fluxes were 4.5, 2.5, 3.7 $\mu g\ C\ gdw^{-1}\ h^{-1}$, respectively. A significant methyl

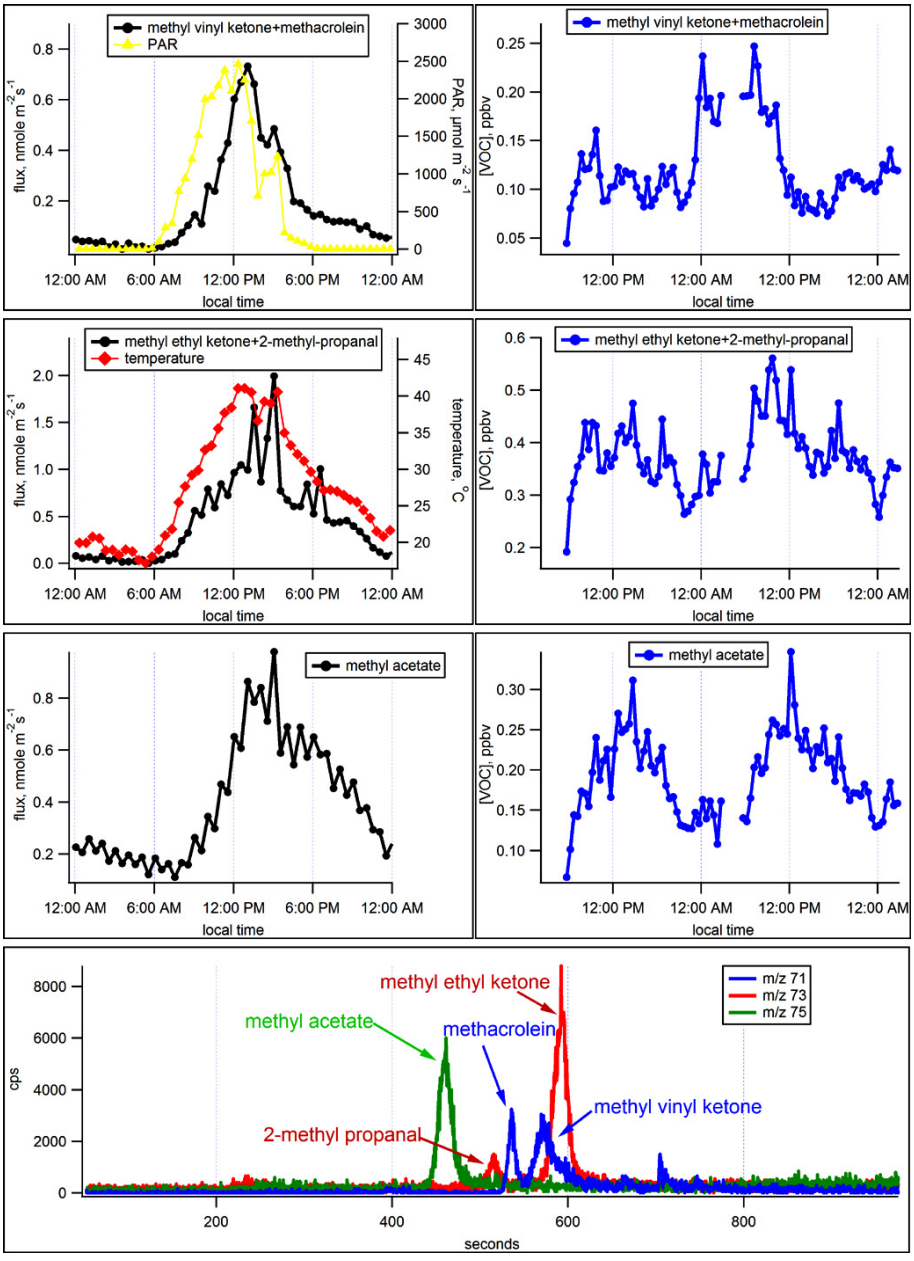

Fig. 4. Branch enclosure flux (left column) and ambient concentration (right column) of methyl acetate, methyl ethyl ketone, and the potential isoprene oxidation products methyl vinyl ketone and methacrolein. PAR at branch height (triangles) and enclosure air temperature (diamonds) are also plotted. GC-PTR-MS chromatogram (bottom).

acetate emission ($0.3\,\mu g\,C\,gdw^{-1}\,h^{-1}$) from creosotebush branches was verified by GC-MS (Fig. 2: Peak 3, top chromatogram) and GC-PTR-MS (Fig. 4). Although rarely reported from plants, methyl acetate has been previously observed in floral scents (Knudsen et al., 2006).

