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Ecosystem-scale volatile organic compound fluxes during an extreme drought in a broadleaf temperate forest of the Missouri Ozarks (central USA)

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Abstract

Considerable amounts and varieties of biogenic volatile organic compounds (BVOCs) are exchanged between vegetation and the surrounding air. These BVOCs play key ecological and atmospheric roles that must be adequately represented for accurately modeling the coupled biosphere–atmosphere–climate earth system. One key uncertainty in existing models is the response of BVOC fluxes to an important global change process: drought. We describe the diurnal and seasonal variation in isoprene, monoterpene, and methanol fluxes from a temperate forest ecosystem before, during, and after an extreme 2012 drought event in the Ozark region of the central USA. BVOC fluxes were dominated by isoprene, which attained high emission rates of up to 35.4 mg m⁻² h⁻¹ at midday. Methanol fluxes were characterized by net deposition in the morning, changing to a net emission flux through the rest of the daylight hours. Net flux of CO₂ reached its seasonal maximum approximately a month earlier than isoprenoid fluxes, which highlights the differential response of photosynthesis and isoprenoid emissions to progressing drought conditions. Nevertheless, both processes were strongly suppressed under extreme drought, although isoprene fluxes remained relatively high compared to reported fluxes from other ecosystems. Methanol exchange was less affected by drought throughout the season, confirming the complex processes driving biogenic methanol fluxes. The fraction of daytime (7–17 h) assimilated carbon released back to the atmosphere combining the three BVOCs measured was 2% of gross primary productivity (GPP) and 4.9% of net ecosystem exchange (NEE) on average for our whole measurement campaign, while exceeding 5% of GPP and 10% of NEE just before the strongest drought phase. The MEGANv2.1 model correctly predicted diurnal variations in fluxes driven mainly by light and temperature, although further research is needed to address model BVOC fluxes during drought events.

Keywords: biogenic emissions, drought, isoprene, isoprene volcano, MEGAN, methanol, monoterpenes, VOC

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Introduction

Plants exchange a wide array of volatile organic compounds (VOCs) with the atmosphere (Kesselmeier & Staudt, 1999), emitting these VOCs in amounts estimated to be an order of magnitude greater than those emitted from anthropic VOC sources on a global scale (Guenther *et al.*, 1995). Thousands of biogenic VOCs (BVOCs) have been characterized, and there is growing evidence that many others are yet to be identified (Goldstein & Galbally, 2007; Park *et al.*, 2013). BVOCs

have ecological functions such as protecting vegetation from abiotic stresses (Singsaas & Sharkey, 1998; Peñuelas *et al.*, 2005; Velikova *et al.*, 2005) or acting as communication signals in plant–plant, plant–animal, and multitrophic relationships (Kessler & Baldwin, 2001; Pichersky & Gershenzon, 2002; Baldwin *et al.*, 2006; Seco *et al.*, 2011a; Filella *et al.*, 2013). In addition, BVOCs can substantially influence atmospheric chemistry and composition (Atkinson, 2000; Tunved *et al.*, 2006; Pryor *et al.*, 2014).

Although the existence of many BVOCs has been known for over a century (e.g. Schreiner & Kremers, 1901), it was during the early 1960s that the first speculations were made concerning the importance of

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isoprenoid emissions (specifically, isoprene and monoterpenes) to the atmosphere and their subsequent photochemical reactions (Went, 1960; Rasmussen & Went, 1965; Sanadze & Kalandadze, 1966; Went *et al.*, 1967). Since Levy (1971) postulated the photochemical production of hydroxyl radical (OH), a strong tropospheric oxidant, the consequences of isoprenoid oxidation by OH have been discussed. For instance, ozone formation due to isoprene photochemistry in rural and urban environments was highlighted by Trainer *et al.* (1987) and Chameides *et al.* (1988), respectively. VOC oxidation produces oxygenated VOCs that usually have lower vapor pressure than the reactant VOCs and hence partition more into the particulate phase in the atmosphere. In fact, Hallquist *et al.* (2009) estimated the annual atmospheric organic aerosol loading from BVOC oxidation processes (88 TgC) to be significantly higher than from anthropogenic VOCs (10 TgC).

