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Large drought-induced variations in oak leaf volatile organic compound emissions during PINOT NOIR 2012

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HIGHLIGHTS

- Leaf level Isoprene emission factors for 4 of 5 oaks were significantly reduced during a severe drought.
- *Quercus stellata* leaf isoprene increased during the drought period.
- Leaf isoprene response to increasing temperature was impacted for most oak species.
- The leaf BVOC emission data supports findings at the canopy level, but discrepancies for monoterpene emissions remain.

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ABSTRACT

Leaf-level isoprene and monoterpene emissions were collected and analyzed from five of the most abundant oak (*Quercus*) species in Central Missouri's Ozarks Region in 2012 during PINOT NOIR (*Particle Investigations at a Northern Ozarks Tower – NOx, Oxidants, Isoprene Research*). June measurements, prior to the onset of severe drought, showed isoprene emission rates and leaf temperature responses similar to those previously reported in the literature and used in Biogenic Volatile Organic Compound (BVOC) emission models. During the peak of the drought in August, isoprene emission rates were substantially reduced, and response to temperature was dramatically altered, especially for the species in the red oak subgenus (*Erythrobalanus*). *Quercus stellata* (in the white oak subgenus *Leucobalanus*), on the other hand, increased its isoprene emission rate during August, and showed no decline at high temperatures during June or August, consistent with its high tolerance to drought and adaptation to xeric sites at the prairie-deciduous forest interface. Mid-late October measurements were conducted after soil moisture recharge, but were affected by senescence and cooler temperatures. Isoprene emission rates were considerably lower from all species compared to June and August data. The large differences between the oaks in response to drought emphasizes the need to consider BVOC emissions at the species level instead of just the whole canopy. Monoterpene emissions from *Quercus rubra* in limited data were highest among the oaks studied, while monoterpene emissions from the other oak species were 80–95% lower and less than assumed in current BVOC emission models. Major monoterpenes from *Q. rubra* (and in ambient air) were p-cymene, α-pinene, β-pinene, D-limonene, γ-terpinene, β-ocimene (predominantly1,3,7-trans-β-ocimene, but also 1,3,6-trans-β-ocimene), tricyclene, α-terpinene, sabinene, terpinolene, and myrcene. Results are discussed in the context of canopy flux studies conducted at the site during PINOT NOIR, which are described elsewhere. The leaf isoprene emissions before and during the drought were consistent with above canopy fluxes, while leaf and branch monoterpene emissions were an order of magnitude lower than the observed above canopy fluxes, implying that other sources may be

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contributing substantially to monoterpene fluxes at this site. This strongly demonstrates the need for further simultaneous canopy and enclosure BVOC emission studies.

1. Introduction

Biogenic Volatile Organic Compound (BVOC) emissions from forests are important inputs to atmospheric chemistry and air quality models, since they can control oxidant chemistry and secondary aerosol formation over many regions of the globe (Guenther et al., 2006). The Model of Emissions and Gases from Nature, (MEGAN) version 2.1 (Guenther et al., 2012), is currently applied to estimate landscape scale emissions of BVOCs. MEGAN results have been compared with measured fluxes of BVOCs at a few global sites, and MEGAN has been found to simulate fluxes and the short-term effects of light and temperature on emissions reasonably well (Müller et al., 2008). We also compared MEGAN2.1 with above canopy BVOC fluxes during the experiment PINOT NOIR (*Particle Investigations at a Northern Ozarks Tower — NOx*, *Oxidants*, *Isoprene Research*) during the summers of 2011 and 2012. MEGAN2.1 BVOC emission estimates agreed well with observed isoprene (2011) and isoprene and monoterpene (2012) emissions during early summer, but over-estimated emissions during mid to late summer droughts in both years (Potosnak et al., 2014; Seco et al., 2015). Here we report leaf level BVOC emission measurements on some important Ozark oak species during pre-drought (June 2012), drought (August 2012), and post-drought senescent (October 2012) conditions to gain insight into the effects of drought on BVOC emissions from individual oak species. We discuss the relationship between leaf—level BVOC emissions and above canopy fluxes and their comparisons with MEGAN2.1.

1.1. Site description

PINOT NOIR was conducted at the Missouri Ozark AmeriFlux (MOFLUX) site, which has been operating since Spring of 2004 with a suite of meteorological and ecological instrumentation. The site is located in the University of Missouri's Baskett Wildlife Research and Education Area (BREA, Lat. 38°44′ N, Long. 92°12′ W), within the Ozark border region of central Missouri. Second-growth upland oak-hickory forests constitute the major vegetation type [Pallardy et al., 1988]. Major tree species include white oak (*Quercus alba* L.), black oak (*Quercus velutina* Lam.), shagbark hickory (*Carya ovata* (Mill.) K.Koch), sugar maple (*Acer saccharum* Marsh.), and eastern red cedar (*Juniperus virginiana* L.). Local ecological studies on the BREA Canopy cover surrounding the flux tower ranges from 85 to 92%, and is composed of at least 66% *Quercus* species, mostly *Q. alba* and *Q. velutina* (Belden and Pallardy, 2009; Pallardy et al., 1988). Regionally, the area is over 80% forested and is also dominated by hardwood species. Table 1 lists the predominant tree species in the proximity of the flux tower and also from the USDA Forest Inventory and Analysis (FIA) Database for the four county area (Boone, Callaway, Cole, and Moniteau) surrounding the BREA. The spatial distribution of *Quercus* species and fraction of non-isoprene-emitting tree species within the flux footprint of the tower is shown in Fig. 1. *Quercus stellata* Wangenh. (post oak), an important oak species in the Ozarks, may be less abundant near the flux tower compared to the regional average as indicated by the FIA data summarized in Table 1 and Fig. 1.

Table 1
Predominant oak species within the flux footprint of the MOFLUX tower and from the USDA Forest Inventory and Analysis Database (FIA) for the four county area (Boone, Callaway, Cole, and Moniteau) surrounding the Baskett Research and Education Area. Basal Area % is the percentage total stem cross-sectional area at 1.37 m tree height. High isoprene emitters (primarily oaks) account for >66% (MOFLUX footprint) and 53% (FIA) of the total basal area and probably a higher percentage of upper canopy area when adjusting for crown form factors and canopy position.

Species	Common Name	% of total basal area	
		MOFLUX	Species
Erythrobalanus	**Red Oak Subgenus**		
Q. imbricaria	Shingle oak	0.1	*Q. imbricaria*
Q. rubra	Northern Red Oak	5.5	*Q. rubra*
Q. shumardii	Shumard Oak	1.8	*Q. shumardii*
Q. velutina	Black Oak	9.8	*Q. velutina*
Leucobalanus	**White Oak Subgenus**		
Q. alba	White Oak	40.2	*Q. alba*
Q. muehlenbergii	Chinkapin Oak	8.5	*Q. muehlenbergii*
Q. stellata	Post Oak	1.7	*Q. stellata*
Other isoprene emitting species		0	4.9
Non-emitting species (Cedar, Hickory, Maple, etc.)		32.4	47.0

The climate of the BREA is warm, humid, and continental, with mean January and July temperatures of 2.2 °C and 25.2 °C, respectively. Annual precipitation averages 940 mm, and moderate to severe droughts commonly occur between July and September. Dominant soils at BREA are Weller silt loam and a broad type classified as “Steep Stony Land” which includes all rocky slopes with a thin soil covering. Clinkenbeard clay soils are found in the area of rocky outcrops to the south and west of the flux tower. The comparatively thin soils of these oak forests often exacerbate plant water stress when droughts occur (from Gu et al., 2007). The BREA experienced a severe drought in mid to late summer of 2011 and an extreme to exceptional drought from mid to late summer of 2012 (http://droughtmonitor.unl.edu, December, 2014 also see Seco et al., (2015) for details of the 2012 drought). In comparing MEGANv2.1 isoprene emission estimates (and total monoterpenes for 2012) with seasonal fluxes measured above the canopy, drought appears to reduce BVOC emissions by more than 50% (Potosnak et al., 2014; Seco et al., 2015). MEGANv2.1 does not currently capture this drought effect using the default global soils data inputs developed for the MM5 mesoscale weather forecasting model (Chen and Dudhia, 2001), probably due to excessively low wilting point values assigned to soils within this study area. Other studies have also found that the Chen and Dudhia (2001) wilting point values applied as defaults in MEGAN2.1 are as much as 50% lower than wilting point values found in other databases (Sindelarova et al., 2014; Huang et al., 2015).

1.2. Variation in tree drought resistance

The Ozarks are located in the transition zone between the eastern forest region and the Great Plains region to the west, and droughts tend to occur frequently. Several oak species have adapted to the stresses associated with these periodic drought conditions (Abrams, 1990). These adaptations include development of drought resistance strategies, which include both drought tolerance and drought avoidance mechanisms. Drought avoidance is defined as

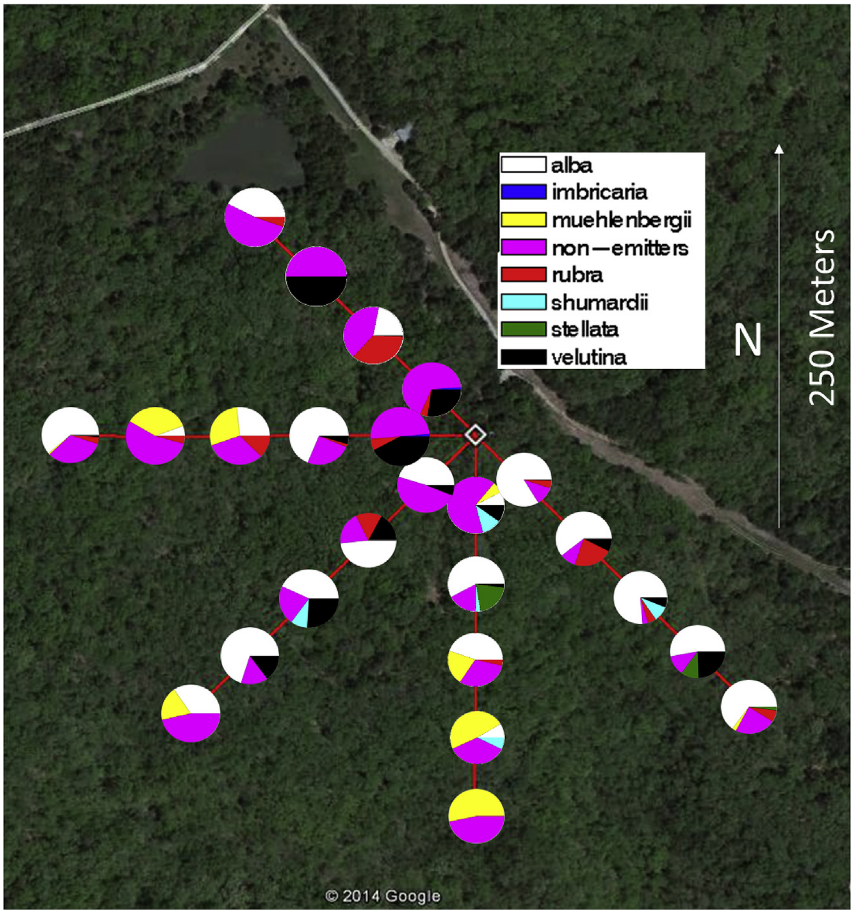

Fig. 1. Proportion of basal area by individual *Quercus* species and the sum of non-isoprene emitting tree species on 1/5 acre (0.081 ha) plots spaced 50 m (center to center) along transects radiating from the MOFLUX tower. The diamond at the transect intersection marks the base of the tower. Data were collected in 2011.