In some of the branch enclosures, water vapor condensed inside the bag during the day due to the high transpiration rates. This resulted in the loss of the highly water soluble VOCs acetic acid, ethanol, and pyruvic acid (data not shown). Therefore, the expected diurnal patterns were only observed from three of the branch enclosures where condensation did not occur (example in Fig. S2). From these branches, average noon time emission rates of acetic acid, ethanol, and pyruvic acid were up to 1.7, 11.7, and $0.2\,\mu g\,C\,gdw^{-1}\,h^{-1}$, respectively. Previous work in our lab using PTR-MS and GC-MS in selected ion mode has shown that pyruvic acid likely contributes to the PTR-MS signal at *m/z* 89 and is a precursor in the biosynthesis of many VOCs

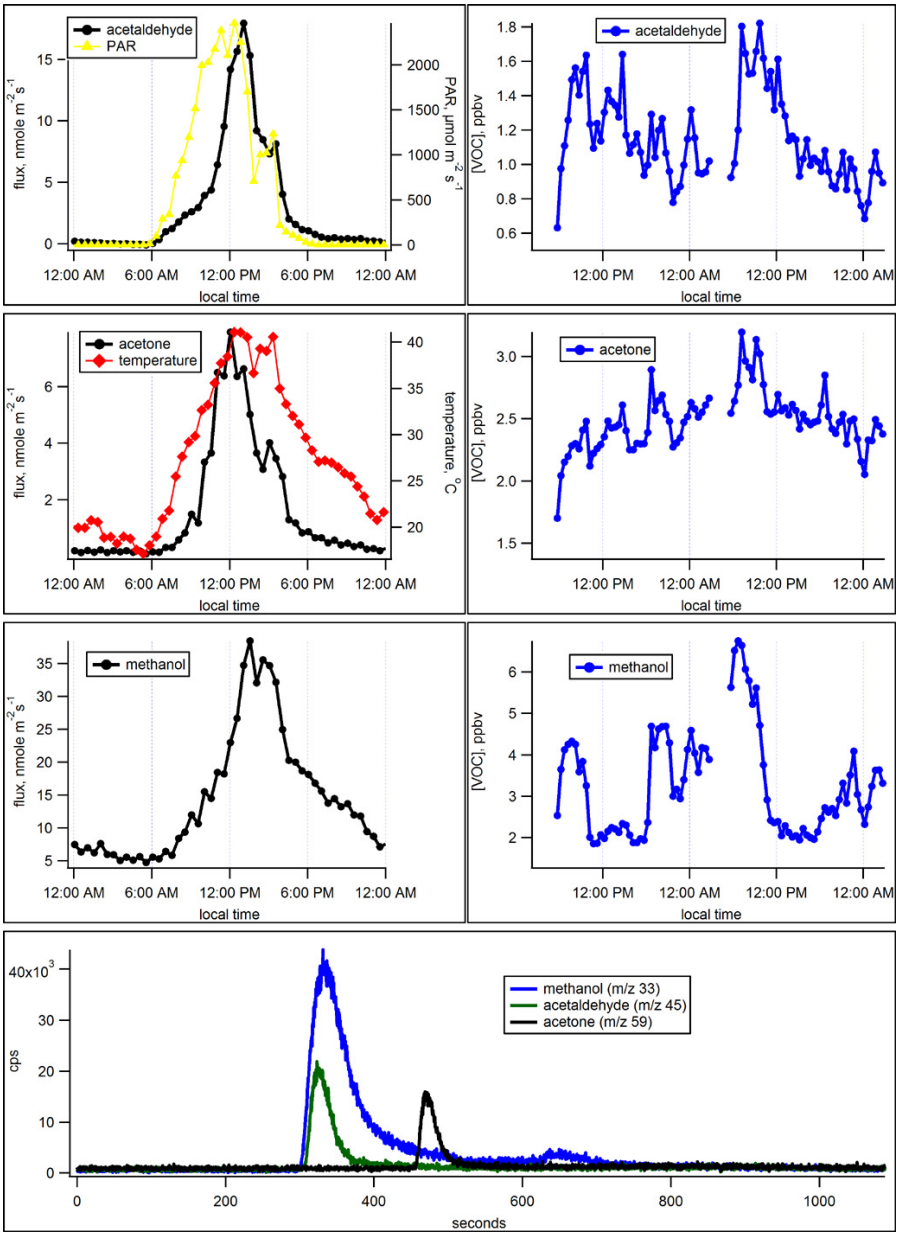

Fig. 5. Branch enclosure flux (left column) and ambient concentration (right column) of select oxygenated VOCs. PAR at branch height (triangles) and enclosure air temperature (diamonds) are also plotted. GC-PTR-MS chromatogram (bottom). GC-PTR-MS chromatogram (bottom).