Tropospheric ozone and aerosols are also considered to be important short-lived climate forcers, although the level of scientific understanding to constrain their roles in the earth's climate system is considered medium to low (IPCC, 2013). All aspects of BVOC tropospheric photochemistry from emission, atmospheric oxidation processes producing tropospheric ozone and secondary organic aerosols (SOAs), to the atmospheric removal processes of those photochemical products are highly uncertain (Arneeth *et al.*, 2010a; Guenther, 2013). BVOC fluxes, especially those of isoprene, are increasingly considered a necessary part of regional and global earth system models, and the response of modeled emissions to global change phenomena such as drought have been identified as a key uncertainty (e.g. Müller *et al.*, 2008; Unger *et al.*, 2013; Sindelarova *et al.*, 2014), highlighting the need for better simulation techniques for the increasing impact of drought (Dai, 2013) and other global change-related stresses on simulated BVOC emissions.

In this study, we report the dynamics of mixing ratios and fluxes of isoprene, monoterpenes, and methanol under extreme drought conditions at a temperate deciduous forest site in the central USA. The measurements were made from May to October 2012 at the Missouri Ozarks Forest AmeriFlux site (MOFLUX, Gu *et al.*, 2006, 2007, 2015) as part of the PINOT-NOIR ('Particle Investigations at a Northern Ozarks Tower: NO_x, Oxidants, Isoprene Research') field campaign. BVOC emission models predict high emissions of isoprene from this region, so high that it has been referred to as an 'isoprene volcano' (Wiedinmyer *et al.*, 2005; Carlton & Baker, 2011). Indeed, at the same Missouri site in 2011, Potosnak *et al.* (2014) measured the highest isoprene fluxes ever reported from a forest canopy with fluxes, measured by means of an eddy covariance

system with a fast isoprene sensor (FIS, Guenther & Hills, 1998), reaching maximum rates of 53 mg m⁻² h⁻¹. In that year, the site experienced abnormally dry to moderate drought conditions during August (The Drought Monitor). In 2012, our present study expanded the VOC species analyzed to include monoterpenes and methanol using virtual disjunct eddy covariance with a proton transfer reaction mass spectrometer (PTR-MS). During August 2012, the drought class reached extreme to exceptional, the highest classes possible (The Drought Monitor). Because the drought conditions in 2012 at the MOFLUX site were extraordinary, the dataset presented here represents an exceptional resource for improving our understanding of the drought effects on ecosystem VOC emissions and for testing the performance of present and future BVOC emission models.

Materials and methods

Site description

The study site (MOFLUX) is located in the Baskett Wildlife Research and Education Area (BWREA), operated by the University of Missouri near the city of Ashland (Lat. 38°44'39"N, Long. 92°12'W). BWREA is within the Ozark border region of central Missouri. Second-growth upland oak-hickory forests constitute the major vegetation type at the BWREA (Rochow, 1972; Pallardy *et al.*, 1988). Major tree species include white, post and black oaks (*Quercus alba* L., *Q. stellata* Wangenh., *Q. velutina* Lam.), shagbark hickory (*Carya ovata* (Mill.) K. Koch), sugar maple (*Acer saccharum* Marsh.), and eastern red cedar (*Juniperus virginiana* L.). The average peak leaf area index (LAI) is approximately 3.7. The climate of the area is classified as warm, humid, and continental (Critchfield, 1966), with monthly mean temperature of -1.3 °C in January and 25.2 °C in July and an annual total precipitation average of 1083 mm (National Climatic Data Center 1981–2010 climate normals, Columbia Regional Airport, Missouri). Two soil types are dominant at the site: Weller silt loam (fine, smectitic, mesic Aquertic Chromic Hapludalf) and Clinkenbeard very flaggy clay loam (clayey-skeletal, mixed, superactive, mesic Typic Argiudoll) (Young *et al.*, 2001). The comparatively thin soils beneath these oak-hickory forests often exacerbate plant water stress when droughts occur (Bahari *et al.*, 1985). Further details about site characteristics can be found in Gu *et al.* (2006, 2007, 2015).

Environmental and ecophysiological parameters

As a member of the AmeriFlux network, the MOFLUX site has been in continuous operation since 2004. The eddy covariance (EC) flux and meteorological measurements were made on a 32-m walkup scaffold tower, approximately 10 m above the top of the canopy (the average height of trees in the top quartile is 22 m). The CO₂ and H₂O flux