growth features that enhance a plant's ability to access moisture or prevent its loss. Major drought avoidance mechanisms include maintenance of high root-to-shoot ratios, reduced effective or exposed leaf surface area by rolling, folding, or shedding of leaves, control of stomatal water loss, development of thick wax cuticles, and root/vascular system development which favors high water extraction ability from soils (Spurr and Barnes, 1980). Drought tolerance refers to the degree to which a plant is adapted to arid or drought conditions via tolerance of dehydration or desiccation. Drought tolerance is less common in trees, but species such as *Q. stellata* can tolerate dehydration for extended periods before closing stomata (Pallardy and Rhoads, 1993). Decreasing leaf osmotic potentials and changes in tissue elasticity during drought are also important drought tolerance mechanisms employed by *Quercus* (Abrams, 1990).

Quercus is generally more drought resistant than co-occurring genera such as *Acer*, *Carya*, *Fagus*, *Juglans*, *Liriodendron*. Pallardy and Rhoads (1993) compared adaptive morphology in seedlings of *Q. stellata* and *Q. alba* with two drought-sensitive species: sugar maple (*Acer saccharum* Marsh.) and black walnut (*Juglans nigra* L.). Seedlings of the *Quercus* species and *J. nigra* tended to have well-developed taproots and to more rapidly explore deep soil layers than did sugar maple seedlings. While *J. nigra* showed the capacity for vigorous root growth, it also exhibited relatively less root length per unit of leaf area when the soil was moist. When established plants were forced to grow in dry soil, downward *J. nigra* root growth was substantially retarded, while *Q. stellata* exhibited a greater capacity than the other species for deep root growth. There was no tendency for drought-tolerant species to possess lower rates of cuticular water loss. The species least effective in curtailing water loss after stomatal closure was *Q. stellata*, the most drought-tolerant species. *Quercus* seedlings showed no evidence of water stress induced leaf abscission, even when plants were subjected to severe drought. In contrast, *A. saccharum* and, particularly, *J. nigra* seedlings showed substantial leaf abscission under water stress. Production of new leaf area after abscission was observed in non-*Quercus* species, but was not adequate to compensate for leaf area loss. Drought-prone sites may present especially detrimental environments for the carbon economy of drought-sensitive species because of the greater probability of recurrent massive leaf abscission.

The four most abundant oaks in the region surrounding the BREA (Table 1) are *Q. alba*, *Q. stellata*, *Q. velutina*, and *Quercus rubra*. *Q. alba* is the most widespread and abundant member of the *Quercus* genus within North America and falls within the white oak subgenus (*Leucobalanus*). *Q. alba* forms tap-roots to depths of 4.5 m and is able to penetrate clay layers to reach deeper water sources (Dougherty et al., 1980; Stone and Kalisz, 1991). It should be noted that variation in rooting habits is not well documented for mature oak trees. Characteristics such as maximum rooting depth and radius (Table 2) have been reviewed by Stone and Kalisz (1991). Many important *Quercus* species have little or no reported dimensional root data, and these authors note that variability in soil conditions (texture, depth to water table, etc.) can be as important as interspecific variability in determining *Quercus* rooting characteristics. *Q. alba* is considered to be drought tolerant by Abrams

Table 2
Some published root dimension, site preference, and water potential data for important *Quercus* species. E = Erythrobalanus, L = Leucobalanus, D/R = maximum observed rooting depth/surface rooting radius in meters (from Stone and Kalisz, 1991 and http://www.na.fs.fed.us/spfo/pubs/silvics_manual/volume_2/quercus/). *A* = Assimilation rate, *Gs* = Stomatal Conductance. T_L = Leaf Temperature. $LWP_{P,M}$ = Lowest observed pre-dawn, midday leaf water potential (MPa, values observed on same day), Values in **bold** are for *in situ* saplings trees, ***bold italics*** denote mature trees. *XWP* = xylem water potential. Site types (X = xeric, M = mesic, H=Hydric). I_L = leaf isoprene, T_L = leaf temperature (C).

Species	D/R (m)	Site	LWP_P/LWP_M	Comments
Eastern North American *Quercus* Species				
L *alba*	4.5/6.7	XM	$-\mathbf{2.2}/-\mathbf{3.0}_{\mathrm{A}}$	LWP_P as low as −4.0 MPa in 2012 at $\mathrm{MOFLUX}_{\mathrm{G}}$
E *coccinea*	7.0/–	XM	–/–	Growth not affected by severe drought in S. Appalachia
E *falcata*	–/–	X	$-1.6/-2.4_{\mathrm{Z}}$	var *Pagodafolia* seedlings. Stomates open when $A<0$
E *ilicifolia*	1.0/	X	$-\mathbf{0.7}/-\mathbf{2.2}_{\mathrm{S}}$	Prefers dry, fire prone sites, thick taproot
E *imbricaria*	–/–	MH	–/–	Prefers moist sites
E *laevis*	–/15	X	$-\boldsymbol{0.4}/-\boldsymbol{2.5}_{\mathbf{D}}$	Dry sandy soils, high root/shoot mass
L *macrocarpa*	4.8/18	XM	$-0.5/-1.7_{\mathrm{B}}$	High T_L tolerant, taproot develops rapidly
E *marilandica*	–/–	X	$-0.4/-1.9_{\mathrm{D}}$	Very drought tolerant
L *michauxii*	>2/–	H	–/–	In habits wet to moist sites but drought tolerant, has allelopathic root exudates
L *muehlenbergii*	–/–	XM	$-0.3/-1.0_{\mathrm{B}}$	High T_L tolerant,
E *palustris*	–/–	H	$-1.5/-2.7_{\mathrm{F}}$	Low pH tolerant, drought intolerant
E *phellos*	–/–	H	$-0.3/-1.8_{\mathrm{P}}$	Hydraulic conductance lower than *L. styraciflua*
L *prinus*	>2/7.3	X	$-\mathbf{1.0}/-\mathbf{2.5}_{\mathrm{L}}$	Limited to rocky thin soils, I_L, *A*, may be lower than other oaks
E *rubra*	3.6/15	M	$-\mathbf{2.0}/-\mathbf{2.7}_{\mathrm{A}}$	Adapted to more mesic sites than other MO oaks
E *shumardii*	–/–	XMH	$-0.3/-1.0_{\mathrm{B}}$	High root/shoot mass
L *stellata*	>4/–	X	$-0.7/-3.7_{\mathrm{V}}$	Very drought tolerant, *A* higher than *A* of *Q. alba* under $\mathrm{drought}_{\mathrm{N}}$
E *velutina*	3.0/–	XM	$-\mathbf{1.6}/-\mathbf{3.0}_{\mathrm{A}}$	$\mathrm{LWP}_{\mathrm{PD}}$ as low as −3.5 MPa in 2012 at $\mathrm{MOFLUX}_{\mathrm{G}}$
E *virginiana*	–/31	XMH	$-2.3/-3.5_{\mathrm{U}}$	Salt, high pH tolerant, I_L strongly correlated with *LWP*
Western North American *Quercus* Species				
E *agrifolia*	9.1/27	M	$-\mathbf{1.0}/-\mathbf{3.5}_{\mathbf{C}}$	Seedling *LWP* significantly lower than concurrent mature tree
E *chrysolepis*	7.3/–	XMH	$-\boldsymbol{1.8}/-\boldsymbol{2.5}_{\boldsymbol{K}}$	Most widely distributed oak in CA, $LWP_{PD}<-3.5$MPa
E *douglasii*	24/–	X	$-\boldsymbol{1.5}/-\boldsymbol{3.4}_{\boldsymbol{K}}$	Water use efficiency constant from $LWP_{\mathrm{P}}>-1$ to <-6 $\mathrm{MPa}_{\mathrm{X}}$
L *dumosa*	8.5/3	XM	$-\boldsymbol{0.5}/-\boldsymbol{3.3}_{\boldsymbol{H}}$	Deepest root penetration of 18 chaparral species
L *gambeliii*	>2.4/–	X	$-\boldsymbol{0.5}/-\boldsymbol{2.8}_{\boldsymbol{O}}$	High root/shoot mass, tolerates $LWP_M < -5.0$, high G_S at −2.5
L *garryana*	>1.5/–	X	$-\boldsymbol{0.5}/-\boldsymbol{3.6}_{\mathrm{J}}$	Most drought tolerant tree in Western Oregon
E *kelloggii*	–/18	XM	$-\boldsymbol{1.5}/-\boldsymbol{3.8}_{\boldsymbol{K}}$	Most important CA oak in volume and range, $LWP_P<-2.5$
L *lobata*	>25/–	M	$-\boldsymbol{0.7}/-\boldsymbol{2.4}_{\boldsymbol{K}}$	Intolerant of salinity, lowering water tables, $LWP_P<-3.5$
E *wislizenii*	24/–	X	$-/-\boldsymbol{2.5}_{M}$	G_S maintained at 9–13% of max. *XWP* of −8 MPa
Asian and European *Quercus* Species				
L *mongolica*	–/–	XM	$-0.7/-1.7_{\mathrm{I}}$	I_L unchanged as *A* declined by 50% in var. *crispula* $_{\mathrm{T}}$
L *serrata*	–/–	XM	$-/-4.0_{\mathrm{T}}$	Isoprene produced at conditions that induced mortality
L petraea	–/–	XM	$-\mathbf{0.5}/-\mathbf{2.5}_{\mathbf{Y}}$	A~0 $@LWP = -2.8$ $_{\mathrm{W}}$
L *pubescens*	–/–	X	$-\mathbf{2.9}/-\mathbf{3.5}_{\mathbf{Q}}$	I_L inc. by ~ 30% under mild drought $\mathrm{stress}_{\mathrm{E,}}$ $A = 0$ $@LWP = -2.5$
L *robur*	9.0/18	XM	$-\boldsymbol{0.9}/-\boldsymbol{2.1}_{\mathrm{W}}$	$A = 0$ $@LWP = -1.3$, I_L decreased @LWP = −2.0

