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Biogenic volatile organic compound emissions from desert vegetation of the southwestern US

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Abstract

Thirteen common plant species in the Mojave and Sonoran Desert regions of the western US were tested for emissions of biogenic non-methane volatile organic compounds (BVOCs). Only two of the species examined emitted isoprene at rates of $10\,\mu g\,C\,g^{-1}\,h^{-1}$ or greater. These species accounted for $<10\%$ of the estimated vegetative biomass in these arid regions of low biomass density, indicating that these ecosystems are not likely a strong source of isoprene. However, isoprene emissions from these species continued to increase at much higher leaf temperatures than is observed from species in other ecosystems. Five species, including members of the *Ambrosia* genus, emitted monoterpenes at rates exceeding $2\,\mu g\,C\,g^{-1}\,h^{-1}$. Emissions of oxygenated compounds, such as methanol, ethanol, acetone/propanal, and hexanol, from cut branches of several species exceeded $10\,\mu g\,C\,g^{-1}\,h^{-1}$, warranting further investigation in these ecosystems. Model extrapolation of isoprene emission measurements verifies recently published observations that desert vegetation is a small source of isoprene relative to forests. Annual and daily total model isoprene emission estimates from an eastern US mixed forest landscape were 10–30 times greater than isoprene emissions estimated from the Mojave site. Monoterpene (and possibly oxygenated terpene and sesquiterpene) emissions may be more comparable, as annual forest terpene emission model estimates were 3–8 times greater than those from the Mojave Desert, and were within a factor of 2 for peak summertime fluxes. Primary productivity and leaf biomass of desert ecosystems are very dependent on annual precipitation, and our model results indicate that there can be at least a three-fold difference in total annual BVOC emissions between dry and wet years. We recommend additional studies of desert plant BVOC emissions, especially those that focus on sesquiterpenes, oxygenated compounds, and the effects of soil moisture, temperature, humidity, and seasonality. Landscape flux studies are needed to test BVOC model estimates and to verify BVOC influences on regional atmospheric chemistry.
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Keywords: Isoprene; Monoterpene; Biogenic volatile organic compounds; Leaf temperature; Photosynthetically active radiation; Emission factor; *Larrea tridentata*; *Ephedra nevadensis*; *Ambrosia dumosa*; *Ambrosia deltoidea*

1. Introduction

Biogenic sources of non-methane volatile organic compounds (BVOCs) exceed anthropogenic sources by approximately an order of magnitude on a global

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basis. The importance of these compounds is amplified by their high reactivity with ozone and the hydroxyl radical compared to most anthropogenic VOCs. It is estimated that over 90% of BVOC emissions are from vegetation (Guenther et al., 1995). Most measurement and modeling studies have focused on forest ecosystems, with a lesser emphasis on grassland, agricultural, and savannah ecosystems (Guenther et al., 1995, 1999, 2000). Arid and semi-arid ecosystems (those receiving <30 cm of precipitation yr^{-1}), on the other hand, have received very little study. Although foliar biomass density of arid ecosystems is low compared to forest systems (Box, 1981), they occupy ~40% of the Earth's terrestrial surface area (Jordan et al., 1999) and typically receive abundant sunshine and warm temperatures throughout much of the year. Here, we present BVOC emission measurements from the most abundant plant species near Tucson, AZ and Mercury, NV, USA. BVOC emission rates (in $\mu g\,C\,g^{-1}\,h^{-1}$) are measured at leaf temperatures of 30–55 °C and photosynthetically active radiation (PAR) of 0–2500 $\mu mol\,m^{-2}\,s^{-1}$. Emission models and comparisons with BVOC emission estimates from eastern US forests are also discussed.

2. Methods

Measurements were conducted on 26–29 April 1999 at the Shoe Box Ranch (32°E18′N, 111°E4.5′W, 860 m above sea level—ASL) in the Sonoran Desert ecosystem near Tucson, AZ. The shrubland community includes mesquite (*Prosopis*) species and primary associated shrub species include creosote (*Larrea tridentata*) and triangle-leaf bursage (*Ambrosia deltoidea*). Annual rainfall is ~28 cm, about half of which falls from July to September. Mean daily maximum air temperatures during this 3-month period are ca. 40 °C, with soil surface temperatures often reaching well over 50 °C. During 14–18 November 2000, additional measurements were taken ~30 km to the north of the Tucson site at the Biosphere II Research Facility near Oracle, AZ. On 22–23 June and 8–9 September 1999, measurements were conducted at the Nevada Desert Free Atmospheric carbon dioxide (CO_2) Exchange Facility (NDFF) near Mercury, NV in the Mojave Desert (36°E49′N, 115°E55′W, 965–970 m ASL). The shrub community was characterized as a *Larrea–Ambrosia–Lycium* species complex (Jordan et al., 1999). Annual precipitation is ~8 cm, and occurs mostly as rainfall during the winter months. Mean summertime daily maximum air temperatures reach ~40 °C, with peaks as high as 48 °C.

2.1. Leaf measurements

Desert plant gas exchange was monitored with a Li-Cor 6400 (Li-Cor Inc., Lincoln, NE) gas exchange measurement system. Two cuvettes were employed, one with a red/blue light source and a $2\times3\,cm^2$ aperture, the other a clear polycarbonate chamber with a $5\times7.5\,cm^2$ aperture (Li-Cor 6400-05 Conifer chamber). The latter was lined with Teflon film and allowed ambient light to pass through the chamber to the enclosed plant. The Li-Cor 6400 system measures water vapor (H_2O) and CO_2 exchange from leaf surfaces with infrared gas analyzers (IRGAs) and allows control of PAR, leaf and air temperature, humidity, CO_2 concentration, and airflow over the plant tissue enclosed in the cuvette. Ambient purge air was drawn by the gas exchange system 2–3 m from the plant being analyzed. This air was passed through a 2-L plastic mixing vessel at a flow rate of 300 $\mu mol\,s^{-1}$ (resulting in a mixing time of ca. 5 min) to help stabilize ambient concentrations of isoprene and CO_2. A three-way Teflon valve was installed to direct exhaust air to either the LI-6400 reference and sample IRGAs (for CO_2 and H_2O analyzer matching purposes) or to chemical analyzers or collection vessels.

Tedlar branch (4 L) enclosures were also used to screen species in the area around Biosphere II. Branches were enclosed for 10 min, after which 2.55 L of air in the enclosure was drawn into evacuated Summa electropolished stainless-steel canisters which were pressurized to 30 psi. Ambient air was used in the static outdoor enclosures and reactive terpene and sesquiterpene emission estimates derived from this technique may be lower than reported. These samples were transported back to the Oregon Graduate Institute Laboratory of Dr. Rei Rasmussen. Tenax cartridges (Greenberg et al., 1999) were also used to collect vegetation enclosure (from the LICOR 6400) and ambient air samples. These were placed in cold storage (−30 °C) immediately after sampling and shipped to NCAR and EPA laboratories for analyses.

2.2. Analytical

Samples contained in *Summa* stainless-steel electropolished canisters were analyzed for C_2–C_{15}

BVOC by gas chromatograph (GC)/mass spectrometer (MS) methods described in Khalil and Rasmussen (1992). Adsorbent cartridges sample tubes using Carbotrap (350 mg) and Carbosieve S-III (180 mg) were analyzed for light oxygenated compounds ($<C_5$) as described in Baker et al. (2001). The methods described by Greenberg et al. (1999) were applied for adsorbent tube sampling and analysis of C_2–C_{11} hydrocarbons. In situ isoprene analyses were conducted using a Photovac Voyager (Perkin-Elmer, Norwalk, CT) portable GC with a photoionization detector (PID). This system was used at the NDFF and Biosphere II to quantitatively screen plants for isoprene emission. The system is very similar to that deployed by Geron et al. (2002). A pump in the GC drew cuvette exhaust air at 200 mL min^{-1} through a 0.5 mL sample loop for 10 s. Gas in the sample loop was injected onto a 0.53 mm i.d. CP-Sil-5 column 10 m in length. Column temperature was isothermal at 60 °C. Zero (hydrocarbon-free) air was used as the carrier gas. The carrier gas flow through the column was reversed after the isoprene eluted. By back-flushing the column, later eluting compounds were prevented from interfering with subsequent analyses. The system was calibrated against a standard containing 460 ± 2 ppb (v/v) isoprene in air (Scott Specialty Gases Inc., Plumsteadville, PA). The standard was referenced to the flame ionization detection (FID) response of a GC (Model HP5890, Hewlett-Packard Inc., Avondale, PA) which was calibrated to a National Institute of Standards and Technology (NIST) propane standard (SRM 1660a, 3 ppm propane in air, Rochester, NY). The Voyager portable GC/PID instrument was calibrated to concentrations of 0, 4, 23, 46, 100, 230, and 460 ppb (v/v) using a dynamic gas calibration system (Model 146, Thermo Environmental Instruments Inc., Franklin, MA). The detector output was linear from 0 to 460 ppb v/v isoprene concentration with an intercept through zero. We estimate that both precision and accuracy were within 2–5% as determined by repeated measurements of the standard gas at these concentrations. The lower detection limit of our analytical system is 1–2 ppb v/v for isoprene. Ambient air samples were drawn through the gas exchange system prior to enclosing a leaf in the cuvette to determine ambient contributions to measured leaf isoprene emissions. Ambient isoprene concentrations were <1 ppb v/v which was verified by other analytical systems cited previously. The PID system was also used to qualitatively screen plants for monoterpene emission.