data used in this study were from an EC system consisting of a 3-D ultrasonic anemometer (model CSAT3, Campbell Scientific, Logan UT, USA) and a fast response, open-path infrared CO₂/H₂O gas analyzer (model LI7500A; Li-Cor, Lincoln NE, USA). The anemometer and gas analyzer were installed at the top of the tower and all sampled at 10 Hz. The gas analyzer was calibrated monthly. The EC system was coupled with a 12-level CO₂/H₂O mixing ratio profile system (Yang *et al.*, 2007) and an eight-level temperature/humidity profile system (Gu *et al.*, 2006). These two profiling systems were used to calculate the changes in the rate of storage of CO₂, water vapor and sensible heat in the air space below the EC instrumentation. The eddy fluxes and the changes in the rate of storage were determined at a half-hourly time step. Spectral and cospectral corrections as detailed in Mauder & Foken (2011) were adopted to correct relevant variances and covariances. The calculations of net ecosystem exchanges (NEE) from eddy fluxes and the changes in the rate of storage followed the fundamental equation of eddy covariance of (Gu *et al.*, 2012), which reformulated the theory of Webb *et al.* (1980) to ensure an internal consistency of the EC technique.

Incoming and reflected photosynthetically active radiation (PAR) were measured at the top of the tower with PAR quantum sensors (model PQS 1; Kipp & Zonen, Delft, Netherlands). Shortwave and longwave radiations were measured with a net radiometer (model CNR 4; Kipp & Zonen). Precipitation was measured with a recording tipping bucket rain gauge (TR-525M; Texas Electronics, Dallas, TX, USA) mounted at the top of the tower. Data were totaled over 30 min periods. Air temperature and relative humidity data used in this study were also measured at the top of the tower. Atmospheric vapor pressure deficit (VPD) was computed from the measured temperature and relative humidity. Volumetric soil water content was measured at multiple depths from 5 to 100 cm with water content reflectometers (model CS616; Campbell Scientific, Logan, UT, USA).

Predawn leaf water potential (Ψ_{pd}) is commonly used by plant physiologists to measure plant water stress (Hsiao, 1973; Pallardy, 2008). The Ψ_{pd} data used in this study were from an ongoing MOFLUX effort that periodically quantifies plant physiological water stress during the growing season at the site. The first measurements occurred in late April and the last measurements took place in late October. Leaf samples were collected before dawn from canopy and sapling individuals of common tree species at the site. A total of 20–21 samples were obtained each day with 6–7 taken from *Quercus alba*, and the rest were distributed among *Q. velutina*, *Acer saccharum*, *Carya ovata*, *Fraxinus americana* (white ash), and *Juniperus virginiana*, roughly in proportion to their relative stem abundance in the stand. Ψ_{pd} was measured with a pressure chamber (Turner, 1981). The Ψ_{pd} data reported in this study were averaged across species.

To compare the amount of carbon emitted as VOC to the amount of carbon fixed by photosynthesis, the ecosystem gross primary productivity (GPP) was calculated using the model described by Gu *et al.* (2002; Eqns 6 and 7 therein). This model takes into account the VPD, which was expected to

play an important role in the calculations of GPP in the drought environment of 2012.

VOC measurements

Volatile organic compound measurements spanned 174 days, between 2 May and 22 October 2012. Air from the top of the MOFLUX tower (32 m agl), next to the sonic anemometer, was drawn by means of a pump through a 1/4 inch OD PFA Teflon tube to a small air-conditioned building located at the base of the tower. VOC quantitation was performed inside the building with a high sensitivity proton transfer reaction quadrupole mass spectrometer (PTR-Quad-MS, Ionicon, Austria) that, in the present configuration, has been described elsewhere (Karl *et al.*, 2001). In short, the instrument generates hydronium ions that transfer a proton to select VOC molecules in a drift tube under a constant electric field (e.g. Hansel *et al.*, 1995; Lindinger *et al.*, 1998). These charged VOC molecules are then detected by the combined effect of a quadrupole mass spectrometer and an ion detector. The drift tube of the instrument used in this study was operated at a pressure of 2.3 mbar, a temperature of 40 °C, and a voltage of 540 V, corresponding to an E/N ratio of 110 Td (E being the electric field strength and N the gas number density; 1 Td = 10⁻¹⁷ V cm⁻²).