Subscripted references: A (Bahari et al., 1985), B (Balok and Hilaire, 2002), C (Coleman et al., 2011), D (Donovan et al., 2000, 2001), E (Genard-Zielinski et al., 2014), F (Timbal and Lefebvre, 1995), G (Gu et al., 2015), H (Burk, 1978), I (Kobayashi and Tanaka, 2001), J (Johnson et al., 2009), K (*XWP* measured, Knops and Koenig, 1994), L (Kloeppel et al., 1993), M (Matzner et al., 2001), N (Ni and Pallardy, 1992), O (Kolb and Stone, 2000), P (Pataki et al., 1998), Q (Damesin and Rambal, 1995), R (Pegoraro et al., 2004b), S (Abrams et al., 1990), T (Tani et al., 2011), U (Cavender-Bares et al., 2007), V (Volder et al., 2010), W (hybrid w/*Q. sessilis*? Cermák et al., 1980), X (Xu and Baldocchi, 2003), Y (Backes and Leuschner, 2000), Z (Pezeshki and Chambers, 1986), 1 (Bruggemann and Schnitzler, 2002).

(1990), although he does not include it as a xeric site species in the central plains. *Q. stellata* is also a member of the *Leucobalanus*, and is known to be more drought tolerant than *Q. alba* (Seidel, 1972). Greater cellular drought tolerance and thick taproot structures that provide access to water up to four meters deep allow *Q. stellata* to form pure stands at the semi-arid forest-prairie transition zones in the central U.S. On poor sites it tends to persist and become dominant because it is more drought resistant than many of its associates. Mignery (1965) found that *Q. stellata* seedlings developed especially thick taproots, usually exceeding the shoot diameter, but overall root development was found to be less than that *Q. rubra*, *Quercus coccinea*, *Q. alba*, and *Quercus marilandica*. Although *Q. stellata* seedlings do become established on sites having a tight clay subsoil, their growth is slow and most roots develop above the underlying clay (Coile, 1937).

Q. rubra is adapted to more mesic sites than other local oak species and is a widespread and abundant member of the *Erythrobalanus* subgenus. *Q. rubra* is typically shallow rooted compared to other *Quercus* species in this region. Although *Q. rubra* roots may penetrate well drained soils to depths exceeding three meters (Stone and Kalisz, 1991), its spreading root system is often limited to the upper 0.7 m, with mature trees not featuring a prominent deep taproot (Lyford, 1980). The Ozarks region is in the southern and western extremes of its North American range, and it has been found to be more susceptible to drought effects, including drought induced mortality, than other oaks (Law and Gott, 1987). *Q. velutina*, also a member of *Erythrobalanus*, is considered to be more drought resistant than *Q. rubra* but often occupies dryer sites on upper slopes and can suffer mortality under severe drought (Dougherty et al., 1980). Another member of the red oak group, Shingle Oak (*Quercus imbricaria*), is adapted to drier, more calcareous sites than *Q. rubra and Q. velutina* (Dickson and Tomlinson, 1996).

Pegoraro et al. (2004b) showed a strong linear relationship between leaf water potential (*LWP*) and leaf isoprene emission (I_L) and concluded that *LWP* could be a useful parameter to include in isoprene emission models to account for effects of drought stress on leaf I_L. However, use of *LWP* as a driving variable would require improved model linkages between *LWP* and soil moisture, spatial characterization of soil texture, and rooting habits of isoprene-emitting plant species. In addition, field measurements of drought-influenced *LWP* are limited, and seedling *LWP* values are often substantially lower than *LWP* observed in conspecific mature trees due to increased water available to the latter (Mahall et al., 2009; Coleman et al., 2011). Abrams et al. (1990) also suggest that larger diurnal variation in *LWP* in drought resistant species may be partly due increased gas exchange, and not water stress. This may account for some of the larger differences between LWP_P and LWP_M (LWP at pre-dawn and mid-day, respectively) for some of the more drought tolerant oaks shown in Table 2. These factors complicate the use of empirical values in establishing relationships between I_L and *LWP*. Nonetheless, interspecific differences in LWP and rooting characteristics may yield useful insight into interspecific and regional differences in I_L as influenced by drought (Table 2). Augé et al. (1998) found that lethal *LWP* for *Q. rubra* (−3.34 MPa), *Q. alba* (−4.60), *Quercus prinus* (−5.73), and *Quercus altissima* (−6.14) decreased with the known increasing drought tolerance of oak species. Gu et al. (2015) noted that *LWP* values for *Q. alba* and *Q. velutina* approached these lethal levels at BREA in the summer of 2012. The apparent similarity of drought influenced *LWP* in eastern vs several of the western US *Quercus* species (Table 2) suggests that greater rooting depths (sometimes to the permanent water table) of the latter is an important drought avoidance strategy during the prolonged annual droughts experienced by the western *Quercus* species in the Mediterranean climates of the western U.S. and southern Europe. California oaks such as *Quercus wislizenii* and *Quercus douglasii* can maintain water use efficiencies during extreme drought, even as LWP_P falls below −6 MPa (Xu and Baldocchi, 2003). It should also be noted that very little information on drought effects on isoprene emission from mature trees is available for any tree species, including those listed in Table 2.

The Ozarks Region suffered extreme droughts in 1980 and 1983. Extensive mortality occurred in the red oak group (*Erythrobalanus*), primarily among scarlet oak (*Q. coccinea* Muenchh.), *Q. velutina*, and *Q. rubra*. Dead and dying volume of these species accounted for 53, 35, and 26% of their respective total volumes. The white oak group (*Leucobalanus*) was much less affected by the drought. *Q. alba* and *Q. stellata* each had only 3% of their volume in the dead and dying classes. Field studies of affected areas on the Mark Twain National Forest revealed most mortality occurred in oak stands over 60 years old with trees more than 14 inches in diameter (Law and Gott, 1987), similar to the size and age of the oaks within the canopy at the MOFLUX tower site.

Given the large variability in physiological, growth, and survival responses to drought between *Quercus* species, it seems reasonable to expect that l I_L and leaf-level monoterpene (M_L) emission rates may also show varying response to drought stress among the oaks. We attempted to characterize this variability by examining I_L and M_L from several oak species before, during and after the severe drought experienced in the Ozarks in the summer of 2012. We compare these observations with the above canopy fluxes of isoprene and monoterpenes measured during the course of the growing season.

2. Methods

Leaf isoprene emission rates (I_L, in μgC (g leaf dry weight)$^{-1}$ h^{-1} unless otherwise specified) were measured by enclosing portions of leaves in the cuvette of two LI-COR 6400 plant photosynthesis systems (Li-Cor, Inc., Lincoln, NE, USA). Exit air was ported to two Photovac (Perkin–Elmer, Norwalk, CT, USA) photoionization detection (PID) systems as described in Geron et al. (2002). Additionally, Tenax TA/Carboxen 563 (Sigma–Aldrich, St. Louis, MO, USA) adsorbent cartridges were used to sample from the Li-Cor exit air for analysis with an Inficon (East Syracuse, NY, USA) HAPSITE ER gas chromatograph and mass spectrometer (GC/MS) system with a thermal desorption unit, which allowed on-site identification and quantitation of isoprene and monoterpenes. Blanks were measured from the empty leaf cuvette system and analyzed on-site with the Inficon GC/MS. Traces of D-limonene were found in these blanks, and a blank taken after a leaf sample indicated that this carryover could be as high as 30–40%. Blank values of other monoterpenes and isoprene were below detection limit (BDL). Photosynthetic Photon Flux Density (PPFD) was held constant at 1000 μmol m^{-2} s^{-1}, while leaf temperature (T_L) was changed gradually between ~20 and 40 °C using the Peltier coolers in the LI-6400. An additional LI-6400 was occasionally used in which a portion of gas exiting the cuvette was diverted to a 2-mL sample loop of a portable, isothermal gas chromatograph, and isoprene was separated on a stainless steel column (1.3 m long x 2 mm i.d.) packed with Unibeads 3S, 60–80 mesh (Alltech Assoc., Deerfield, IL, USA). Isoprene eluting from the column was measured with a reduction gas detector (Model RGD2, Trace Analytical, Menlo Park, CA, USA), and peak integration was accomplished using PeakSimple Chromatography Software (SRI Instruments, Las Vegas, NV, USA). Because the sensitivity of the analytical system varied with ambient temperature, the isoprene detection system was calibrated after approximately every fifth measurement using a standard cylinder containing 45 ppbv isoprene, referenced to an NIST Butene/Benzene standard using gas chromatography (Model 7890a, Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with both a flame ionization detector and an electron ionization mass-selective detector.

In August, an additional photosynthesis system (MPH-1000, Campbell Scientific, Logan, UT, USA) was deployed. Leaves were enclosed in a custom-built temperature-controlled, fan-stirred glass cuvette (Allen Scientific Glass, Boulder, CO, USA) 12.5 cm in diameter (volume of 425 cm^3) and concentrations of CO_2 and H_2O measured using an Infrared Gas Analyzer (IRGA, Model LI-6262, Li-Cor, Lincoln, NE, USA, see Harley et al., 2014 for complete description). Exhaust gas leaving the cuvette was ported to an Ionicon proton transfer time of flight mass spectrometer (PTR-TOF-MS 8000, Ionicon Analytik, Austria) and isoprene concentrations were monitored at protonated m/z 69.066. A thorough description and characterization of the PTR-TOF-MS instrument is given by Graus et al. (2010) and the data reduction was performed with the software developed by Müller et al. (2013). The drift tube of the PTR-TOF-MS was operated at 2.3 mbar, 520 V, and 75 °C, producing an E/N ratio of 118 Td. Background of the instrument was measured regularly by passing ambient air through a platinum catalyst heated to 415 °C. Sensitivity calibrations for the PTR-TOF-MS were performed by dynamic dilution of VOCs using a house-made VOC gas standard (5 ppmv of isoprene) into zero air generated by the catalytic converter.