including volatile isoprenoids (isoprene, monoterpenes, and sesquiterpenes) and several oxygenated VOCs (acetaldehyde, acetone, acetic acid, and ethanol) (Jardine et al., 2010).

3.3 Nitriles and sulfides

Using GC-MS, we discovered that creosotebush emits measurable quantities of isobutyronitrile and 2-methyl butanenitrile (Fig. 2). Although isobutyronitrile (*m/z* 70) and 2-methyl butanenitrile (*m/z* 84) were measured with PTR-MS mass-scans from creosotebush branch emissions, these nitriles were not included in the ambient air measurements. Due to the interference by ^{13}C-isoprene at *m/z* 70 measured by PTR-MS, we subtracted 5.5% of the signal at *m/z* 69 from *m/z* 70 to estimate the concentration of isobutyronitrile using *m/z* 70. A similar subtraction to quantify 2-methyl butanenitrile was done for the influence on *m/z* 84 by 3-methyl furan. The average noon time emission rate of isobutryonitrile was 0.7 µg C gdw^{-1} h^{-1}. More importantly, this represents a large loss of nitrogen from these ecosystems of 8.4 ngN m^{-2} s^{-1} with a maximum loss rate of 35 ngN m^{-2} s^{-1} (normalized to leaf area). Assuming a

creosotebush leaf area index of 0.45 and a 14 % cresotebush land cover (Kurc and Benton, 2010), this corresponds to a nitrogen loss rate of 0.5 ngN m^{-2} s^{-1} with a maximum loss rate of 4.4 ngN m^{-2} s^{-1} (normalized to ground area). For comparison, at a Mohave Desert site dominated by creosotebush, total reactive nitrogen ($NO + NH_3$) emissions were measured from dry and artificially wetted soils (McCalley and Sparks, 2009). They found a maximum emission rate of 5 ngN m^{-2} s^{-1} (ground area) was measured from dry soils and 150 ngN m^{-2} s^{-1} was measured from wetted soils. While the authors claimed that these emissions dominate arid-land nitrogen export, our observations suggest that nitrile emissions from creosotebush are also present.

Another surprising result from the CREATIVE 2009 field campaign are the large emission rates and ambient concentrations of dimethyl sulfide (DMS) and 2,4-dithiapentane measured with PTR-MS at *m/z* 63 (0.2 µg C gdw^{-1} h^{-1}) and *m/z* 109 (1.2 µg C gdw^{-1} h^{-1}) respectively. DMS has a potentially potent effect on climate by forming sulfate aerosols in the atmosphere that can act as cloud condensation nuclei (Lovelock, 1976). While very few DMS emission rate measurements from terrestrial plants exist, it is generally thought that most plants are a source of DMS to the atmosphere, but that terrestrial vegetation is considered a minor source compared with the oceans (Watts, 2000). While several studies using GC techniques have measured DMS from terrestrial plants, only a few species studied release small amounts of it (Yonemura et al., 2005; Geng and Mu, 2006). For example, when 19 tree species were surveyed, the maximum DMS emission rates (0.4 pmol m^{-2} s^{-1}) were more than three orders of magnitude lower than measured here for creosotebush (0.8 nmol m^{-2} s^{-1}) (Geng and Mu, 2006). DMS fluxes from several plants were also shown to be light and temperature dependent with the highest fluxes measured from corn at 30 °C (30 ngS gdw^{-1} h^{-1}) (Fall et al., 1988). In comparison, noon time emission rates from creosotebush reached values up to 585 ngS gdw^{-1} h^{-1}; (a branch exposed to field temperatures up to 48 °C), nearly twenty times larger than those reported for corn. Therefore, DMS emissions from creosotebush should be taken into account when constructing terrestrial emission inventories in North and South America.