Instrument background was measured daily by diverting the inlet air through a platinum catalyst heated to 380 °C. Calibration of the PTR-MS was performed by dilution of a house-made VOC gas standard into zero air generated by a second heated catalytic converter (415 °C). Two mass flow controllers (MKS Instruments, Andover MA, USA) were used for the dilution. The gas standard contained approximately 5 ppmv each of isoprene, camphene, and benzene. The calibration factors measured for camphene were used to calculate the total monoterpene mixing ratios in ambient air, and the calibration factor for methanol was calculated from the calibration factor of benzene taking into account the transmission efficiency of the detection system and the reaction rate of each compound with H₃O⁺ ions (Cappellin *et al.*, 2012). The main *m/z* (mass to charge ratios) monitored during this study were *m/z* 21 (H₃O⁺ isotope, 0.5 s dwell time), *m/z* 33 (methanol, 0.1 s dwell time), *m/z* 39 (water cluster, 0.1 s dwell time), *m/z* 69 (isoprene, 0.1 s dwell time), and *m/z* 81 and *m/z* 137 (monoterpenes, 0.1 s dwell time each). The cycle scanning through all the *m/z* ratios had a duration of approximately 1.2 s (i.e. each *m/z* was measured once every 1.2 s), and measurements for EC were recorded for 25 minutes of each half-hour.

Fluxes of VOCs were calculated using the virtual disjunct eddy covariance technique (vDEC), also known as disjunct eddy covariance by mass scanning (Karl *et al.*, 2002). The disjunct time series that was generated for each *m/z* every half-hour was time aligned with the vertical wind data from the sonic anemometer by shifting one time series relative to the other until the absolute maximum covariance between the two time series was determined. Using this procedure, the time lag between the two measurements was found to be approximately 4 s. In the case of methanol, we used the lag time of isoprene when the absolute covariance peak was difficult to find. Previously, the wind data had been rotated according to the

planar fit method (Wilczak *et al.*, 2001). Computed fluxes were excluded from further analysis if any of the following conditions occurred: (i) turbulence was low ($u^* < 0.15$); (ii) vertical wind rotation exceeded 5° ; and (iii) results of the stationarity test (Foken *et al.*, 2004) were higher than 30% for isoprene and monoterpenes or higher than 50% for methanol. Half-hour EC fluxes excluded by these conditions represented 38%, 61%, and 51% of the total calculated for isoprene, monoterpenes, and methanol, respectively. The flux detection limit was calculated according to the approaches of Spirig *et al.* (2005) and Billesbach (2011). However, no computed flux was excluded from analysis for being below the detection limit to avoid discarding net fluxes close to zero (e.g. at nighttime or small deposition fluxes for methanol) that otherwise were accepted following the conditions explained above.

High-frequency losses due to the instrument gas exchange time in the drift tube were not corrected for because comparison to temperature cospectra showed that the contribution of high frequencies to fluxes was typically under 5%, as expected for such an environment. The measurement tower was surrounded by forest in a continuous radius of 1 km, which mainly contained the 90% flux recovery footprint as modeled by Hsieh *et al.* (2000), so no VOC data were filtered out on the basis of wind direction. vDEC calculations were performed with MATLAB software (Mathworks, Natick, MA, USA).

Representative episodes along the season

To allow a better interpretation of the results, three main and three secondary episodes were selected along the measurement season, and they are represented in Fig. 1 by colored backgrounds.

The three main episodes identified were as follows: (i) *MaxCO₂* (11–21 May) when ecosystem net CO₂ assimilation and H₂O evapotranspiration were at their peak; (ii) *MaxVOC* (18 June–8 July) when isoprene and monoterpene fluxes were at their seasonal maxima; and (iii) *Drought* (7–27 August) when the highest drought stress on the ecosystem was recorded.

The three secondary episodes were *T1* (31 May–14 June) and *T2* (16–28 July), which essentially were transitional periods between *MaxCO₂* and *MaxVOC*, and between *MaxVOC* and *Drought*, respectively, and *Recovery* (18–27 September). The *Recovery* period was characterized by an increase of net CO₂ flux after the occurrence of some rain events that mitigated the drought experienced by the ecosystem.

VOC flux modeling

Two modeling approaches were applied to analyze this dataset: a simple big-leaf model and a site-specific version of the MEGANv2.1 model. The simple approach used a big-leaf model (Geron *et al.*, 1997) to assess the responses of canopy-level VOC fluxes to light and temperature, using the leaf-level algorithms developed by Guenther *et al.* (1991, 1993, 1999) and described by the following expressions (Eqns 1–3).

The response of isoprene and monoterpene fluxes to light was modeled as follows:

$$C_L = \frac{\alpha \cdot C_{L1} \cdot L}{\sqrt{1 + \alpha^2 \cdot L^2}} \quad (1)$$

where C_L is a scalar representing electron transport rates to simulate the response (nondimensional) of isoprene emission to light (Guenther *et al.*, 1991), α and C_{L1} are empirical parameters, and L is PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$).