Measurements were conducted on June 17–18, August 8–12, and October 19–22 (Table 3). Sunlit leaves of sapling oaks at the north and west edges of a clearing 1 km north of the MOFLUX tower were examined for I_L and M_L as well as CO_2 and H_2O exchange. IRGA instability induced high variability in leaf CO_2 and H_2O flux, and these data are not reported for June measurements. Maximum canopy-level isoprene fluxes, measured at the MOFLUX tower, were observed from mid-June through early July. The peak of the drought occurred between early and late August, when leaf water potentials fell below −3.5 MPa. Senescence was underway during the October measurements, following a drought recovery period in late August and September when rainfall re-charged soil moisture. In June, August, and October, response of I_L to T_L variations was determined by increasing T_L (from ~30 to 40 °C in June and August, ~15–25 °C in October), in 2–3 °C increments over the course of 1–2 h using the LI-6400 systems. In August, using the MPH-1000 system, light was rapidly cycled several times at varying T_L from high PPFD (1200–1500 μmol m^{-2} s^{-1}) to zero, to examine light/dark response of I_L.

SUMMA (Biospherics Research Corp., Portland, OR, USA) canisters (850 mL) were also used to collect ambient air and small branch enclosure air samples. Branches of sapling *Q. alba*, *Q. rubra*, and *Q. stellata* were enclosed in five liter Teflon bags using the

Table 3
Oak (*Quercus* spp) species examined at the leaf level during the 2012 PINOT NOIR growing season using the Li-Cor 6400, PID, and Inficon instruments. June, August, and October sampling dates and local times are listed. The same leaves of each species (with the exception of *Q. imbricaria*) were tagged and re-measured during the peak of drought conditions, and again during October.

Q. alba		Q. rubra		Q. velutina		Q. stellata		Q. imbricaria	
6/17	15:00–18:00	6/17	18:30–20:00	6/18	11:00–13:00	6/17	12:30–14:30		
8/09	16:00–19:00	8/08	16:30–19:00	8/09	10:00–13:00	8/08	12:30–14:30	8/12	10:30–13:00
10/20	12:30–15:00	10/22	13:00–15:00	10/20	15:30–17:30	10/19	13:30–15:30		
10/21	13:00–15:30			10/22	15:30–17:30	10/21	10:30–12:30		

methods described in Geron and Arnts (2010). The SUMMA canisters were pressurized to 10–26 psig using ambient air or a subsample of the exit air from the dynamic branch enclosure system. Canisters were transported to the laboratory in Portland, OR, USA, and within two weeks were evacuated onto a two-bed (Tenax TA and Carbotrap) Markes cartridge and desorbed using a Markes-1 thermal desorption/preconcentration system. Output was analyzed on an Agilent 6980N gas chromatograph and Agilent 5973 mass selective detector operated in selected ion mode (SIM). The SIM detector response to BVOCs relative to CCl_4 (assumed to be 100 ppt) was used to approximate BVOC concentrations in the canister samples, although these samples were used primarily to analyze ratios of isoprene to monoterpene (MNT) and relative abundance of individual MNT compounds.

3. Results

3.1. Leaf isoprene emissions

The June I_L measurements using the PID and LICOR systems showed basal emission rates (I_L at PPFD = 1000 μmol m^{-2} s^{-1} and $T_L = 30$ °C) that ranged from 80 to 120 μgC g^{-1} h^{-1} (Table 4). These rates fall within the range observed by Geron et al. (2001) for *Q. alba*, *Q. rubra*, *Q. stellata*, and *Q. velutina* in North Carolina, USA. During the wet summer of 1998, I_L from both *Q. stellata* and *Q. marilandica* in the Ozarks (late July) was 66 ± 10 μgC g^{-1} h^{-1}, although the *Q. stellata* leaves studied were not entirely exposed to the sun, which may have affected I_L (Wiedinmyer et al., 2005). Here, responses of I_L to changing T_L were also very similar to patterns typically observed in other studies (Sharkey et al., 1991; Guenther et al., 1993; Harley et al., 1996; Geron et al., 2000a) and were reasonably well described by the default Guenther et al. (1993, or G93) function (Fig. 2). *Q. rubra* I_L data were very well described by G93, as was *Q. alba* except for a slight overestimation at higher T_L. *Q. velutina* I_L exhibited a decline at temperatures slightly less than 40 °C. *Q. stellata*, on the other hand, did not exhibit any decline at T_L values which exceeded 41 °C in the June data.

Drought conditions appeared to influence both basal emission rates and the shape of the temperature response. During drought conditions on August 11, basal I_L from the same *Q. rubra* leaf measured in June decreased by ~30% and showed very little response to increasing leaf temperature above 30 °C (Fig. 2). Despite prolonged slightly negative values of net photosynthesis (A), substantial amounts of isoprene were emitted at higher T_L from *Q. rubra* and *Q. velutina* in Fig. 2, suggesting the possibility that isoprene was produced from a source other than recently fixed carbon. On August 9, another *Q. rubra* leaf on a different tree was held at approximately constant temperature and PPFD (33 ± 2 °C and 2000 μmol m^{-2} s^{-1}) using the Li-Cor 6400 (Fig. 3). At 10 AM, when the first measurements were made, isoprene was emitted at 40 μgC g^{-1} h^{-1} but was already declining steeply, and it is likely the early morning peak in emissions was missed. Isoprene continued to decline steadily, to 20 μgC g^{-1} h^{-1} by 1 PM, and fell to 13 μgC g^{-1} h^{-1} through the afternoon (5 PM). Stomatal conductance (G_S) and A were both extremely low and unstable (less than 0.5 μmol m^{-2} s^{-1} and 10 mmol m^{-2} s^{-1}, respectively; not shown) throughout the day, although again it is likely that early morning maxima may have been missed (see below).

Measurements on a third leaf of *Q. rubra* were initiated at 8 AM on Aug. 10, at which time, A and G_S were both positive, although quite low (Fig. 4). Isoprene emission rates were relatively high and comparable to isoprene emission rates observed the previous day. As PPFD was reduced from 2000 to 0 μmol m^{-2} s^{-1} over the next four hours, A and G_S both declined as one would expect, but it is difficult to know if this decline is wholly due to declining PPFD, or if the decline is, at least in part, simply due to severe water stress, resulting in extremely low midday values as seen the day before. Neither A nor G_S recovered when PPFD was increased to 800 μmol m^{-2} s^{-1} at 1 PM and held there for several hours, suggesting that stress effects predominated. Isoprene emission rates also declined with decreasing PPFD in the morning, but in contrast to CO_2 and H_2O exchange, exhibited a substantial, although incomplete, recovery in the afternoon.

Overall, basal isoprene I_L declined by over 30% between the June and August periods, and emission rates appeared to decline over the course of the day as leaf water status declined, largely

Table 4
Isoprene Emission factors (basal I_L) calculated using PID data and standardized using the Guenther et al. (1993) temperature algorithm for data where T_L was within 30 °C ± 2 °C. PPFD was held constant at 1000 μmol $m^{-2}s^{-1}$. No data were collected for *Q. muehlenbergii* or *Q. shumardii*, which together accounted for about 10% of the MOFLUX footprint basal area. Standard deviation is given in parentheses. LMA is leaf mass (dry weight) per unit area (fresh punch) in g m^{-2}. Values in parentheses after species name indicates number of leaves sampled. (* Includes branch enclosure samples). Basal I_L for the *Erythrobalanus* species determined in August using the MPH-1000 and PTRMS systems was considerably (~20–60%) lower than the corresponding August values shown below.

	June		August		October		% Change (June–Aug)	% Change (June–Oct)	LMA
	μg C g^{-1} h^{-1}	Nmol m^{-2} s^{-1}	μgC $g^{-1}h^{-1}$	Nmol m^{-2} s^{-1}	μgC g^{-1} h^{-1}	nmol m^{-2} s^{-1}			
Erythrobalanus									
Q *Q. imbricaria* (2)	–	–	50.5 (0.8)	12.0 (0.2)	–	–	–	–	47
Q *Q. rubra* (5*)	101.7 (16.7)	35.9 (5.9)	74.2 (5.1)	26.2 (1.8)	5.1 (2.2)	1.8 (0.8)	−27	−95	70
Q *Q. velutina* (3)	88.9 (5.2)	38.1 (2.2)	75.9 (4.5)	32.5 (1.9)	12.7 (7.7)	5.5 (3.3)	−15	−86	85
Leucobalanus									
Q *Q. alba* (4*)	90.6 (5.1)	35.6 (2.0)	60.2 (3.4)	23.7 (1.3)	8.4 (2.7)	3.3 (1.1)	−34	−91	78
Q *Q. stellata* (5*)	93.6 (4.8)	36.3 (1.9)	131.9 (7.6)	51.2 (2.9)	11.9 (4.0)	4.6 (1.6)	+41	−87	77