A PTR-MS signal at *m/z* 63 attributed to DMS blown inland from the coast was also observed in forest ambient air (Jordan et al., 2009). One possibility is that the signal at *m/z* 63 arises from a water-acetaldehyde-H^+ cluster. However, previous research found no humidity dependence on acetaldehyde (*m/z* 45) and DMS (*m/z* 63) concentration measurements by PTR-MS (Warneke et al., 2001). In this study, when 19 ppbv acetaldehyde was introduced into zero air humidified to 20 °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 DMS in cyclohexane was used for calibration, we conclude that significant VOC-water cluster formation does not occur during ambient air and branch flux measurements under our operating drift tube conditions (E/N 117 Td, 600 V, 2.1 mb). See Fig. S7 in the Supplement.

3.4 Aromatics and chlorocarbons

Aromatic compounds in the atmosphere are widely considered to be primarily of anthropogenic origin (Na et al., 2005; Hellen et al., 2005; Burstyn et al., 2007), and are generally not considered in discussions of biogenic emissions from plants (Kesselmeier and Staudt, 1999). These compounds are a concern for air quality because of their carcinogenic effects in animals (Mehlman, 1991). Several aromatic compounds have been shown to be emitted from plants including toluene (White et al., 2009), benzaldehyde (Batten et al., 1995), and phenol (Holzinger et al., 2000). A survey of seven Mediterranean woody species revealed only a few species emitted phenol (Penuelas and Llusia, 2001). We found that average noon time emissions of aromatic VOCs (5.5 µg C gdw^{-1} h^{-1}) represent 8.0% of the total noon time VOC emissions from creosotebush (Fig. 6).

While volatile components make up a significant portion of creosotebush resin, the majority consists of a variety of non-volatile polyphenolic compounds such as flavonoids and lignin produced from the Shikimic acid pathway. Volatile aromatic compounds that are emitted into the atmosphere in measurable quantities from creosotebush including benzene, phenol, xylene, benzaldehyde, acetophenone, and 1-chloro-2-methoxy-benzene (Table 1, Fig. S1) are possibly also produced from the Shikimic acid pathway. To our knowledge, these are the first emission rate estimates of the halocarbon 1-chloro-2-methoxy-benzene from any plant. Previous work has identified creosotebush scrub ecosystems in Southern California to be a source of chloroform, methyl chloroform, and carbontetrachloride (Rhew et al., 2008). GC-MS measurements from the Southern Arizona creosotebush branch enclosure sample collected in the field reveal the presence of elevated carbon tetrachloride (Fig. 2, bottom chromatograph, peak 8). While previously often considered strictly anthropogenic, our results demonstrate that aromatic compounds in the atmosphere can have a measurable biogenic source. Additional research is necessary to determine whether these emissions are unique to creosotebush or are also released from other plants. The presence of volatile aromatic compounds in essential oils from multiple plant species suggests that many plants may produce and emit volatile aromatic compounds (Chiu et al., 2009).

3.5 Volatile isoprenoids

A large list of volatile isoprenoids including isoprene, monoterpenes, oxygenated monoterpenes, sesquiterpenes, and oxygenated sesquiterpenes were found to be produced by creosotebush. While previous studies did not detect isoprene emissions from creosotebush, we found a substantial average

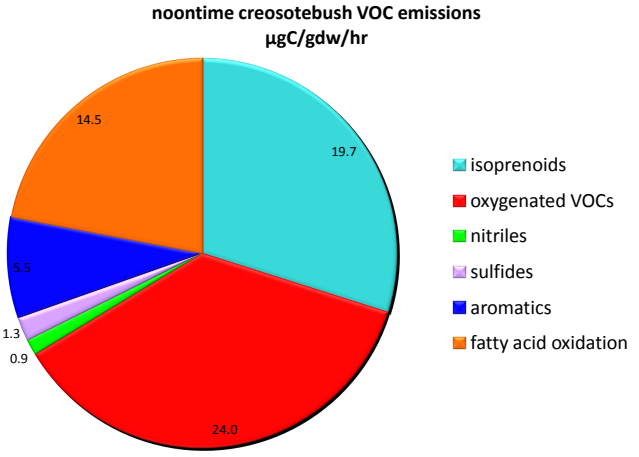

Fig. 6. Piechart showing average noontime VOC fluxes from seven creosotebush branches (by mass of carbon).