In addition to sampling intact plants in field settings, shoots of desert plants near Biosphere II were cut and stems placed in flasks of distilled water. The foliated portion of the shoot was then enclosed in the Teflon lined conifer chamber of the LI-6400 and illuminated using two white light sources which generated PAR levels of 400–700 μmol m^{-2} s^{-1}. BVOC emission measurements from these plants were performed by porting the Li-Cor 6400 cuvette exhaust to a proton transfer reaction–mass spectrometer (PTR–MS) system which allows for on-line monitoring of the concentrations of VOCs. The system and analytical procedure have been described earlier (Lindinger et al., 1998). The air to be investigated was sampled with a pumping speed of 0.2 l min^{-1} through a Teflon line of 1 mm i.d., from which a small fraction of ca. 15 STP cm^3 min^{-1} was led into the PTR–MS system. The response time of the system is ca. 0.1 s. Lower detection limits for this system are on the order of 20 ppt v/v for isoprene and monoterpenes and oxygenated compounds, such as methanol and acetone.

Following enclosure of vegetation, purge samples were taken to test "carryover" or residual terpene content remaining in the chamber or sampling lines. This appeared to be a minimal problem, although occasionally oxygenated terpenes and small amounts (5–20% of direct plant emission) of *d*-limonene were detected. Following an enclosure emission sample of *Larrea tridentata*, the oily foliage of this plant was intentionally rubbed on the chambers walls to test the maximum residual effect. Camphene levels were ~10% of those in emission samples, while *d*-limonene concentrations were comparable to those from enclosed plants. This suggests that caution must be used when using emission rates from enclosure experiments, as has been discussed previously by Juuti et al. (1990) and Arey et al. (1995). Since we were careful to minimize disturbance and contact with the enclosed plants, these effects are thought to be minor in this study. However, for some plant species with heavily branching architecture and oily surfaces, such as *Hymenoclea salsola* and *Chrysothamnus nauseosus*, disturbance was inevitable and its effects could be more substantial, resulting in elevated emission rates of mono- and sesquiterpenes compared to natural conditions. When ambient purge air was used in these chamber blank tests, the aldehydes

non-anal and decanal were present at levels lower than those detected in plant emissions. No 6-methyl-5-hepten-2-one was detected in the majority of these tests, although small amounts were found in a few blanks. We have found that ambient ozone is strongly reduced by the pump of the LI-6400, thereby reducing ozone exposure of the enclosed plant.

Leaf BVOC emission sampling was initiated after allowing leaf gas exchange (internal CO_2 concentration, photosynthesis, and stomatal conductance) to stabilize. This usually occurred within 2–10 min of enclosure. Ambient air samples were drawn from the sample line downstream from the mixing vessel before leaf measurements were performed on a given plant species. Only samples on intact foliage in the field were taken at the SBR and NDFF sites. Both in situ measurements as well as investigations on cut shoots were performed at the Biosphere II. The latter were analyzed in a Biosphere II laboratory. Leaf mass per unit leaf area was determined on the enclosed leaves. The area of these leaves was measured within a few hours after harvest using an LI-3000a leaf area scanner (Licor Inc. Lincoln, NB, USA). These leaves were then dried at 80 °C for 48 h and weighed. Leaf mass per unit leaf area ($g\,m^{-2}$) was then determined by dividing the dry leaf mass by the area.

BVOC emission rate E ($nmol\,m^{-2}\,s^{-1}$) was calculated as

$$E = f(C_o - C_i)m^{-1}, \quad (1)$$

where f is the flow rate ($mol\,s^{-1}$) into the cuvette, C_o and C_i are the outlet (exhaust air) and inlet BVOC concentrations ($nmol\,mol^{-1}$), respectively, and m is the enclosed dry leaf mass (g). As each BVOC emission sample was being drawn from the cuvette exhaust, leaf environment and gas exchange data were logged with the gas exchange system.

2.3. BVOC emission model

Leaf-level VOC fluxes measured at NDFF were extrapolated to the ecosystem scale for the surrounding Mojave Desert environment using modeling methods similar to those of Guenther. The mean above-ground biomass density of $166\,g\,m^{-2}$ (dry weight) used here is from litterfall studies of the eight NDFF circular plots summarized by Zitser et al. (2000). (http://130.199.4.11/FACE_Site_Data_Archive/FACESites/DesertFace.htm). These plot biomass densities ranged from 119 to $222\,g\,m^{-2}$. We performed BVOC emission measurements on genera which account for 82% of the above-ground plant biomass found on these plots. Biomass statistics for individual species are given in Table 1. The leaf fraction of total above-ground biomass varies strongly with precipitation. Hydrologic year 1998 (1 October 1997 to 31 September 1998) was much wetter than normal, and the leaf fraction of total above-ground biomass for *Larrea tridentata* and *Ambrosia dumosa* was ~0.35 and 0.15, respectively. For 1998, we use a mean fraction of 0.25 for all other species except *Chrysothamnus nauseosus*, *Ephedra nevadensis*, and *Hymenoclea salsola*, to which we assign a value of 1.0 consistent with the emission rate measurements, where the entire above-ground portion of the plant was similar in composition to the enclosed sample. Conversely, 1999 was drier than normal, and the above-ground leaf biomass fractions were roughly 0.20 and 0.08 for the mean plant size of *Larrea tridentata* and *Ambrosia dumosa*, respectively, on the NDFF plots. For 1999, we use a mean fraction of 0.15 for all other species except *Chrysothamnus nauseosus*, *Ephedra nevadensis*, and *Hymenoclea salsola*. The vegetation cover is apportioned into species-level foliage quantities according to these ratios and above-ground biomass from the NDFF plots for both 1998 and 1999. Basal isoprene emission rates for emitting species are 10 and 35 $\mu g\,C$ (g-foliar dry mass)$^{-1}\,h^{-1}$ standardized for PAR values of $1000\,\mu mol\,m^{-2}\,s^{-1}$ and leaf temperatures of 30 °C as determined by the isoprene measured from *Ephedra nevadensis* and *Psorothamnus fremontii*, respectively (Table 2). For other species found at the site, a basal isoprene emission factor of ~0.1 $\mu g\,C\,g^{-1}\,h^{-1}$ was observed. Based on our emission measurements and the NDFF species composition for this site, 28% (of the $34\,g\,m^{-2}$ of the estimated leaf dry mass) emits significant isoprene resulting in a site average basal isoprene emission factor of about $3\,\mu g\,C\,g^{-1}\,h^{-1}$, or $106\,\mu g\,C\,m^{-2}\,h^{-1}$ for the estimated 1998 and 1999 average foliar density and plant composition at the NDFF site. Individual results for the years 1998 and 1999 are discussed later.