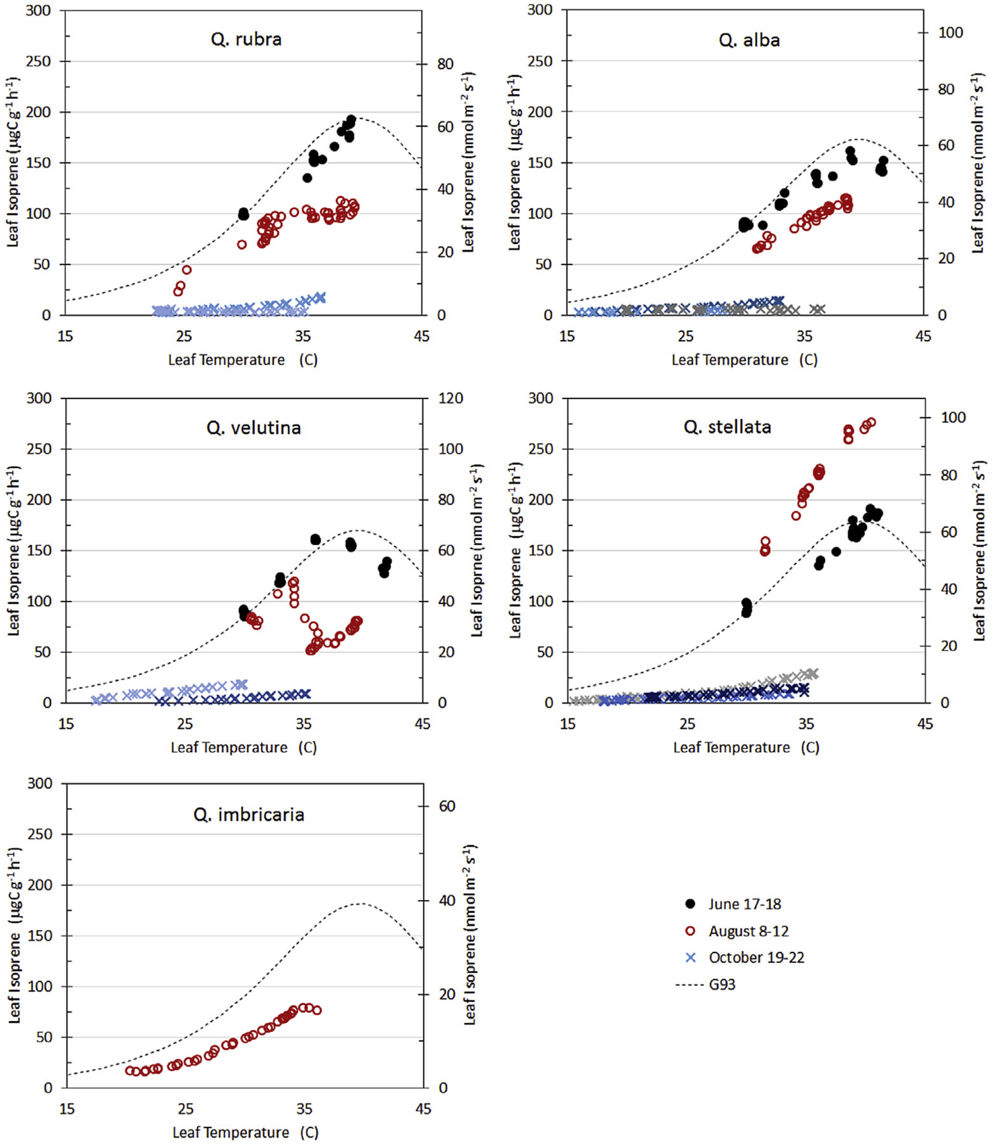

Fig. 2. Leaf isoprene emission (I_L) measurements during PINOT NOIR. PPFD was held constant at 1000 μmol m^{-2} s^{-1}. Black dots, red circles and blue-gray X's (shades indicate individual leaves) represent June, August, and October measurements, respectively. The black line represents the fit of the Guenther et al. (1993) temperature response algorithm to the June measurements, fit through the mean I_L at $T_L = 30$ °C for each species. The fit for *Quercus imbricaria* is derived from the mean of *Q. rubra* and *Q. velutina* since June data are not available for that species. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

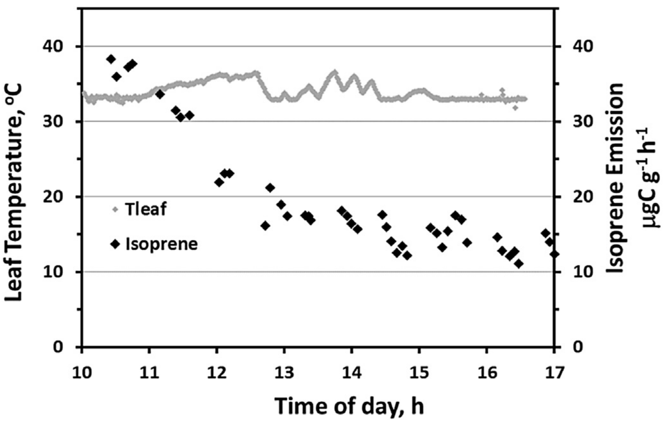

Fig. 3. Diurnal variation in I_L from a *Quercus rubra* leaf on August 9, 2012. Leaf temperature was 33 ± 2 °C.

independent of variations in light or temperature (Figs. 3 and 4). Response of I_L, A, and Gs to PPFD and T_L changes, especially in the August PM hours, was greatly reduced. *Q. rubra* was considerably less responsive to increasing leaf temperature during the drought, although it remains difficult to distinguish between temperature effects versus water stress effects. In either case, isoprene emissions were substantially reduced below emission model estimates, particularly at the high temperatures experienced during the drought period (Fig. 2).

I_L from *Q. velutina* on August 9 initially increased when temperature increased from 30 to 34 °C in the AM hours and then rapidly declined by ~50% (Fig. 2). From 36 to 40 °C, I_L gradually increased to rates initially observed at 30 °C. At T_L of 30 °C G_s (20–25 mmol H_2O m^{-2} s^{-1}) and A (3–4 μmol CO_2 m^{-2} s^{-1}) were near rates typically observed for oaks, but then decreased rapidly at T_L above 30 °C by a factor of 3–4 and remained low at higher leaf temperatures. Basal I_L declined by 15% between the two periods, but the response to increasing T_L (similar to *Q. rubra*), probably

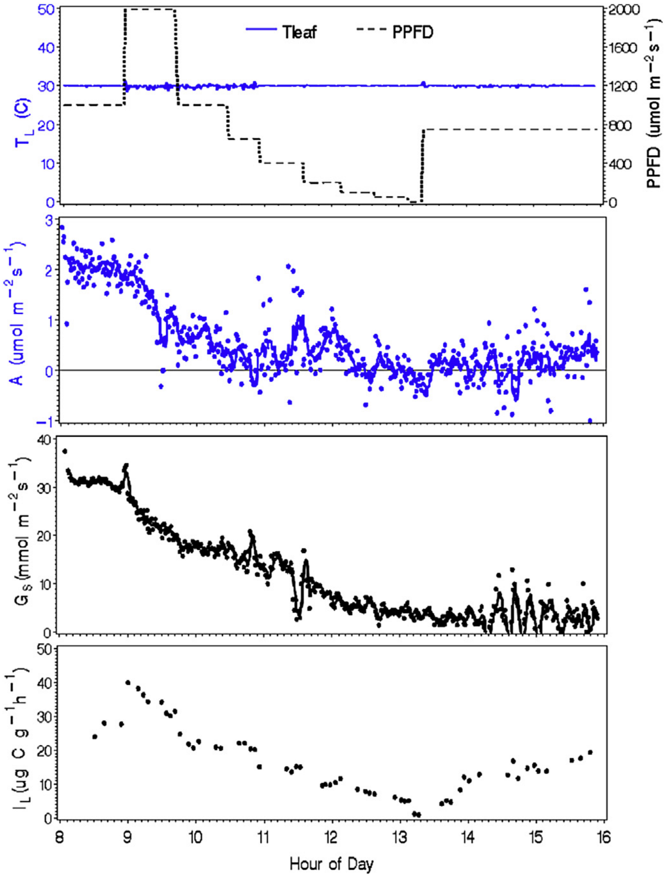

Fig. 4. I_L response of a *Quercus rubra* leaf to fluctuations in PPFD (gray line in top panel) at a constant temperature of 30 °C on August 10, 2012. Net photosynthesis (A) is shown as blue line in second panel from top, stomatal conductance (G_S) is shown as black line in third panel from top. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

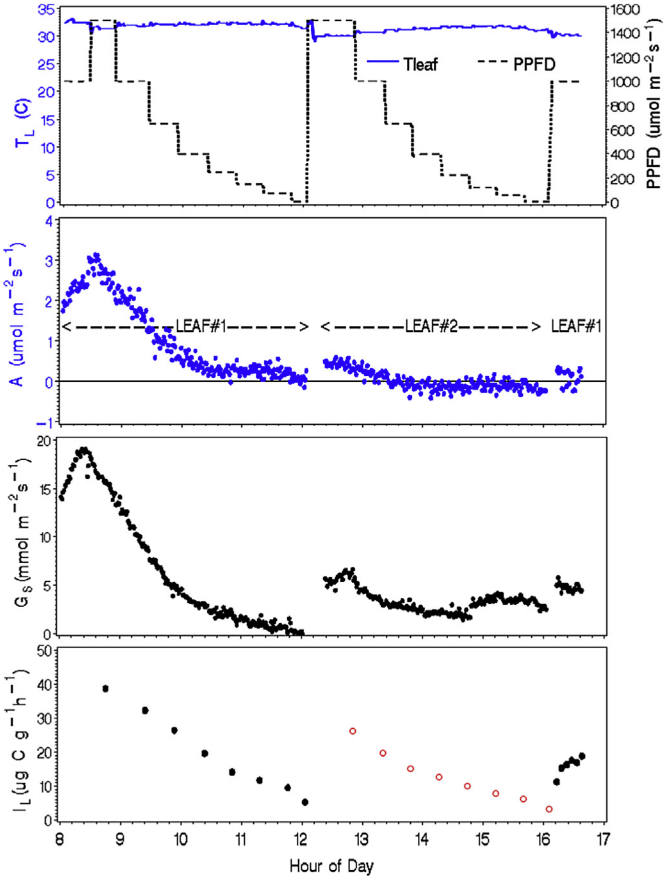

Fig. 5. I_L, A (net photosynthesis), and G_S (stomatal conductance) response of 2 *Quercus velutina* leaves to fluctuations in PPFD at a temperature of 30–32 °C on August 14, 2012. Black dots and red circles denote I_L for leaf #1 leaf #2, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

confounded with early PM drought effects on leaf physiology, was quite different in August. Additional data obtained from two leaves of *Q. velutina* on Aug. 14 (Fig. 5) also demonstrate the apparent effects of drought. The first leaf, inserted into the leaf chamber at approximately 8 AM, exhibited low but positive rates of A and G_S, and as PPFD was reduced over the subsequent four hours (T_L constant at 30 °C) both declined to near zero, as expected. However, when the leaf was reinserted in the leaf chamber at 4:30 PM, with PPFD set to 1000 μmol m^{-2} s^{-1}, neither A nor G_S showed significant levels of recovery, presumably as a result of leaf water status. At approximately 12:30 PM, a second, adjacent, leaf was placed in the chamber with PPFD set to 1000 μmol m^{-2} s^{-1}, but by that time of day, both A and Gs were already depressed to extremely low values of approximately 0.5 μmol m^{-2} s^{-1} and 5 mmol m^{-2} s^{-1}, respectively. Significant levels of isoprene emissions were again observed for both leaves, although the rate of the second leaf was approximately 30% lower than the rate of the first under identical conditions (PPFD = 1000 μmol m^{-2} s^{-1}; 30 °C). Emissions from both leaves continued even after approximately 30 min in darkness, in contrast to what is expected for an unstressed leaf. In addition I_L from the second leaf in Fig. 5 was significant even as A was negative as PPFD declined from 600 to 0 μmol m^{-2} s^{-1}. When the first leaf was reinserted into the leaf chamber late in the day, isoprene emission slowly recovered, reaching approximately 50% of the morning value after 90 min (Fig 5).