The response of isoprene and monoterpene fluxes to temperature was modeled as follows:

$$C_T = \frac{E_{\text{opt}} \cdot C_{T2} \cdot e^{C_{T1} \cdot x}}{C_{T2} - C_{T1} \cdot (1 - e^{C_{T2} \cdot x})}, \quad x = \frac{\frac{1}{T_{\text{opt}}} - \frac{1}{T}}{R} \quad (2)$$

where C_T is a scalar representing an enzyme activation to simulate the response (nondimensional) of isoprene emission to temperature (Guenther *et al.*, 1991), E_{opt} ($\text{nmol m}^{-2} \text{s}^{-1}$) is the maximum normalized emission capacity at temperature T_{opt} (K), C_{T1} (kJ mol^{-1}) and C_{T2} (kJ mol^{-1}) are empirical parameters, T is the current temperature (K), and R is the ideal gas constant ($= 0.008314 \text{ kJ K}^{-1} \text{ mol}^{-1}$).

The response of monoterpene and methanol fluxes to temperature was modeled as follows:

$$F_{\text{VOC}} = F_{\text{ref}} \cdot e^{\beta \cdot (T - T_{\text{ref}})} \quad (3)$$

where F_{VOC} is the actual VOC emission flux ($\text{mg m}^{-2} \text{h}^{-1}$) at temperature T (K), F_{ref} is the VOC emission ($\text{mg m}^{-2} \text{h}^{-1}$) at T_{ref} ($= 303 \text{ K}$), and β (K^{-1}) is an empirical coefficient.

For the big-leaf model used in this analysis, which considers the canopy as a single multispecies layer of foliage, above-canopy PAR was used in Eqn 1 instead of leaf-level PAR, and temperature values used in Eqns 2 and 3 were above-canopy air temperature instead of leaf temperature. To calculate light dependence (Eqn 1), flux data measured in a narrow range of air temperatures ($23\text{--}27^\circ\text{C}$) were binned into $100 \mu\text{mol m}^{-2} \text{s}^{-1}$ groups. For the temperature dependencies (Eqns 2 and 3), only VOC flux data for which PAR exceeded $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ were grouped in 1°C bins. The binned flux data were averaged and subsequently those averages were fitted to the algorithms using nonlinear least squares regression to determine the best fit parameter values using the software Igor Pro (Wavemetrics Inc., Portland, OR, USA).

The second modeling approach was a single location version of the widely used MEGAN version 2.1 model (Guenther *et al.*, 2012) that includes an explicit canopy environment model with a canopy radiation transfer and energy balance scheme to calculate direct and diffuse light and leaf temperature of sun and shade leaves at each of five layers. The model calculates fluxes as the product of a fixed canopy emission factor and nondimensional emission activity factors. For this study, we used the model's global default canopy emission factors assigned to broadleaf deciduous temperate forests, with values of 10, 0.99, and $0.8 \text{ mg m}^{-2} \text{h}^{-1}$ for isoprene, monoterpenes, and methanol, respectively. The environmental conditions measured at the tower (Figs 1 and 2) were used to constrain the driving variables of the model's emission activity factors (air temperature, PAR, LAI, wind speed, etc.). Additionally, the temperature and light emission activity