Emission factors for acetone ($0.09\,\mu g\,g^{-1}\,h^{-1}$) and methanol ($0.6\,\mu g\,g^{-1}\,h^{-1}$) are derived from Guenther et al. (2000) and are applied to all plant species. Emissions of these compounds are highly uncertain and may be strongly influenced by factors, such as leaf age, stress, herbivory, or mechanical disturbance. They are thought to be especially

Table 1
Above-ground biomass by plant species at the Nevada Desert FACE facility

Species	Freq.	Density	Std.dev.	Pct.	FDens.
Acamptopappus shockleyi	8	1.32	1.15	0.794	0.1–0.3
Achnatherum hymenoides	8	0.36	0.23	0.217	0.03–0.09
Ambrosia dumosa	8	11.9	10.30	7.14	0.6–1.8
Argemone corymbosa	2	0.003	0.0042	0.002	0.001–0.0003
Atriplex canescens	2	0.030	0.0205	0.018	0.003–0.009
Baileya multiradiata	8	0.124	0.206	0.074	0.01–0.03
Delphinium parishii	3	0.018	0.020	0.011	0.001–0.003
Encelia virginensis	1	0	—	0	Not Quantified
Ephedra nevadensis	8	9.22	8.12	5.54	4–12
Eriogonum inflatum	6	1.68	3.94	1.01	0.2–0.6
Erioneuron pulchellum	8	0.009	0.008	0.006	0.001–0.003
Grayia spinosa	3	0.715	0.241	0.430	0.06–0.18
Hymenochlea salsola	1	1.96	—	1.18	0.7–2.1
Krameria erecta	8	13.1	13.8	7.89	1.2–3.6
Krascheninnikovia lanata	8	2.50	2.47	1.50	0.3–0.9
Larrea tridentata	8	38.0	8.93	22.8	5–15
Lycium andersonii	8	38.1	16.0	22.9	4–10
Lycium pallidum	8	21.8	14.0	13.1	2–6
Mirabilis pudica	5	1.13	1.11	0.678	0.1–0.3
Opuntia basilaris	3	0.027	0.0093	0.016	0.2–0.4
Opuntia echinocarpa	5	0.016	0.0131	0.009	0.1–0.2
Opuntia ramosissima	4	0.206	0.128	0.124	0.1–0.2
Pleuraphis rigida	8	19.9	10.2	11.9	2–6
Polygala subspinosa	7	1.10	1.03	0.662	0.1–0.3
Psorothamnus fremontii	6	2.61	3.26	1.57	0.2–0.6
Salazaria mexicana	1	0.336	—	0.202	0.03–0.09
Sphaeralcea ambigua	4	0.001	0.0025	0.001	0.0001–0.0003
Sphaeralcea grossulariaefolia	2	0.033	0.0460	0.02	0.003–0.009
Stephanomeria pauciflora	5	0.073	0.118	0.044	0.006–0.018
Thamnosa montana	1	0.212	—	0.13	0.02–0.06

Freq. is the number of plots inhabited by each species. Density is the mean above-ground total biomass ($g\,m^{-2}$) for each species, Std.dev. is the standard deviation (between plots) of the above-ground total biomass ($g\,m^{-2}$) for each species, Pct. is the percentage of the total above-ground biomass composed by each species among the eight plots, and FDens. is approximate range in foliage biomass density (dry weight) in $g\,m^{-2}$ for extremes in meteorological year precipitation.

influenced by phenological stage, with highest emissions from young expanding foliage (Guenther et al., 2000). Emission of methanol is assumed to be influenced by PAR in a manner similar to isoprene, while acetone emission is allowed to increase exponentially with increasing leaf temperature (Guenther et al., 1993, Eq. (5)). We measured emissions of acetone and methanol considerably higher than the factors cited above (discussed later); however, the plants studied were cut branches placed in water which likely influenced the emission rates of these compounds. Nonetheless, the emission factors applied in this model may be lower limits.

The empirical algorithms of Guenther were used to adjust emission rates to ambient PAR and temperature conditions. Parameters for the leaf temperature effect on isoprene emission were derived from the data shown in Fig. 1, as discussed later. Direct beam and diffuse fractions of measured total above-canopy PAR and sunlit/shaded fractions of leaf area were estimated using the techniques described in Guenther et al. (1995). Since the plant canopy was very sparse and the dry crustal soils very reflective, shading at lower levels within the plant canopy is considered to be negligible. Leaf temperatures were calculated from above-canopy radiation, temperature, relative humidity, and wind speed values using iterative methods described in Guenther et al. (2000). Calculated leaf temperatures were typically within 1.5 °C of ambient air temperatures. Hegazy and El Amry (1998) found that foliage of desert vegetation was often warmer than ambient air during winter months except during midday, when slight cooling occurred. Maximum

Table 2
Summary of plant family, genus, and species screened, location sampling/analytical methods used

Family	Species	# Plants	Location	Environ.	Enclosure	Detection
Asteraceae	*Ambrosia deltoidea* (Torrey) Payne	5	AZ	I, C	RA, RB, TB	FM, PI, PT, SI
Asteraceae	*Ambrosia dumosa* (A. Gray) Payne	2	NV	I	RA, RB	FM, PI, SI
Fabaceae	*Artemisia tridentata* (A. Gray)	1	AZ	C	RB	FM
Chenopodiaceae	*Atriplex canescens* (Purch) Nutt.	3	AZ, NV	I, C	RA, RB, TB	FM, PI, PT, SI
Compositae	*Chrysothamnus nauseosus* (Pallas ex Pursh) Britt.	2	AZ, NV	I	RA, RB	FM, PI, SI
Compositae	*Encelia farinosa* (A. Gray)	1	AZ	I	TB	FM
Ephedraceae	*Ephedra nevadensis* (S. Watson)	2	NV	I	RB	FM, PI, SI
Asteraceae	*Hymenoclea salsola* (Torrey & A. Gray)	2	AZ, NV	I,C	RA, RB, TB	FM, PI, PT, SI
Krameriaceae	*Krameria erecta* (Willd. Ex J.A. Schultes)	2	NV	I	RA, RB	FM, PI, SI
Zygophyllaceae	*Larrea tridentata* (Moc. amd Ses.) Coville	6	AZ, NV	I,C	RA, RB, TB	FM, PI, PT, SI
Solanaceae	*Lycium andersonii* (A. Gray)	2	NV	I	RA, RB	FM, PI, PT, SI
Fabaceae	*Olneya tesota* (A. Gray)	1	AZ	I	RB	PI
Fabaceae	*Psorothamnus fremontii* (Torrey) Barneby	2	NV	I	RA, RB	FI, FM, PI, SI

Enclosure type is indicated as: RA, rigid transparent cuvette with ambient light; RB, rigid enclosure with artificial red/blue or white light; and TB, Teflon bag with ambient light. Methods of detection and quantitation are denoted by: FI, ozone chemiluminescent fast isoprene detection; FM, gas chromatography/flame-ionization/mass spectroscopy; PI, gas chromatography/photo-ionization; PT, on-line proton-transfer mass spectroscopy; and SI, gas chromatography/selected-ion mass spectroscopy. Environ denotes measurement environment of I (in situ) or C (cut branch in laboratory environment).

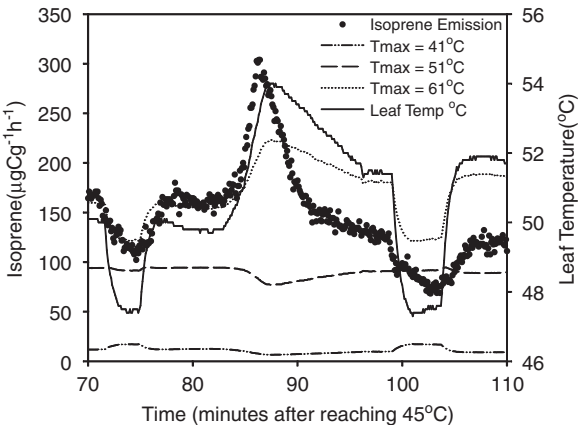

Fig. 1. Response of *Psorothamnus fremontii* isoprene emission (determined using the FIS) to changing leaf temperature. Leaf temperature was maintained at >45 °C for 70 min prior to collection of the data shown. Also shown are the temperature response curves from the Guenther et al. (1993) equation using T_{MAX} values ranging from 41 °C to 61 °C.

differences were at night and sometimes approached 10 °C. They found leaves to be cooler than ambient air during summer months, although differences were minimal (1–5 °C) during midday and greater at night (up to 8 °C). These differences were caused by morphological and physiological characteristics of the leaves. Crustal soils in these environments can be 20 °C higher than air temperatures above, which may affect the leaf temperatures of the low lying vegetation, although Gates et al. (1968) found this effect to be small for most plant species. Considered together, these effects would tend to negate each other, especially during the midday hours, although the net effects are very uncertain. The leaf age activity factors, ratio of current to peak foliar density, and escape efficiency factors described in Guenther et al. (2000) are incorporated here. These factors probably have minimal effect on net estimated flux (ca. 5–10%) since leaf senescence and litterfall appear to be fairly uniformly distributed throughout the year, although small peaks in litterfall may be observed during very dry foresummers for some species in the Mojave Desert (Strojan et al., 1979). Surface PAR, temperature, wind speed, and relative humidity measurements from the NDFF were used as inputs to the model to estimate hourly BVOC emissions.