I_L from *Q. imbricaria* was examined at midday on August 12. Basal emission rates were approximately 50% lower than would typically be expected from *Quercus*, consistent with the August decline observed in *Q. rubra*, *alba*, and *velutina*. I_L increased as T_L increased from 28 to 35 °C, which was consistent with G93, although there was some indication of the onset of I_L decrease at 34–35 °C. A further series of measurements carried out using the MPH-1000 and PTR-TOF-MS on a leaf of *Q. imbricaria* further highlights the breakdown of the normal temperature response under extreme drought conditions, and the difficulty of distinguishing between drought and high temperature effects. A leaf was placed in the leaf chamber at approximately 8:30 AM and measured for nine hours under a high PPFD (1200–1500 μmol m^{-2} s^{-1}) while T_L was varied with brief darkness periods (Fig. 6). When gas exchange measurements began, leaf temperature was set to 20 °C and both A (6 μmol m^{-2} s^{-1}) and G_S (30 mmol m^{-2} s^{-1}) were quite high for this period of high water stress. However, left at 20 °C, A and Gs were both unstable and declined over time. When T_L was increased in a series of steps after 11:00 AM to a maximum of 32.5 °C, A fell to values less than 1 μmol m^{-2} s^{-1} and G_S to values close to zero and remained at those levels for the rest of the measurement period. I_L measurements commenced at 10:45 and as T_L was increased from 20 °C to 30 °C, isoprene increased as expected, with a Q_{10} of approximately 3.2. When T_L was raised to 32.5 °C, emissions initially increased but then fell rapidly to levels below those measured at 30 °C. When T_L was returned to 30 °C, there was no recovery and when T_L was

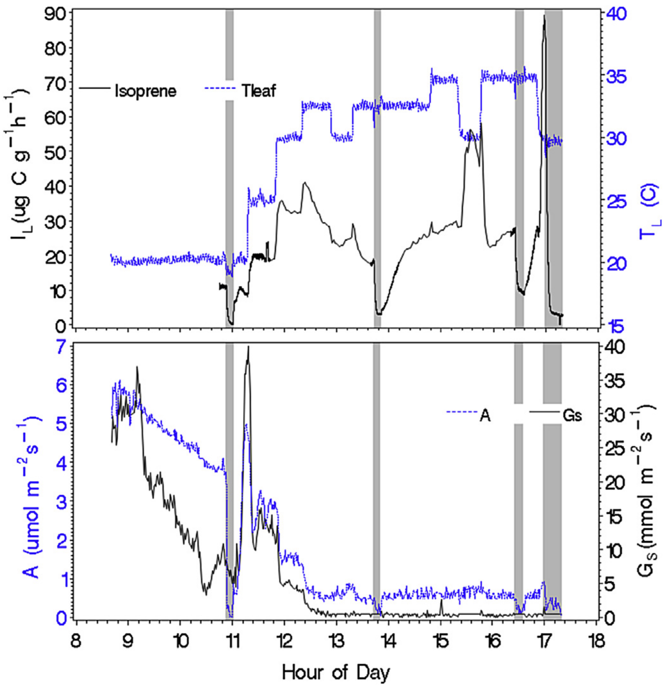

Fig. 6. Leaf isopene emission (I_L), net photosynthesis (A) and stomatal conductance (G_S) response of a *Quercus imbricaria* leaf to fluctuations in leaf temperature (T_L) under high PPFD (1200–1500 μmol m^{-2} s^{-1}) on August 12, 2012. Shaded areas indicate periods of darkness (PPFD<1 umol m^{-2} s^{-1}).

raised again to 32.5 °C, I_L fell further, indicating initiation of a decline in emission capacity rather than a simple steady-state response to temperature. These results are consistent with the observed loss of temperature sensitivity and reduced temperature optima shown in Fig. 2 for *Q. rubra*, *Q. velutina*, and *Q. imbricaria*. Following a brief period of darkness in early afternoon (shaded areas in Fig. 6) emission slowly recovered even as T_L was increased to 35 °C, but a series of unexpected responses to T_L manipulations followed. When T_L was lowered from 35 °C to 30 °C a large burst of emissions was observed lasting half an hour and reaching substantially higher rates than any I_L observed previously. Later in the afternoon, this step change from 35 °C to 30 °C was repeated, resulting in another, even larger, burst of emissions. Four times during the day, and at different T_L, light was rapidly reduced to zero. Except under cooler T_L (20 °C), isoprene emissions did not fall to zero after 10 min or more in the dark (Fig. 6). This level of I_L in the dark was particularly high at a leaf temperature of 35 °C. Significant dark emissions, when DMAPP production should rapidly drop to zero, further support the idea that under these extreme stress conditions of drought and high temperature, DMAPP for isoprene production may derive from a source other than immediately fixed photosynthetic products. The non-enzymatic reaction of DMAPP to isoprene, known to be acid catalyzed (Silver and Fall, 1991), may partly account for this isoprene, although at physiologically relevant pH levels this source is expected to produce emissions at levels lower than we observed in the dark (Fig. 6). Alternatively, Li and Sharkey (2013) find that large pools of methylerythritol cyclodiphosphate (MEcDP) may explain transient and dark emissions of I_L from hybrid aspen (*Populus tremula* × *alba*).

During the drought conditions on August 8, I_L from the same *Q. alba* leaf measured in June decreased by 34%, but unlike *Erythrobalanus* (red oak) species, showed a relative temperature response similar (although somewhat dampened) to the June observations (Fig. 2). The I_L temperature optimum exceeded T_L values of 40 °C in June, and these values were not attained in the LICOR 6400 cuvette system during the August measurements. Although *Q. alba* is likely to be more drought tolerant than the red oaks present on this site, a decrease in I_L associated with severe drought is suggested by these data.

In contrast to the other *Quercus* species, I_L from the *Q. stellata* leaf measured on August 8 actually increased by ~40% relative to June and also showed a response to increasing T_L similar to the June observations. This I_L was higher than the rates measured for any other oak species at any time during the study. No obvious I_L temperature optimum below approx. 41 °C could be detected in either time period. Drought adaptation in this species may lead to seasonal variation in I_L considerably different from other *Quercus* species at this site.

3.2. Monoterpene emissions

Q. rubra emission samples analyzed on-site with the Inficon instrument indicated that this species may contribute to the observed above canopy MNT flux (Seco et al., 2015). A *Q. rubra* emission sample at $T_L = 30$ °C and PPFD of 1000 μmol m^{-2} s^{-1} collected on June 18 indicated total M_L of 1 μgC g^{-1} h^{-1}, which increased to 4 μgC g^{-1} h^{-1} at $T_L = 39$ °C. Primary MNT compounds emitted were p-cymene, α-pinene, β-pinene, D-limonene, γ-terpinene, β-ocimene (predominantly1,3,7-trans-β-ocimene, but also 1,3,6-trans-β-ocimene), tricyclene, α-terpinene, sabinene, terpinolene, and myrcene (Fig. 7). Camphene and Δ3-carene were also detected. All MNT emissions (except p-cymene) increased with increasing T_L, and maintained a constant emission rate relative to isoprene at higher T_L in June. Under drought conditions in August, M_L from *Q. rubra* was only 12–25% of June values at similar T_L. However, the D-limonene and β-ocimene emission rates were higher than p-cymene, pinenes and terpinenes from the same *Q. rubra* leaf in the drought measurements. The β-ocimene compounds in particular, have previously been linked to stress response (Harley et al., 2014). Ortega et al. (2007) found light-dependent MNT from *Q. rubra* in Michigan, which was dominated by *trans*-ocimene. M_L found by those investigators were somewhat higher than observed here. Similar to isoprene, there was little response to increasing T_L during the August drought. The M_L from *Q. rubra* are equivalent to 1–2.5% of I_L from this species on a C basis and exhibit the highest M_L of the *Quercus* species examined here.

M_L from *Q. velutina* in June was an order of magnitude lower (0.08 μgC g^{-1} h^{-1}) than *Q. rubra* at 30 °C and consisted of D-limonene and α-pinene. M_L (primarily D-limonene) from this species increased somewhat in August but was only slightly correlated with T_L.

M_L from *Q. alba* in June (at $T_L = 30$ °C and PPFD of 1000 μmol m^{-2} s^{-1}) was 0.04 μgC g^{-1}h^{-1}, increasing to 0.25 μgC g^{-1} h^{-1} at $T_L = 42$ °C, and was positively correlated with T_L. Dominant MNTs were p-cymene, D-limonene and α-pinene, while 1,3,7 trans-β-ocimene and terpinolene were also present at elevated T_L. During drought conditions in August, M_L increased to 0.1 μgC g^{-1} h^{-1} at $T_L = 31$ °C, and was almost entirely composed of D-limonene. The August M_L remained constant with increasing T_L.

Similarly to *Q. alba*, M_L from *Q. stellata* was composed primarily of p-cymene, D-limonene and α-pinene. M_L from *Q. stellata* in June at $T_L = 30$ °C and PPFD of 1000 μmol m^{-2} s^{-1} was 0.12 μgC g^{-1} h^{-1}. The D-limonene and α-pinene showed little response to increasing T_L, while p-cymene decreased with increasing T_L. During August drought conditions M_L decreased by 50% to 0.05 μgC g^{-1} h^{-1}, almost entirely composed of D-limonene. Additionally, the emission of D-limonene decreased with increasing T_L, although blank levels of this compound complicate interpretation of M_L and T_L response for this compound.