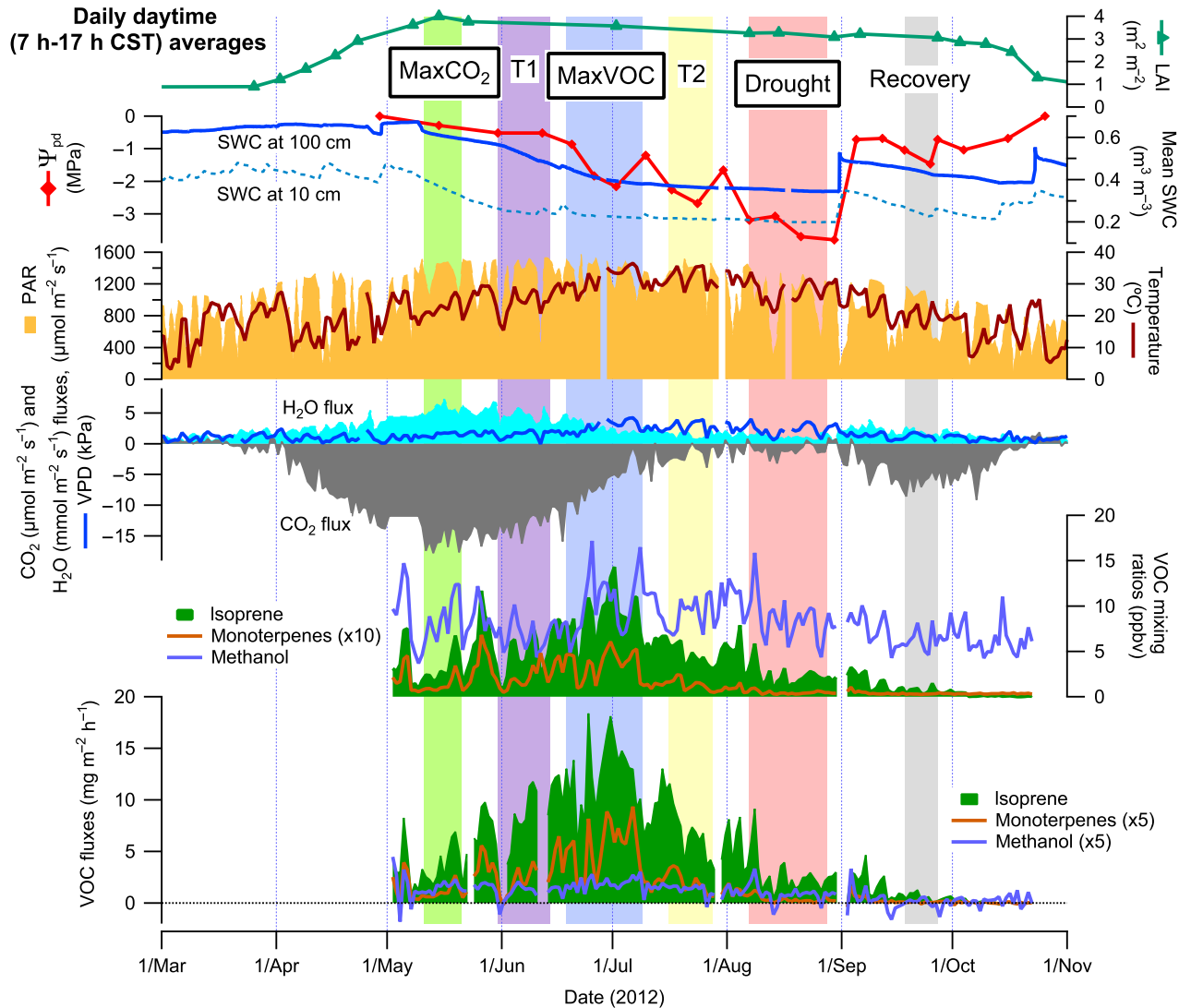


Fig. 1 Daily daytime (7–17 h CST) averages of environmental and physiological parameters, VOC mixing ratios, and VOC canopy-level fluxes measured at the MOFLUX site. The different episodes (see main text) are identified by their name and marked by colored backgrounds. Isoprene mixing ratios and fluxes (lower panels) are shown with filled traces—highlighting the seasonal shape—to allow a better visual comparison to PAR and CO₂ and H₂O flux seasonal shapes. Note that monoterpene mixing ratios (×10) and methanol and monoterpene fluxes (×5) have been multiplied for clarity. Date labels indicate 00:00 h CST. LAI: leaf area index; Ψ_{pd}: predawn leaf water potential; SWC: soil water content; PAR: photosynthetically active radiation; VOC: volatile organic compounds; CST: Central Standard Time (UTC-6 h).

factors include the influence of the past 24 and 240 h of temperature and light conditions. The version 2.1 of the MEGAN model also incorporates a drought activity factor that is driven by soil volumetric moisture content and is used to linearly decrease to zero the calculated flux of isoprene when soil water content falls between 0.04 m³ m⁻³ above the soil wilting point and the wilting point itself. Potosnak *et al.* (2014) used a wilting point value of 0.084 m³ m⁻³ for the MOFLUX site, taken from a global dataset for wilting points (Chen & Dudhina, 2001), and found that the drought activity factor had no effect on modeled isoprene fluxes because the soil moisture in 2011 was always above the threshold value. Similarly in 2012, soil moisture was always above the 0.124 m³ m⁻³ needed to

trigger the drought activity factor using the 0.084 m³ m⁻³ wilting point value even though the ecosystem was in an extreme to exceptional drought status as confirmed by the Ψ_{pd} and daytime net CO₂ flux measurements. Instead, by examining the Ψ_{pd} and SWC data (at 10 cm of soil depth), we took as wilting point a value of 0.23 m³ m⁻³ for use in MEGAN's drought activity factor algorithm, consistent with values of soil moisture at wilting point for combined silt-loam (Weller series) and rocky clay-loam (Klinkenbeard series) soil types found at the site (Spurr & Barnes, 1980). This value also corresponded to a Ψ_{pd} of -1.5 MPa, equal to the commonly used value of soil matrix potential that defines the permanent wilting point (Soil Science Society of America, 1997) beyond

which a plant wilts and is not able to recover its turgidity when placed in a saturated atmosphere.