3. Results and discussion

3.1. Plant-scale BVOC emissions

Creosote bush (*Larrea tridentata*) is one of the most widespread and abundant species in the

semi-arid regions of the southwestern US. This genus has been the subject of extensive phytochemical study because external leaf resins compose 10–15% of the dry weight of leaves (Sakakibara et al., 1976). These resins are composed of nodirhydroquaeiretic acid (a powerful antioxidant), kaempferol and quercitin (plant growth inhibitors and UV absorbers) and a variety of C_{15} and heavier compounds. However, little information is available concerning more volatile compounds from this genus. We found negligible isoprene emission rates from this species, but significant monoterpene emissions of ca. $2.0\,\mu g\,C\,g^{-1}\,h^{-1}$. The dominant compounds were *d*-limomene, α-pinene, and camphene, with lesser amounts of β-pinene, myrcene, and γ-terpinene (Table 3). Knowlton et al. (1999) also observed a similar mix of monoterpenes emitted from *Larrea tridentata* in New Mexico. They report somewhat lower emission rates (at lower temperatures), but these are within the limits of uncertainty in the respective data sets. The sesquiterpene β-caryophyllene was emitted from this species at rates ranging from 0.5 to $2\,\mu g\,C\,g^{-1}\,h^{-1}$. Mass spectra of emissions from this species also indicated the presence of its oxidation product caryophyllenyl alcohol. Lesser amounts of a second sesquiterpene, eluting in the region of α-caryophyllene, were also detected.

Some samples indicate a significant emission of 6-methyl-5-hepten-2-one, which has been previously identified as a possible product of O_3 reaction with leaf cuticular waxes (Fruekilde et al., 1998). We quantitatively removed ozone and background VOC from the purge air of one *Larrea tridentata* emission sample using an activated carbon filter. *Z*-β-ocimene was the most abundant terpene in this sample, and its concentration was over 10 times greater than *d*-limonene, the next most abundant monoterpene, indicating that complete O_3 removal may have allowed increased recovery of this highly reactive compound. 6-methyl-5-hepten-2-one was also not detected, suggesting that its production may indeed be O_3 limited. Mass spectra data for *Larrea tridentata* emission also indicated substantial emission of 2-ethyl-1-hexanol. Peaks eluting in the regions of oxygenated terpenoids camphor, linalool, and β-terpineol were also observed, and were confirmed by mass spectrometry. These peaks were approximately equivalent to those of the monoterpenes, indicating that oxygenated terpenes may be significant from this species. However, smaller peaks in these regions were sometimes detected in sample blanks, and further interference from co-eluting contaminants from the silicon oils used in the LI-Cor 6400 gas exchange system further complicates quantitation of these compounds. Knowlton et al. (1999) found that creosote bush emitted formic and acetic acids (0.6 and $0.7\,\mu g\,g^{-1}\,h^{-1}$, respectively) as well as significant emissions of formaldehyde ($3.1\,\mu g\,g^{-1}\,h^{-1}$). Acetaldehyde emissions were not detected from this species by Knowlton et al. (1999), but we observed it to be emitted at rates of ca. $1\,\mu g\,g^{-1}\,h^{-1}$. Acetaldehyde emissions are typically dependent on the ambient air vs. internal leaf concentrations, which determine an emission compensation point that varies with environmental conditions, such as

Table 3
Summary of BVOC emission rates ($\mu g\,C\,g^{-1}\,h^{-1}$, standard error in parentheses) adjusted to leaf temperature of 30 °C and PAR of $1000\,\mu mol\,m^{-2}\,s^{-1}$ using algorithms of Guenther et al. (1993)

Species	Isoprene	α-Pinene	β-Pinene	Camphene	Myrcene	*d*-Limonene	Γ-Monoterpenes
Ambrosia deltoidea	<0.1	0.06 (0.02)	0.31 (0.18)	0.51 (0.18)	2.3 (1.1)	1.0 (0.32)	4.1 (1.6)
Ambrosia dumosa	<0.1	1.6 (0.93)	3.0 (1.5)	0.06 (0.03)	1.1 (0.82)	2.0 (0.87)	7.9 (3.4)
Atriplex canescens	<0.1	0	0	0.17 (0.17)	0.13 (0.12)	0	0.31 (0.29)
Chrysothamnus nauseosus	<0.1	0.28 (0.28)	0	0	0.16 (0.16)	0.21 (0.02)	0.65 (0.46)
Ephedra nevadensis	10 (4.0)	0.05 (0.01)	0.03 (0.017)	0.01 (0.006)	0.09 (0.06)	0.11 (0.06)	0.30 (0.04)
Hymenoclea salsola	<0.1	1.4 (0.31)	0.06 (0.06)	0.02 (0.02)	0.35 (0.26)	0.30 (0.30)	2.6 (0.57)
Krameria erecta	<0.1	0.02 (0.02)	0.06 (0.001)	0.03 (0.003)	0.14 (0.05)	0.05 (0.003)	0.30 (0.03)
Larrea tridentata	<0.1	0.37 (0.18)	0.12 (0.04)	0.44 (0.18)	0.30 (0.13)	0.74 (0.31)	2.0 (0.48)
Lycium andersonii	<0.1	0.10 (0.03)	0.27 (0.10)	0.11 (0.01)	0.39 (0.02)	0.27 (0.06)	1.1 (0.18)
Psorothamnus fremontii	35 (10)	0.50 (0.19)	0	0	1.0 (0.24)	0.50 (0.18)	2.0 (0.2)

T_{MAX} in the temperature correction for isoprene was assumed to be 51 °C, however, data collected at temperatures below 40 °C were used in estimation of isoprene emission factors. *Encelia farinosa*, *Olneya tesota*, and *Artemisia tridentata* emissions were determined from a branch of one plant of each species and are regarded as highly uncertain due to probable high disturbance. Results are not given here but are discussed in the text.

light, temperature, nutrients, stress, etc. (Kesselmeier and Staudt, 1999). Our measurements were performed using acetaldehyde-free air and therefore might represent an upper limit. Knowlton et al. (1999) found that these oxygenated compounds were emitted as functions of light and temperature, which were reasonably well simulated using the equations and parameters of Guenther et al. (1993). Since Knowlton et al. (1999) used ambient purge air in their enclosure, compensation point dependence of acetaldehyde, acetic acid, and formic acid was probably minimized.

At the SBR site we examined possible short-term humidity effects by passing the purge air over distilled water added to the mixing chamber. This increased the relative humidity of the purge air from $<20\%$ to over 70% and induced a brief spike in stomatal conductance which quickly fell back to pre-humidified rates (within ca. 60 s). Humidification appeared to increase monoterpene emission by a factor of 2–3, without significantly affecting the relative abundance of individual terpene compounds. However, it could not be determined to what degree increased humidity may have increased monoterpene recovery efficiency from our sampling/analytical systems. The humidified emission rates were not included in estimation of the basal emission factors. However, Dement et al. (1975) found similar humidity effects on camphor emissions from live and dead branches of California black sage (*Salvia mellifera*). Schade et al. (1999) also observed increases in monoterpene emission from *Pinus ponderosa* with increasing relative humidity. Diem (2000) attributed humidity induced increases in BVOC emissions during the summer monsoon season to transition from VOC dependence of O_3 production to a NO_X limited O_3 production regime in the Tucson area. The late April measurements from *Larrea tridentata* are prior to the July/August monsoon season and may represent conditions conducive to terpene emission response to humidity in some of these species. More work is needed on the effects of changing humidity on BVOC emissions in semi-arid regions, as this is suspected to impact ambient VOC reactivity and possibly air quality (Diem, 2000). Emissions of methanol were substantial from a cut branch of *Larrea tridentata* examined at the Biosphere II facility (Fig. 4a). These emissions were detected using the PTR–MS, and the identity of methanol was confirmed qualitatively using GC/MS. Methanol emissions appeared to be highly correlated with stomatal conductance, which has also been observed in other species. Significant emissions of ethanol and a compound tentatively identified as 1,8-cineole were also detected from the cut branch.