noon time emission rate of 7.5 µg C gdw^{-1} h^{-1}. Monoterpene fluxes detected by Geron et al. (5.0 µg C gdw^{-1} h^{-1}, adjusted to 40 °C for comparison), are within the range of noontime fluxes measured in this study (range: 2.2–21.9 µg C gdw^{-1} h^{-1}, average of 10.4 µg C gdw^{-1} h^{-1}). In addition, our average estimate for sesquiterpene emissions (0.8 µg C gdw^{-1} h^{-1}) falls within the emission range (0.5–2.0 µg C gdw^{-1} h^{-1}) of β-caryophyllene (a sesquiterpene) made by Geron et al. (2006). Two sesquiterpenes including β-caryophyllene were detected from branch enclosure samples by GC-MS analysis at Biosphere 2 (Fig. 2) whereas at least 15 different sesquiterpenes and oxygenated sesquiterpenes (data not shown) were detected from branch enclosure samples analyzed at NCAR using GC-MS. In addition, emissions of 2-methyl-3-buten-2-ol (MBO, Fig. 2, bottom chromatogram, peak 7) were likely significant but could not be separately determined due to the presence of 2-pentanone, pentanal, and MBO at the PTR-MS signal at *m/z* 87 (average noon time emissions of 0.7 µg C gdw^{-1} h^{-1}). Although MBO emissions are generally considered to be isolated to Pine trees, our results demonstrate that this assumption is incorrect and highlights the need to screen more plants for MBO emissions to the atmosphere. Because the emission rates of isoprenoids can be tightly linked with carbon assimilation rates or unlinked by evaporation from storage pools (resins), future research could address this question by using $^{13}CO_2$ labeling and PTR-MS analysis to separate de novo and pool isoprenoid emissions (Ghirardo, 2010).

In Amazonia, inverse modeling of vertical concentration gradients of methyl vinyl ketone + methacrolein concentrations suggested a source from isoprene oxidation above the canopy (Karl et al., 2009). This agrees with the general assumption that methyl vinyl ketone and methacrolein are secondary oxidation products of isoprene in the atmosphere (Pang et al., 2009; Helmig et al., 1998). However, primary emissions of the isoprene oxidation products methyl vinyl ketone + methacrolein (0.4 µg C gdw^{-1} h^{-1}) and 3-methyl furan (1.0 µg C gdw^{-1} h^{-1}) were found to be directly emitted in significant quantities from creosotebush; representing ∼19% of the branch level isoprene emission rates on average. Given the air residence time in the enclosure of approximately one minute and the likely low ozone concentrations, we assume gas phase oxidation of isoprene is negligible. Past studies have shown negligible (<2%) gas phase isoprene oxidation reactions using dynamic plant enclosures even during ozone fumigation (Fares et al., 2008). Isoprene produced by plants has been shown to reduce ozone damage in leaves, but the mechanism are not yet fully understood (Loreto and Velikova, 2001; Loreto and Fares, 2007). Isoprene oxidation products may be produced during reactions with reactive oxygen species (ROS) which are known to accumulate in plants during stress (Kotchoni and Gachomo, 2006). During metabolism at elevated temperatures, mitochondria may become sources of ROS which could react with isoprene within the plant to produce the oxidation products methyl vinyl ketone, methacrolein, and 3-methyl furan; thereby protecting important cellular components from oxidative damage. Our observations provide the first direct evidence that this protection is mediated by isoprene oxidation reactions. However, methacrolein and methyl vinyl ketone may also be produced from fatty acid oxidation (Almeras et al., 2003). Other studies have suggested that primary branch emissions (Holzinger et al., 2000) and ambient concentrations (Jordan et al., 2009; Holzinger et al., 2002) of a VOC detected at *m/z* 71 with PTR-MS correspond to methyl vinyl ketone and methacrolein. We used GC-MS and GC-PTR-MS to verify their identities (Fig. 2, bottom chromatogram, peaks 3 and 4; Fig. 4). Therefore, our results call into question the idea that isoprene oxidation products derive exclusively from isoprene photooxidation in the atmosphere and supports the hypothesis that one of the major functions of volatile isoprenoids in plants is to act as an antioxidant (Vickers et al., 2009).