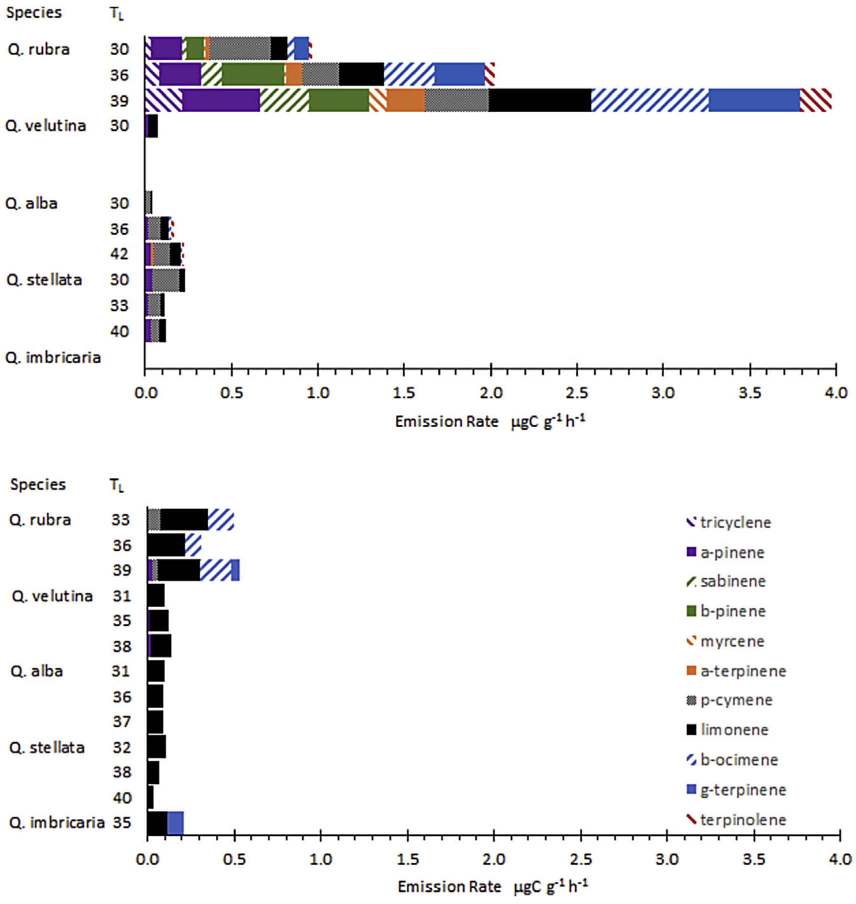

Fig. 7. Monoterpene emissions by species and leaf temperature during PINOT NOIR in June prior to drought (top) and August during drought (bottom).

Q. imbricaria, sampled only during drought conditions in August, showed moderate M_L emissions of 0.20 µgC g^{-1} h^{-1} at 35 °C and PPFD of 1000 µmol $m^{-2}s^{-1}$. Similar to the other *Quercus* species, M_L was dominated by D-limonene during drought conditions, with lower levels of γ-terpinene.

SUMMA canister samples taken from branch enclosures in August indicated that I_L to M_L ratios from *Q. alba* and *Q. stellata* were factors of 2 (~400:1) and 3 (600:1) times higher respectively, compared to *Q. rubra* (200:1) on a carbon basis. These ratios are similar in magnitude and species rank to the ratios from the Inficon on-site analyses. The MNT compounds α-pinene, D-limonene, p-cymene, and 1,3,7-trans-β-ocimene were the most abundant in the canister analyses, in agreement with the June and August Inficon data for *Q. rubra*. However, a suite of additional MNT compounds similar to the June Inficon data were also present at low levels in the August canister samples for *Q. alba* and *Q. stellata*, while the Inficon analyses indicated mainly D-limonene emissions from these species in August. The Agilent GC/MS system used to analyze these samples is more sensitive to MNT than the Inficon GC/MS, and also more foliage was enclosed in the branch system, increasing overall sensitivity to the MNT compounds. A large peak eluting just before β-myrcene indicated emission of an unidentified MNT compound, which was present in all branch samples and was the most abundant MNT emitted from *Q. alba*.

The aromatic p-cymene has been found in *Quercus* emissions in previous studies (Geron et al., 2000b). In this study p-cymene emissions appeared to decline at higher temperatures relative to isoprene emission and showed an inconsistent response to increasing T_L from each species with the exception of *Q. alba* in June. The p-cymene was comparable to the pinenes in both the ambient and branch enclosure canister samples.

3.3. Comparison of leaf vs canopy monoterpene fluxes

Canopy average M_L rates (Table 4) are at least an order of magnitude lower than the rates used in MEGAN for North American broadleaf deciduous temperate forest canopies and warrant additional attention. MEGAN appears to simulate observed above canopy MNT fluxes (Seco et al., 2015) reasonably well, although MEGAN assumes that only 50% of the MNT flux is light dependent. The flux data indicate a much higher percentage of light-dependent MNT, consistent with MNT emissions from foliage such as oaks, maples, and poplars with no known storage structures. The biomass of conifers is low (*J. virginiana* composes 7% of the basal area) and is not expected to make a large contribution to the observed above canopy MNT flux. *Acer saccharum* accounts for 10% of the basal area at the MOFLUX site, so it is possible that light-dependent MNT emissions from this species could explain some of the above-canopy MNT fluxes reported by Seco et al. (2015). Clement et al. (1990) report MNT mixing ratios of several ppb in an *A. saccharum* forest near Quebec, Canada. However, Ortega et al. (2008) reported very low (<0.01 µgC g^{-1} h^{-1}) M_L rates from *A. saccharum* in a branch enclosure study, where enclosure temperature ranged from 22 to 30 °C.

3.4. October leaf BVOC emissions

Mid to late October I_L measurements were conducted after significant rainfall recharged soil moisture. However, senescence was affecting leaf physiology by the time of these measurements. For each cuvette enclosure, the T_L temperature program ranged from ~15 °C to 35 °C. Several cuvette experiments were performed on leaves at varying stages of senescence (Fig. 2). Green leaves displayed physiological activity, although A and G_s were lower than observed in June and August. Similarly, I_L (at PPFD = 1000 μmol m^{-2} s^{-1} and T_L = 30 °C) was also reduced dramatically, with rates from *Q. rubra*, *Q. velutina*, *Q. alba*, and *Q. stellata* observed at 4.5, 7.5, 7.5, and 12 μgC g^{-1} h^{-1}, respectively. Monoterpenes were below detection limits during the October measurements. This could be an additional indication of summertime, light-dependent *de novo* MNT production and emission since autumn emissions from stored MNT pools would likely be similar to summertime emissions.

4. Discussion

The patterns illustrated above suggest a drought-induced breakdown of the dependence of I_L on T_L in the *Erythrobalanus* subgenus of *Quercus*. This drought-induced breakdown has been observed experimentally by Fortunati et al. (2008) in *Populus nigra* seedlings, and by Tani et al. (2011) in East Asian *Quercus serrata* and *Quercus crispula*. Their results showed that under drought severe enough to completely inhibit A, I_L is also reduced by 65–75%. Fig. 8 illustrates these effects from 10 previously published seedling/drought experiments. This plot indicates that I_L is relatively unaffected when A is within 40% of control (well-watered) values. In several cases, I_L increases with the onset of drought (Tingey et al., 1981; Fang et al., 1996; Funk et al., 2004; Pegoraro et al., 2004b; Genard-Zielinski et al., 2014; Sharkey and Loreto, 1993 *Pueraria lobata* data not shown). As A continues to decline, however, I_L begins to decline more rapidly. Even when A reaches 0 μmol m^{-2} s^{-1}, I_L is within 30–70% of control values. The I_L reductions shown bracket the reduction observed in the PINOT NOIR above canopy isoprene fluxes. Brilli et al. (2007) found that under these severe conditions, the residual I_L can be derived from non-photosynthetic cytosolic carbon entering the DOXP/MEP pathway. Fortunati et al. (2008) showed that this A—independent I_L is also independent of T_L. These patterns are consistent with the decoupled I_L - T_L relationships observed during the peak drought period of PINOT NOIR in 2012. Although we observed low positive rates of A and a positive I_L correlation with T_L before midday during the severe PINOT NOIR drought, the declines in A through the day may limit A-derived carbon sources available for isoprene production, decoupling I_L from T_L. Reductions in T_L initially induced in the leaf cuvette systems during T_L response experiments appeared to stimulate A, as observed in *Q. alba*, *Q. imbricaria*, and *Q. rubra*, and under these conditions, may produce enough substrate to drive isoprene production, at least temporarily.

In contrast to the other *Quercus* species studied, *Q. stellata* I_L increased under drought stress and high temperature conditions, indicating tolerance for drought. Other *Quercus* species at the plains-deciduous forest interface have been found to be similarly tolerant of such stress. Following prolonged exposure to T_L of 47 °C, Bur oak (*Quercus macrocarpa* Michx.) and chinquapin oak (*Quercus muehlenbergii* Engl.) leaves showed A values (measured at optimum ambient temperatures of 22–30 °C) similar to those observed for other *Quercus* and hardwood species at optimum temperatures (Hamerlynck and Knapp, 1996, and references therein). The thermal tolerance characteristics of these oaks contributes to their persistence in deciduous forest, extending west into the hot, semi-arid grasslands of the North American central plains. Although these species have not been quantitatively studied for isoprene