Triangle-leaf bursage (*Ambrosia deltoidea*) is also a dominant plant species in the arid southwestern US. We measured negligible isoprene emission rates from this species in the field, as did Rasmussen (1978). However, a significant signal at AMU 69, which was later confirmed to be protonated isoprene, was detected in emissions from a cut branch examined indoors at the Biosphere II facility (Fig. 4a). Peak emissions ranged from 10 to $15\,\mu g\,C\,g^{-1}\,h^{-1}$ and were at least an order of magnitude greater than isoprene emissions measured from other *Ambrosia deltoidea* plants examined in situ using other techniques. Standardized monoterpene emissions of $4.1\,\mu g\,C\,g^{-1}\,h^{-1}$ were observed. The dominant compounds were myrcene, *d*-limomene, and camphene, while lesser amounts of β-pinene and α-pinene were also emitted (Table 3). Δ^3-carene and γ-terpinene were also detected in some samples, and in a few samples *Z*-β-ocimene was the most abundant monoterpene. At least $1\,\mu g\,C\,g^{-1}\,h^{-1}$ of the sesquiterpene β-caryophyllene was emitted from this species, and lesser amounts of a second sesquiterpene eluting in the region of α-caryophyllene, were also detected. Similar to isoprene, much larger quantities of monoterpenes (indicated by AMU 81 and 137) and sesquiterpenes (AMU 205) were detected from the cut branch sample (Fig. 4b). These emissions seemed to be largely temperature dependent (Fig. 4a and b). We speculate that placement of the cut end of the branch in water may have hydrated the plant and induced abnormally large release of these compounds. The PTR–MS measurements also indicated a very high methanol emission flux which again was highly correlated with stomatal conductance. Compounds with AMU of 59, possibly protonated acetone or propanal, were also emitted from the cut branch of *Ambrosia deltoidea* (Fig. 4a). Several samples indicate emission of 6-methyl-5-hepten-2-one at levels of ca. $1\,\mu g\,C\,g^{-1}\,h^{-1}$, but quantitative estimates of this compound are difficult to resolve due to background and blank concentrations. Significant peaks eluting in the regions of oxygenated terpenoids camphor, linalool, terpin-4-ol, and α,β-terpineol were also observed. However, as in the case of *Larrea tridentata*, smaller peaks in these regions were sometimes detected in sample blanks,

and the identification of these compounds were not consistently confirmed by mass spectra analyses of *Ambrosia deltoidea* emission samples. Knowlton et al. (1999) also noted that desert shrubs in New Mexico, which included species common to this study, often emitted several unidentified C_{10} terpenoids. NCAR GC/FID analyses indicated that significant amounts of a compound tentatively identified as 1,8-cineole was also emitted at rates equivalent to *d*-limonene. This was confirmed by GC-MS. As with *Larrea tridentata*, we also tested humidity effects on monoterpene emission. We observed no increase in monoterpene emission with the increased humidity, and likewise saw only a small increase in stomatal conductance of water vapor. This may be partly due to the fact that conductance rates were already fairly high prior to addition of humidity to the purge air stream, although previous studies have found humidity related increases in terpene emissions to be unrelated to stomatal conductance or transpiration (Dement et al., 1975).

White bursage (*Ambrosia dumosa*) is a dominant species in the drier Mojave Desert. Its smaller, scaly leaves have abundant surface glandular hairs. This species also emits abundant terpenes, but seems to emit more pinenes than *Ambrosia deltoidea* (Table 3). We found it to be an insignificant isoprene emitter, as did Rasmussen (1978).

Four-winged saltbush (*Atriplex canescens*) is a common associate of *Artemisia* in the higher elevations of the Sonoran and Mojave deserts. This species was examined for BVOC emission at NDFF and Biosphere II. We found this species to emit small amounts of monoterpenes, mostly camphene and myrcene. Knowlton et al. (1999) also found very low monoterpene emission rates from *Atriplex canescens*, mostly α-pinene and myrcene. They also noted that myrcene emissions were apparently negatively correlated with temperature. Helmig et al. (1999) reported much higher terpene emission rates from a single enclosure (cut branch) of *Atriplex canescens*, which were dominated by α-pinene. These authors also report high ($15\,\mu g\,g^{-1}\,h^{-1}$) total sesquiterpene emissions. Knowlton et al. (1999) found that saltbush emitted formic and acetic acids (0.43 and $0.35\,\mu g\,g^{-1}\,h^{-1}$, respectively) as well as formaldehyde and acetaldehyde (1.0 and $0.27\,\mu g\,g^{-1}\,h^{-1}$, respectively). These oxygenated compounds were emitted as functions of light and temperature, which were reasonably well simulated using the equations and parameters of Guenther et al. (1993). We observe similar emission rates of acetaldehyde, as well as methanol and acetone. Isoprene was identified in two of the nine samples by Knowlton et al. (1999). They attributed the observed isoprene to inadvertent placement of the sweep air inlet near a *Quercus turbinella* shrub, a strong isoprene emitter. However, we observe isoprene on some occasions from *Atriplex canescens*, but not on others under similar light and temperature conditions. Additional measurements are needed to resolve this issue. Similar to *Larrea tridentata*, ethanol emissions from cut branches were often highest of all compounds. However, excess water availability, such as in flooded soils, has been found to greatly increase plant ethanol and acetaldehyde production (Kreuzwieser et al., 2000), so these results cannot be reliably extrapolated to field conditions.

Rabbit brush (*Chrysothamnus nauseosus*) emitted fairly low levels of monoterpenes ($0.65\,\mu g\,C\,g^{-1}\,h^{-1}$). These emissions were composed of α-pinene, *d*-limonene, and myrcene (Table 3). Helmig et al. (1999) found that this species emitted $110\,\mu g\,g^{-1}\,h^{-1}$ of total BVOC, about 70 of which was monoterpenes. These were dominated by the same three compounds we quantified, and also included α-phellandrene, α-terpinene, and ρ-cymene, among others. These authors could not rule out substantial disturbance effects. They also reported $3.2\,\mu g\,g^{-1}\,h^{-1}$ of total sesquiterpenes and $0.5\,\mu g\,g^{-1}\,h^{-1}$ of acetone emission.

Burrobush (*Hymenoclea salsola*) is a common member of the family Asteraceae and is found on both the Sonoran and Mojave sites. This species colonizes disturbed sites, such as stream beds, alluvial soils, and abandoned farms. Its green twigs contribute significantly to gas exchange (Turner et al., 1995), and we enclosed twigs during our BVOC emissions measurements as well as foliage. We found *Hymenoclea salsola* to emit monoterpenes at rates of $2.6\,\mu g\,C\,g^{-1}\,h^{-1}$, the most abundant of which is α-pinene. Due to the branching architecture and oily surfaces of this species, it was difficult to rule out disturbance as a perturbing factor in the terpene emission rates.

Littleleaf ratany (*Krameria erecta*) is a member of the family Krameriaceae. It accounts for ~8% of the above-ground biomass at NDFF. We could find little evidence of previous VOC emission or essential oil study of this species. We found it to be a low emitter of monoterpenes at $0.3\,\mu g\,C\,g^{-1}\,h^{-1}$. Myrcene was the most common compound observed.

Isoprene was not detected in emissions from this species.

Fremont dalea (*Psorothamnus fremontii*), common at the NDFF, was found to emit significant isoprene. This species is in the family Papilionaceae, and Harley et al. (1999) found that the majority of genera in this family contained isoprene-emitting species, so our finding is not surprising. Emission rates determined using the LI-6400 and Voyager GC/PID measured at standard conditions ($T_L = 30\,^{\circ}C$ and PAR of $1000\,\mu mol\,m^{-2}\,s^{-1}$ in this study, to which we refer hereafter as 30/1000) were $\sim 35\,\mu g\,C\,g^{-1}\,h^{-1}$. Knowlton et al. (1999) found that the parameters of the Guenther et al. (1993) equation were not suitable for desert vegetation in New Mexico, USA, as isoprene emission continued to increase with increasing temperature to 55 °C. Using the FIS and a flow-through (dynamic) glass cuvette system, we see similar results from a *Psorothamnus fremontii* branch. After over an hour of being held at leaf temperature of 45 °C or more, isoprene rate continued to fluctuate with temperature, even when temperatures were held at 50 + °C for several minutes (Fig. 1). This indicates that the T_{MAX} parameter of the temperature algorithm is probably determined in large part by a plant's developmental environment. Pétron et al. (2001) also found that T_{MAX} varied directly as a function of growth conditions of *Quercus macrocarpa*, although this does not rule out a genetic contribution to this variability. Knowlton et al. (1999) also found that the temperature response of isoprene emission from *Quercus turbinella* in the arid lands of New Mexico was accurately reproduced using a T_{MAX} value of 61 °C. We see similar results here, as a T_{MAX} value of 61 °C seems to explain the temperature response of isoprene emission quite well (Fig. 1). Isoprene emission from *Psorothamnus fremontii* continued to increase with increasing temperature up to 54 °C and then declined as leaf temperature decreased to 48 °C. A subsequent increase in leaf temperature to 52 °C again resulted in increased isoprene emission, although emission levels were somewhat lower than when this temperature was attained 20 min earlier, which may be partly due to the artificially rapid increase in T_L induced by the glass enclosure. Fig. 2 (from minutes 120 to 130) also indicates that reducing PAR from 2000 to $1000\,\mu mol\,m^{-2}\,s^{-1}$ has the effect of reducing isoprene emission by ca. 40%, which indicates that parameters of the Guenther et al. (1993) light response equation may also be different