Results

Drought intensity

The total accumulated rainfall for the whole year 2012 was 563 mm, the lowest amount of at least the last decade. In particular, small was the summer precipitation amount for 2012, a fact that had a big impact on the ecosystem drought intensity (Gu *et al.*, 2015). Also important was that the precipitation events in 2012 were unusually sporadic. L. Gu *et al.* (manuscript in

preparation) applied several indices to show that the high unevenness in stress-releasing precipitation events was an essential factor in defining the intensity of the 2012 drought.

Soil water content started to decrease at the beginning of May and reached its minimum (0.2 and $0.35 \text{ m}^3 \text{ m}^{-3}$ at 10 and 100 cm depth, respectively) at the end of August (Figs 1 and 2). Likewise, Ψ_{pd} decreased gradually until the end of August when it reached a minimum of -3.79 MPa (Fig. 1). Plants are typically classified to be under severe water stress when leaf water potential drops below -1.5 MPa , according to the commonly accepted criteria suggested by Hsiao (1973). In addition, the mean ($\pm \text{SE}$) Ψ_{pd}

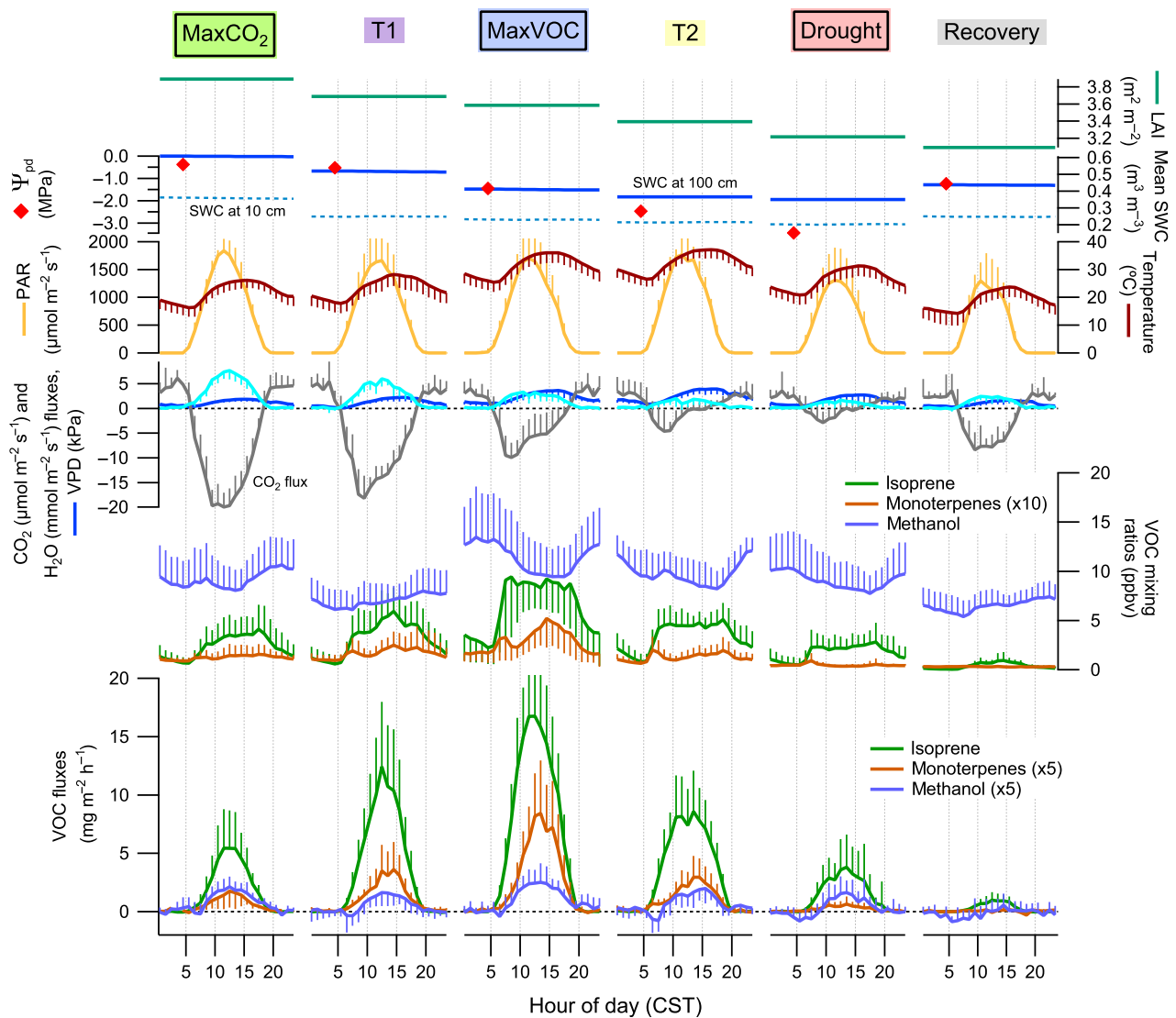


Fig. 2 Hourly averaged diel cycles of the environmental and physiological parameters and VOC mixing ratios and fluxes measured at the MOFLUX site. Each vertical panel shows the diel cycle for each episode (see main text). Error bars indicate plus or minus one standard deviation for each hourly average. See caption of Fig. 1 for the meaning of symbols and acronyms.

seasonal minimum for the preceding years (2004–2012) was -1.91 ± 0.41 MPa. Therefore, the 2012 minimum Ψ_{pd} value was more than 4 SE below the seasonal mean which highlights the severity of the drought of 2012 at the MOFLUX site. Air VPD values also reflected the dryness: between the end of June and the end of August, when VPD reached its highest values, 26 days had half-hour peaks higher than 4 kPa, of which 10 days exceeded 5 kPa. As a result, VPD hourly averages corresponding to *MaxVOC* and *T2* episodes showed values between 3 and 4 kPa in the afternoon hours (Fig. 2).

Water and carbon dioxide fluxes