3.6 Fatty acid oxidation products

The stress-induced activation of the octadecanoid pathway in plants leads to the biosynthesis of metabolites from the oxidation of fatty acids termed oxylipins including volatile C_6 aldehydes and alcohols (Vick and Zimmerman, 1989; Hatanaka et al., 1987). This ubiquitous pathway has been shown to be elicited following a wide range of stresses including wounding (Farmer and Ryan, 1992), herbivory (Schmelz et al., 2003), and desiccation (de Gouw et al., 1999). Emissions of volatile oxylipins from plants have been measured at the ecosystem scale during the harvesting of alfalfa for hay (Warneke et al., 2002). Although the octadecanoid pathway appears to be a general response of plants to stress, we measured high average noon time creosotebush emissions (14.5 µg C gdw^{-1} h^{-1}) and ambient concentrations of a large group of VOCs which we have

loosely termed fatty acid oxidation products (Figs. S3 and S4). These include the classic C_6 green leaf volatiles and their acetate esters (hexanal, 3-hexen-1-ol acetate, hexyl acetate) but more generally, C_2–C_{18} alkenes, aldehydes, ketones, alcohols, and acetate esters. Therefore, emissions of these VOCs may derive from enzymatic reactions (lipoxygenase) or non-enzymatic reactions (reactions with ROS). Although the branches were not under any obvious mechanical or herbivory stresses while in the enclosure, other abiotic stresses may have been present such as elevated light and temperature typical of noon time conditions. We suggest that one possible role for the oxidation of fatty acids is the protection of creosotebush from oxidation by ROS generated during metabolism at high temperatures, exposure to UV light, and atmospheric oxidants like ozone. In addition, the presence of these compounds in the resin likely contributes to an increase in water use efficiency.

4 Conclusions

Although desert ecosystems are generally considered small sources of reactive hydrocarbons in the atmosphere, we find substantial branch-scale emissions of a wide variety of compounds from creosotebush which were also detected in the ambient air above the canopy. Additional research to quantify ecosystem-scale VOC fluxes, preferably over a full annual cycle, is needed to understand the impact that these emissions may have on regional air quality and climate. Previous research on creosotebush VOC emissions have reported no isoprene emissions, but with significant monoterpene, sesquiterpene, and oxygenated VOC emissions. During CREATIVE 2009, we observed large branch emission rates of a wide range of VOCs including volatile isoprenoids (including isoprene), oxygenated VOCs, aromatics, sulfides, nitriles, and fatty acid oxidation products. Emissions and ambient concentrations followed ambient temperature and light and displayed strong diurnal patterns with maxima during midday. Unlike other field sites where volatile isoprenoids are the dominant compounds released, average emissions from creosotebush are divided roughly equally into oxygenated VOCs, volatile isoprenoids, and fatty acid oxidation products + aromatics + sulfides + nitriles. Several new compounds of biogenic origin including 1-chloro-2-methoxybenzene and isobutyronitrile are reported here for the first time. Emissions of nitriles from creosotebush represent a significant loss of nitrogen from desert ecosystems that may reinforce nitrogen limitations in desert environments. While aromatic compounds in the atmosphere are generally considered to be of anthropogenic origin, the wide array of aromatic and phenolic VOCs emitted by creosotebush suggests that this assumption needs to be revisited in certain ecosystems. We also provide the first primary emission rate estimates of isoprene together with its three oxidation products 3-methyl furan, methyl vinyl ketone, and methacrolein. Together with primary emissions of a wide group of compounds we have roughly classified as fatty acid oxidation products, these observations provide the first direct evidence that volatile isoprenoids and fatty acids may function as antioxidants in plants.

Of potential significance for the formation of cloud condensation nuclei, we found that maximum dimethyl sulfide emissions from creosotebush are higher than reported from any plant. Creosotebush emissions may be higher than other reported species in part because of the high ambient temperatures and solar insolation experienced during the summer in the desert southwest, but also because of their potential protective roles against abiotic and biotic stresses (herbivory, UV light, desiccation, oxidants). Some of these stresses may not be as severe in plants growing in cooler, non-water limited ecosystems. However, because branch enclosures may induce physiological stresses in some plants, our branch emission rate measurements should be considered as an upper limit.

In conclusion, given its vast distribution in North America, additional research is needed to understand the physiological, ecological and atmospheric impacts of creosotebush VOC emissions. For example, more research is needed to understand the relationship between abiotic stress and ROS/VOC metabolism and to understand the potential influences of summer monsoons and winter frontal storms on creosotebush VOC emissions and their potential impact on air quality and precipitation dynamics.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/10/12191/2010/acp-10-12191-2010-supplement.pdf.

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