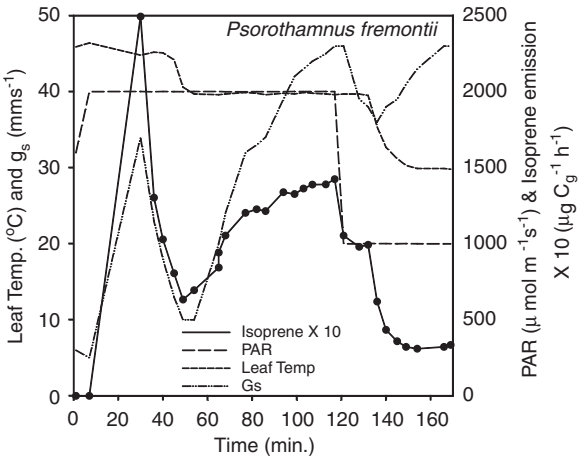

Fig. 2. Response of isoprene emission (determined using the Li-Cor 6400 and GC/PID) from a second *Psorothamnus fremontii* plant to changing leaf temperature and PAR. Early correlation of isoprene emission with stomatal conductance (g_S) may indicate foliage acclimation to the cuvette environment.

for desert plants. Substantial differences in isoprene emission response to increasing PAR above $1000\,\mu mol\,m^{-2}\,s^{-1}$ has also been documented recently in plants from other ecosystems (Guenther et al., 2000; Geron et al., 2002; Lerdau and Throop, 1999; Harley et al., 1997).

Monoterpene emissions from *Psorothamnus fremontii* were also fairly high ($2.0\,\mu g\,C\,g^{-1}\,h^{-1}$) and consisted mainly of myrcene, *d*-limonene, and α-pinene (Table 3). Light dependence of emission was tested by turning the light source off on the LI-6400 and then setting it to $2000\,\mu mol\,m^{-2}\,s^{-1}$ for two cycles. No light dependence of these monoterpene emissions was detected, and in fact on the second cycle myrcene emissions appeared to increase in the dark. As noted earlier, Knowlton et al. (1999) reported negative correlations of myrcene emissions with temperature from *Atriplex canescens*.

Mormon tea (*Ephedra nevadensis*) is widespread throughout much of the Mojave Desert. Members of the *Ephedra* genus are found throughout the southwestern US and the northern half of Mexico. Rasmussen (1978) reported five *Ephedra* species, including *Ephedra nevadensis*, to be isoprene emitters. We observed two plants to emit isoprene at a rate $10\,\mu g\,C\,g^{-1}\,h^{-1}$ at standard conditions. Light and temperature response of isoprene emission were similar to *Psorothamnus fremontii*. Isoprene emission from *Ephedra nevadensis* increased at temperatures well in excess of 45 °C. Fig. 3 also shows that decreasing PAR from 2000 to $1000\,\mu mol\,m^{-2}\,s^{-1}$

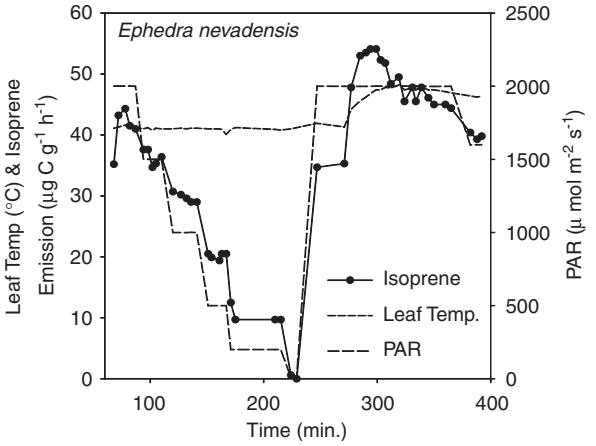

Fig. 3. Response of *Ephedra nevadensis* isoprene emission (determined using the Li-Cor 6400 and GC/PID) to changing leaf temperature and PAR.

results in a 50% decrease in isoprene emission rate, suggesting that, like *Psorothamnus fremontii*, the isoprene emission from this species is also more sensitive response to light levels above 1000 µmol $m^{-2} s^{-1}$. Monoterpene and oxygenated VOC emission rates were found to be negligible from this species.

We found that isoprene emitted in situ from *Psorothamnus fremontii* at 30 °C was equivalent to 1–2% (on a carbon basis) of measured CO_2 assimilation (A) rates. This is similar to other percentages of carbon lost as isoprene from plants in temperate and tropical environments (Geron et al., 2002; Sharkey et al., 1996). As leaf temperatures increased up to 40 °C, both *Ephedra nevadensis* and *Psorothamnus fremontii* species emitted linearly increasing amounts of isoprene (5–30%) relative to A. Thus, isoprene emission may be a substantial carbon loss from these species on hot days.

Brittlebush (*Encelia farinosa*), another member of the Compositae family, was found to be a high (6 ± 3 µg $g^{-1} h^{-1}$) monoterpene emitter by Winer et al. (1983). No isoprene emission was detected. We also detected negligible isoprene emission from this species, but very high monoterpene emission. In fact, the emission was so high as to exceed the analytical capabilities of our GC system, although we cannot rule out the possibility that physical disturbance may have influenced this observation.

Big sagebrush (*Artemisia tridentata*) emitted high levels of mono- and sesquiterpenes from a cut branch at Biosphere II. Total terpenoid emission rates exceeded 100 µg $g^{-1} h^{-1}$ and were probably influenced by cutting and enclosure as was discussed by Arey et al. (1995). Helmig et al. (1999) found that this common desert species emitted monoterpenes at rates exceeding 7 µg $g^{-1} h^{-1}$, most of which were tricyclene, camphor, 1,8-cineole, and camphene. These authors also reported total sesquiterpene emission rates of 1.3 µg C $g^{-1} h^{-1}$ as well as 0.4 µg $g^{-1} h^{-1}$ of acetone and 0.2 µg $g^{-1} h^{-1}$ of acetic acid. Arey et al. (1995) also reported high (47 ± 19 µg $g^{-1} h^{-1}$ at 30 °C) BVOC emissions from *Artemisia californica* which were dominated by ketones, alcohols, oxygenated terpenes, monoterpenes, and sesquiterpenes. They note, however, that disturbance of glandular trichomes on the leaf surfaces may influence these rates. Lu et al. (2002) found that the contents of (−)-β-pinene in juvenile *Artemisia annua* leaves and in emitted volatiles also varied in a diurnal rhythm, correlating strongly with mRNA accumulation. The presence of such controls in western North American species in this family has not been investigated, although Arey et al. (1995) speculated that diurnal variability in emission from *Artemisia californica* may be due to larger pools of VOC available for volatilization in the morning.

PTR–MS measurements of BVOC emissions from cut branch of ironwood (*Olneya tesota*), a member of the Fabaceae family, were performed at the Biosphere II facility. Fig. 4 illustrates the temporal pattern of emissions and corresponding environmental data. Methanol emission was stimulated by high temperature and increased rapidly as stomatal conductance increased. The experiments illustrated in Fig. 4 were performed to examine methanol and acetone emission variations, especially at high temperatures, and are not intended to establish emission factors. Isoprene (AMU 69) emission was also observed but, unlike *Ephedra nevadensis* and *Psorothamnus fremontii*, emission did not increase above leaf temperatures of 40 °C. This plant is indigenous to the somewhat cooler climatic regions of southern Arizona and may indeed have cooler temperature optima than the former species, which grow near the seasonally hot crustal soils in the Mojave Desert. However, the effects of cutting may also be responsible for this difference.