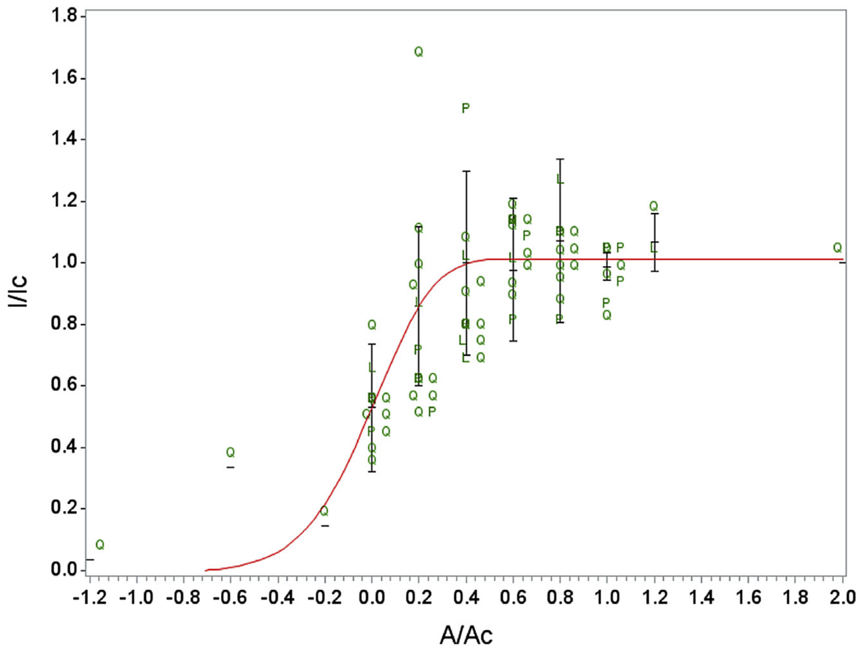

Fig. 8. Isoprene emission versus carbon assimilation from published tree seedling drought exposure studies. I_L from drought stressed leaves divided by I_L from leaves of well-watered control plants (I/Ic) is plotted versus A from the drought stressed leaves divided by A from the leaves of well-watered control plants (A/Ac). Data are from Brilli et al. (2007, *Populus alba*), Bruggemann and Schnitzler (2002, *Quercus pubescens* and *Q. robur*), Fang et al. (1996, *Liquidambar styraciflua*), Funk et al. (2004, *Populus deltoides*), Funk et al. (2005, *Quercus rubra*), Genard-Zielinski et al. (2014, *Quercus pubescens*), Pegoraro et al. (2004a, *Populus deltoides*), Pegoraro et al. (2004b, *Quercus virginiana*), Tani et al. (2011, *Quercus crispula* and *Q. serrata*), and Tingey et al. (1981, *Quercus virginiana*). Vertical lines are ± one standard deviation of I/Ic for binned A/Ac values. Solid line represents fit of the Richards function to 114 data points ($I/Ic = a(1-[e(A/Ac+1.2)^{b}]^{c}$ where $a = 1.011$, $b = -0.2410$, and $c = 6.1316$ are parameter estimates from an iterative non-linear least squares fit. Green letters denote genus (L = *Liquidambar*, P = *Populus*, Q = *Quercus*) means for each study within each A/Ac bin. Some of these symbols are slightly offset to avoid overlap. Single dash symbols with no vertical bars denote bins with a single observation.

emission, it is possible that these species also produce isoprene during severe thermal and drought stress environments similar to *Q. stellata*. *Q. muehlenbergii* occupies the dry limestone outcrops near the MOFLUX tower and is a significant component of the flux footprint (Fig. 1) and surrounding forest (Table 1). Additional measurements are needed to determine if these species may contribute disproportionally to BVOC fluxes during drought at this site and regionally.

Estimates of *Quercus* species abundance and distribution within the flux footprint of the tower is illustrated in Fig. 1 and Table 1. An estimate of the contribution of the mean reduction in the oak isoprene emission factor to the above-canopy isoprene flux could be approximated as a basal area-weighted average of the *Q. alba*, *Q. stellata*, *Q. rubra* and *Q. velutina* emission factor reduction between June and August (see Table 4). This reduction, on the order of 30%, would explain much of the observed 50–70% reduction in whole-canopy flux measurements between the two periods (Seco et al., 2015). Given the reduced I_L response to increasing leaf temperature during the drought, the difference between pre-drought and drought conditions may be exacerbated on days when the canopy temperature exceeds 30 °C. This response also helps explain the 40% over-prediction by MEGAN for the 2012 growing season (Seco et al., 2015). The soil water content needed to trigger the wilting point function with the default MEGAN2.1 soils data was never reached, probably because the soil water content at the wilting point was actually higher at this site than the value of 8% soil volumetric water content assumed in the model. This has also been documented by Sindelarova et al. (2014) and Huang et al. (2015), where alternate wilting point datasets were evaluated and found to yield higher values of soil moisture at wilting point than the default database currently used in MEGAN2.1. I_L data, especially within the red oak species, would also suggest that diurnal effects of severe drought might be more significant in the afternoon hours compared to morning emissions. However, comparison of above canopy flux estimates before and during the drought showed no obvious drought-related shifts in diurnal patterns of isoprene flux, possibly due to species composition being dominated by *Q. alba* near the tower (Fig. 1). *Q. alba* did not show as severe a decline at higher temperatures or during the PM hours compared with the *Erythrobalanus* species. Several leaves tagged for analysis in June were actually lost prior to the August measurements due to early abscission related to the drought. This rough estimate of overall canopy isoprene emission reduction does not take into account the loss of foliage in the canopy due to drought-related abscission or tree mortality. Tree and leaf mortality could explain the difference between the 30–40% decreases in I_L versus the 70% reduction in above-canopy isoprene fluxes observed from June to August, 2012 by Seco et al. (2015).

Previous droughts in this region demonstrate that this mortality can be very high among the *Erythrobalanus*. Visual observation from the MOFLUX tower in August of 2012 indicated that foliage of several tree crowns was wilting and turning brown, suggesting that mortality may have also affected the canopy during this drought as well. These observations are confirmed by Gu et al. (2015), who observed considerable mortality among various tree species as a result of the 2012 drought, including *Q. velutina* and *Q. alba*, which suffered 20% and 7% of basal area mortality, respectively. Overall 17% and 7.8% of *Erythrobalanus* and *Leucobalanus* trees, respectively, suffered mortality, although not all mortality was apparent until spring of 2013. Presumably, leaf mortality was greater than tree mortality, so a significant reduction of isoprene-emitting leaf biomass is likely.

Above-canopy monoterpene fluxes observed during PINOT NOIR are among the highest observed anywhere in North America. Peak MNT fluxes exceeded 3.75 mgC m^{-2} h^{-1} in late June (Seco et al., 2015). These fluxes exceed extrapolations of the leaf and branch enclosure emission data by at least an order of magnitude, although the canopy MNT fluxes are given only as total monoterpenes (AMU 136) from the PTRMS as determined from the main MNT fragment ($m/z = 81$) and protonated parent mass ($m/z = 137$). MNT compounds have been observed as light- and temperature-dependent emissions from flowering plants such as deciduous broadleaf trees and are thought to be under synthesis and environmental controls similar to isoprene emission. The above-canopy diurnal MNT flux profile is very similar to the isoprene flux profile at this site, suggesting that MNT emission from the Ozark deciduous canopy is indeed under similar controls. The Inficon emission samples suggest that, compared to *Q. rubra*, MNTs are less abundant relative to isoprene from *Q. velutina*, *Q alba* and *Q. stellata*, by factors of approximately 7, 35 and 4 in June and 6, 5, and 10 in August, respectively. The branch enclosures yielded MNT compound profiles similar to MNT compound profiles from the leaf enclosure samples analyzed on the Inficon. Relative differences in I_L:M_L between species was higher by a factor of 2–3 for *Q. rubra* compared to *Q alba* and *Q. stellata*. These differences may be at least partly due to self-shading in the branch enclosure and natural variability between leaves.

Mixing ratios of isoprene to MNT (I/M) were considerably lower in the ambient air above the canopy relative to the enclosures. These ratios suggest that MNT emissions from other species (possibly *Acer saccharum*) within the footprint of the flux tower may be considerably higher than MNT emissions from *Quercus* species examined here. Canister samples were collected at two heights on the MOFLUX tower; at the canopy crown and co-located with the PRTMS inlet (Seco et al., 2015). The Isoprene mixing ratio in a canister sample (3.6 ppb) taken near the PTRMS inlet at 1:20 PM on August 9, 2012 was in reasonable agreement with the PTRMS (2.8 ppb). However, the canister yielded an I/M signal of approximately 2, which is lower than the observed PTRMS I/M for above-canopy mixing ratios (34). MNT mixing ratios were much higher in the canister (1.7 and 0.065 ppb from the canister and PTRMS, respectively). Camphene was the dominant MNT compound in the canister sample followed by α-pinene, D-limonene, 1,3,7-trans-β-ocimene, and 1,3,6-trans-β-ocimene. Other significant unidentified MNT compounds were present as well, as indicated by peaks at mass 93 in the SIM analysis. A "green" (low oxidant) solvent, ρ-chlorotriflouromethylbenzene, was also detected in this sample, and offsite contamination cannot be ruled out for this measurement. Interestingly, a second canister sample taken later in the afternoon (3:30 PM LST) at canopy level showed a higher I/M of 17:1. Isoprene mixing ratios were 3.3 and 3.4 ppb from the canister and PTRMS, respectively. MNT was higher in the canister (0.195 and 0.060 ppb from the canister and PTRMS, respectively). These ratios are in better agreement with the observed PTRMS above-canopy mixing ratios (56:1), and 4–40 times lower than observed in the enclosure measurements. The β-ocimene mixing ratios in the canister at canopy level were 15% higher than observed at the PTRMS inlet. Ocimene has higher reaction rates with O_3 and the hydroxyl radical than most of the other MNTs and may be lost to reactions farther above the canopy, although sample variability and footprint effects may also contribute to these differences. Conversely, camphene mixing ratios were 100 times greater at the PTRMS inlet compared to canopy level. The isoprene/monoterpene values in ambient measurement mixing ratios and fluxes appear to be significantly lower than the corresponding ratios from the leaf and branch enclosure measurements, suggesting: 1) a large unexplained monoterpene source in the tower footprint, 2) perturbation of emissions by the enclosure techniques, 3) greater branch to branch emission variability of MNT emissions, 4) variable intraspecific tree to tree emissions due to highly variable stress levels, or

5) differences in analytical techniques between enclosure and above canopy measurements.

5. Conclusions

The data presented here suggest that drought had a significant effect on I_L and M_L basal emission rates as well as temperature and light response. These effects varied significantly between species, and it is important to note that such effects cannot be detected from whole-canopy flux studies. Even within an oak canopy classification, variation in species composition could result in significant differences in response to drought and high temperatures. For instance, a forest stand composed of *Q. stellata*, *Q. muehlenbergii*, and *Q. macrocarpa* could produce dramatically different isoprene fluxes during dry, hot conditions compared to a forest dominated by *Q. alba*, *Q. rubra*, and *Q. velutina*. Taken together, however, the drought responses of the individual species at MOFLUX are generally consistent with canopy fluxes of isoprene given the *Quercus* species composition near the tower. The leaf level data are also consistent with laboratory effects of drought on I_L documented in previous studies, suggesting a drought-induced breakdown of the dependence of I_L on T_L particularly within the *Erythrobalanus* subgenus of *Quercus*. Low levels of leaf monoterpene emissions measured before and during the drought of 2012 suggest that non-oak sources of these compounds may be controlling above canopy fluxes. Additional leaf-level studies are needed in the field for both I_L and M_L during drought-affected growing seasons. Screening of other species with thermal and drought stress tolerance similar to *Q. stellata*, which are adapted to the semi-arid eastern deciduous forest-prairie Great Plains interface, is also warranted. Quantitative soil to leaf water relationships and their impacts on BVOC emissions are needed to improve BVOC emission model performance under drought stress conditions.

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