3.2. Ecosystem-scale BVOC emissions

Mojave Desert ecosystem litterfall and net primary productivity are strongly influenced by

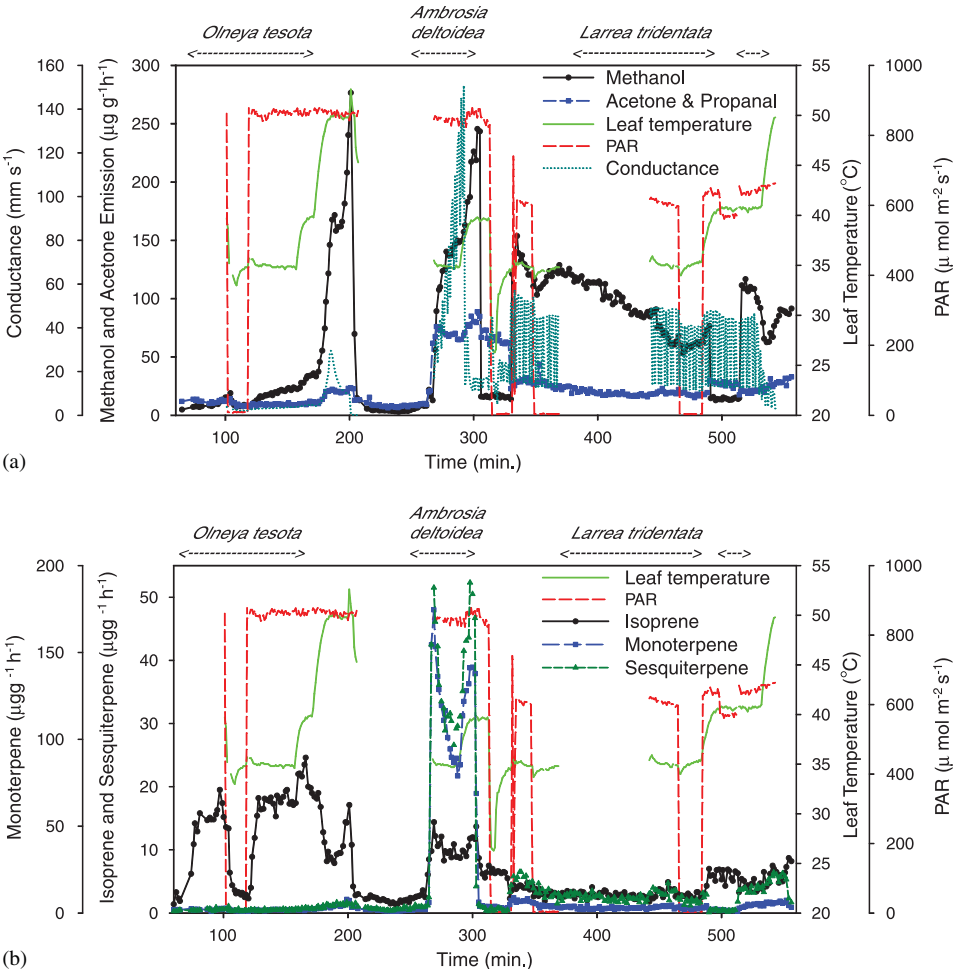

Fig. 4. PTR–MS emission data from cut branches of *Olneya tesota*, *Ambrosia deltoidea*, and *Larrea tridentata* at Biosphere II. Methanol, acetone/propanal, stomatal conductance, photosynthetically active radiation (PAR), and leaf temperature are shown in (a), isoprene, monoterpenes, and sesquiterpenes are shown in (b).

annual rainfall (Strojan et al., 1979). These authors, working in the same ecosystem a few kilometers from the NDFF, found that leaf litterfall biomass varied linearly and by more than a factor of 3 with annual precipitation total. Hydrologic year 1998 was wetter than normal (309 mm of precipitation as rain), while Hydrologic year 1999 was dryer than normal (107 mm). Our estimates of leaf biomass $48\,g\,m^{-2}$ for the wet year are consistent with $43\,g\,m^{-2}$ estimated by Strojan et al. (1979) during a year with 223 mm of precipitation. During the dry year we estimate leaf biomass of $16\,g\,m^{-2}$, Strojan et al. (1979) measured leaf litterfall of $11.4\,g\,m^{-2}$ during a year when only 62 mm of precipitation was observed. These comparisons indicate that the leaf/total above-ground biomass fractions used here produce reasonable results for hydrologic years of contrasting moisture availability.

Fig. 5 shows that the resulting variability in leaf biomass resulted in corresponding increases in isoprene and monoterpene emissions. Annual total isoprene and monoterpene emissions were 0.316 and $0.281\,g\,C\,m^{-2}\,yr^{-1}$ in 1998 and 0.117 and $0.107\,g\,C\,m^{-2}\,yr^{-1}$ for isoprene and monoterpenes, respectively, in 1999. The emissions due to increased leaf biomass dwarfed the effects of higher temperatures (mean maximum daily temperature of 22.2 °C in 1998, 24.7 °C in 1999) and PAR (annual mean of $420\,\mu mol\,m^{-2}\,s^{-1}$ in 1998 and $429\,\mu mol\,m^{-2}\,s^{-1}$ in 1999) measured at NDFF. Annual isoprene emissions were reduced by 8–9% if the PAR response function parameters of Guenther et al. (1993) were

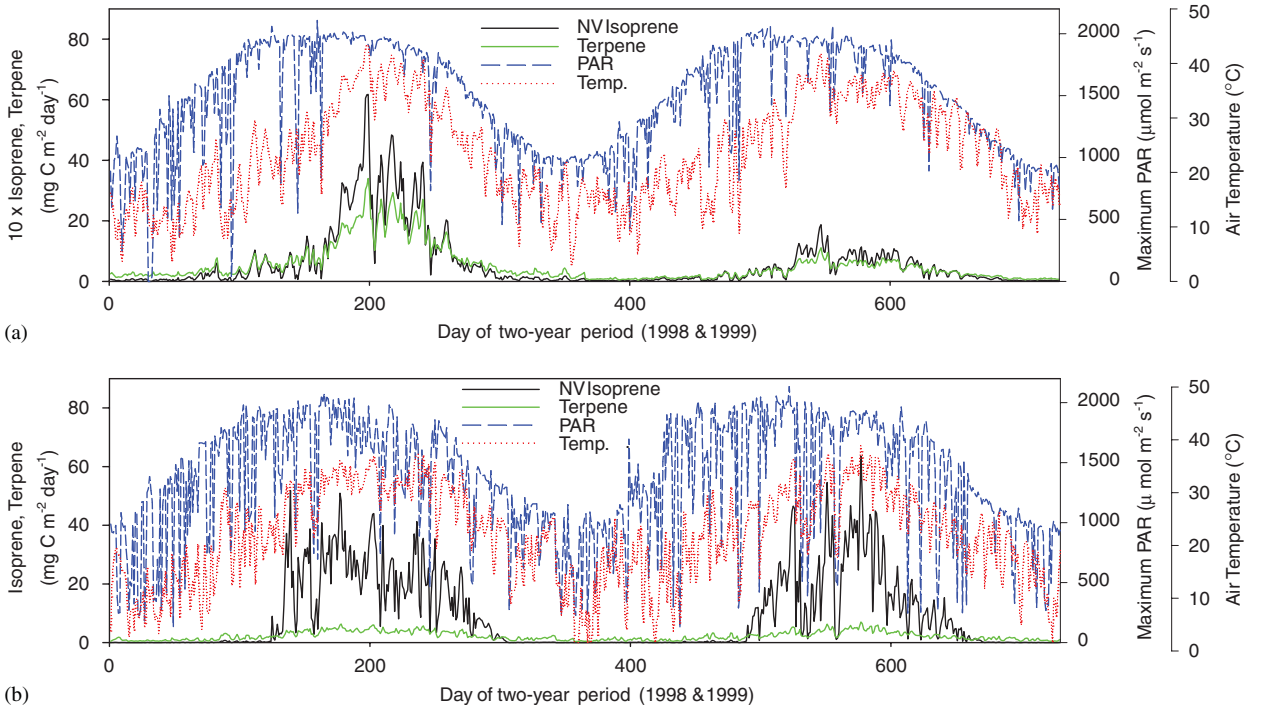

Fig. 5. Model (Guenther et al., 2000) comparison of BVOC emissions (isoprene and total monoterpene) and PAR and ambient temperature for 1998 and 1999 from (a) Mojave Desert based on emission factor, vegetation composition and density, and climate data from the NDFF (top panel) and (b) Orange County, NC based on forest composition data from Geron et al. (1994) and meteorological data from FACTS1 (bottom panel). Note the factor of 10 difference in emission scale.

used. The use of these parameters results in a smaller increase (<10%) in isoprene emission rate as PAR increases from 1000 to 2000 $\mu mol\,m^{-2}\,s^{-1}$. The temperature maximum (T_{MAX}) in the temperature correction function was set to 61 °C for the simulation presented in Fig. 5. If a value of $T_{MAX} = 51$ °C was used isoprene emissions were reduced by ~1%, however, at $T_{MAX} = 41$ °C, isoprene emissions were reduced by 17% in 1998 and 10% in 1999.

The North American model described by Guenther et al. (2000) estimated July isoprene emissions for these areas to be between 4 and 40 $mg\,C\,m^{-2}\,d^{-1}$ for mean July conditions. Our estimates for the NDFF are at or below the low end of this range. Site-specific biomass composition data are not available for the study sites near Tucson, however, since annual precipitation is 3.5 times that of the NDFF site, BVOC emissions likely are greater by a similar factor. The global BVOC emission model described by Guenther et al. (1995) estimated isoprene fluxes in the desert southwestern US of ca. 0.1–0.3 $g\,C\,m^{-2}\,month^{-1}$ for July and negligible emission in January. Our July predicted daytime average fluxes at NDFF ranged from ~0.03 to 0.1 $C\,m^{-2}\,month^{-1}$. Monoterpene emissions are predicted by Guenther et al. (1995) to range from 0.02 to 0.06 $g\,C\,m^{-2}\,month^{-1}$ for July and were again negligible in January. Our NDFF monoterpene emission estimates fell within this range, with July estimates for the wet 1998 year falling in the upper half of the range and emissions in the drier 1998 falling near the low end. Although NDFF monoterpene emissions appeared to be in better agreement with published regional and global model predictions, the estimates for both isoprene and monoterpenes were within uncertainty estimates for these models.

To compare BVOC emissions from desert ecosystems with more productive eastern US forests, we estimate daily isoprene and monoterpene emissions from NDFF and a forested county at a similar latitude in North Carolina for 1998 and 1999. Forest cover data and leaf biomass density estimates were taken from Geron et al. (1994) for Orange County, NC. The isoprene emission rates by genus of Geron et al. (1994) were updated according to Geron et al. (2001). Thirty-five percent of the forest

canopy of Orange County, NC is composed of species with high isoprene emission capacity ($70\,\mu g\,C\,g^{-1}\,h^{-1}$ at PAR = $1000\,\mu mol\,m^{-2}\,s^{-1}$, leaf temperature of 30 °C) while 65% of the canopy area is occupied by species with negligible ($0.1\,\mu g\,C\,g^{-1}\,h^{-1}$) emission capacity. These percentages are within 1% of the average values for North Carolina. We estimate that Orange County is 54% covered by forest canopy, which is ~10–15% lower than the statewide average. BVOC emissions from agriculture and non-forest ecosystems are not considered in this comparison but are thought to be negligible compared to forests in this region (Guenther et al., 2000). The methods of Guenther et al. (2000) were used to estimate isoprene and total monoterpene emissions as a function of $\frac{1}{2}$h meteorological data collected at a CO_2 exposure system similar to NDFF. This system, the free atmosphere carbon transfer scheme (FACTS1, http://c-h2oecology.env.duke.edu/Duke-Face/main.cfm), is located in Duke Forest in Orange County, NC (35.98EN, 79.09EW). The resulting emission comparison is illustrated in Fig. 5.

Estimated annual total isoprene emissions in the FACTS1 region (Orange County, NC) are 11 times higher than the NDFF total in 1998 (3.5 vs. $0.32\,g\,C\,m^{-2}\,yr^{-1}$) and 26 times higher (3.1 vs. $0.12\,g\,C\,m^{-2}\,yr^{-1}$) during 1999, the dry year at NDFF. Daily summertime peak isoprene totals ranged from 40 to $60\,mg\,C\,m^{-2}\,d^{-1}$ at FACTS1 compared to 4–6 $mg\,C\,m^{-2}\,d^{-1}$ during the wetter 1998 season. Peak estimates ranged only from 1 to $2\,mg\,C\,m^{-2}\,d^{-1}$ during the summer of 1999. Monoterpene emissions at NDFF were similar to isoprene at NDFF. Moisture driven biomass variation again determined interannual variability, with total monoterpenes estimated at 0.28 and $0.11\,g\,C\,m^{-2}\,yr^{-1}$ in 1998 and 1999, respectively. Annual total monoterpene emission estimates from the FACTS1 region were 0.84 and $0.78\,g\,C\,m^{-2}\,yr^{-1}$ in 1998 and 1999, respectively. Peak daytime monoterpene emission totals were comparable between sites for 1998, ranging from 2 to $3\,mg\,C\,m^{-2}\,d^{-1}$ at NDFF compared to 3–5 $mg\,C\,m^{-2}\,d^{-1}$ at FACTS1. Average daily maximum temperatures at NDFF were 22.2 °C in 1998 and 24.7C in 1999, compared to 22.0 and 20.0 at FACTS1. Average annual PAR was 420 and 429 $\mu mol\,m^{-2}\,s^{-1}$ in 1998 and 1999, respectively, at NDFF, and 357 and 358 $\mu mol\,m^{-2}\,s^{-1}$ at FACTS1.

Diem and Comrie (2000) developed BVOC emission estimates for the Tucson area as a whole, including substantial exotic plantings in urban Tucson. They report isoprene emissions for a typical summer day of ca. $1.2\,mg\,C\,m^{-2}\,d^{-1}$, which is at the low end of our range for NDFF. The desert landscapes of the Sonoran Desert near Tucson do not feature the abundance of *Psorothamnus* and *Ephedra* that the Mojave Desert does. On the other hand, typical summer day emissions of monoterpenes in the Tucson area were estimated to be $3.3\,mg\,C\,m^{-2}\,d^{-1}$, which is greater than we estimate for the Mojave Desert and comparable to eastern US mixed forest landscapes. In addition to higher biomass densities measured in the Tucson area, Diem and Comrie (2000) use substantially higher monoterpene emission rates than we observed (25 vs. $4.1\,\mu g\,C\,g^{-1}\,h^{-1}$) for the common desert shrub *Ambrosia deltoidea*. This substantial difference in monoterpene emission factor may warrant additional investigation.

Methanol and acetone emissions remain highly uncertain in BVOC emission models. We estimate annual methanol and acetone fluxes from the Mojave Desert of 0.085 and $0.018\,g\,m^{-2}\,yr^{-1}$, respectively, in 1998 and 0.032 and $0.007\,g\,m^{-2}\,yr^{-1}$ in 1999. Methanol and acetone emissions from the FACTS1 region were 0.18 and $0.11\,g\,C\,m^{-2}\,yr^{-1}$, respectively, although agricultural and harvesting emissions are not included in this estimate. Martin et al. (1999) found that low molecular weight organic acids, aldehydes, and ketones were important emissions from tree species in Central New Mexico. Ambient concentrations of these compounds were in the 0.5–2 ppb range, while isoprene and monoterpene concentrations were below detection limits. Our PTR–MS data and limited data from other studies suggest that emission of oxygenated compounds should be a focus of further study in arid as well as other ecosystems.

Daytime soil surface temperatures in deserts of the southwestern US can exceed ambient air temperatures by >20 °C (Gates et al., 1968). These authors found that the leaf temperatures of most plant species were within 3 °C of ambient air temperatures, including those within a few centimeter of the soil surface, such as *Ephedra* species. However, *Opuntia* species (present but with low biomass at NDFF) exhibited leaf temperatures 10–16 °C above air temperature. Such differences can have large impacts on BVOC emission estimates. Using the model described above, we estimate that a gradual daytime increase in leaf temperature that peaks at 2 °C (above current model

estimates) at noon will increase annual desert isoprene and monoterpene fluxes by 18% and 7%, respectively. This likely affects emission of sesquiterpenes and oxygenated BVOC emissions as well. Seasonal effects of vegetation phenology and humidity impacts also warrant additional attention, as do emissions of sesquiterpenes and oxygenated compounds. Desert plant growth, reproduction, and physiological activity peak during and immediately following wet seasons, and additional measurements are needed during these periods. Vegetation distribution and biomass information are less available for arid environments than for more commercially valuable forest and agricultural systems. Improvements in these databases are necessary for realistic estimation of BVOC inventories from arid ecosystems.

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