Ecosystem daytime net CO_2 fluxes started to increase at the beginning of April with leafout and increasing LAI values (Fig. 1). Daytime CO_2 fluxes increased in magnitude gradually until mid-May (*MaxCO₂* period) when daily average net assimilation of $17.8 \mu\text{mol m}^{-2} \text{s}^{-1}$ (and 30-min peaks of up to $30 \mu\text{mol m}^{-2} \text{s}^{-1}$, data not shown) were measured (Fig. 1). The diel cycles of hourly CO_2 fluxes (Fig. 2) revealed that starting in June (*T1* episode) and continuing until the end of August (*Drought* episode), the CO_2 net assimilation showed a peak in the morning before 10:00 h, and then declined to lower levels of CO_2 exchange between 10:00 and approximately 15:00 h. Net water flux average daily maxima (occurring between 10 and 15 h) also declined as the season progressed until the *Drought* episode, starting with hourly maxima of $7.7 \text{ mmol m}^{-2} \text{s}^{-1}$ during *MaxCO₂* and declining to $1.7 \text{ mmol m}^{-2} \text{s}^{-1}$ during *Drought* (Fig. 2). After the rain events at the end of August, net CO_2 assimilation and water flux hourly maxima recovered to $8.4 \mu\text{mol m}^{-2} \text{s}^{-1}$ and $2.4 \text{ mmol m}^{-2} \text{s}^{-1}$ on average, respectively, during *Recovery* (Fig. 2).

Measured VOC fluxes and mixing ratios

Ambient mixing ratios of the measured VOCs were dominated by methanol, with half-hour average ranges of 1.9–26 ppbv and daytime average ranges of 3.6–17 ppbv (Fig. 1). Mixing ratios of isoprenoids reached half-hour maxima of 28.9 and 1.37 ppbv for isoprene and monoterpenes, respectively, with minima near zero (< 10 pptv) in both cases. Daytime average maxima were half of the half-hour maxima for both isoprene and monoterpenes with values of 14.3 and 0.68 ppbv, respectively (Fig. 1). The diel cycle of methanol revealed higher mixing ratios during nighttime hours, while isoprenoids showed the opposite behavior (Fig. 2).

Isoprene was the main VOC emitted. Its half-hour maximum flux was $35.4 \text{ mg m}^{-2} \text{h}^{-1}$ at midday on 1 July. On that same day, the highest daytime average

flux was also recorded, with $14.3 \text{ mg m}^{-2} \text{h}^{-1}$. The magnitude of isoprene fluxes increased from the beginning of the VOC measurements in May until the beginning of July (*MaxVOC* episode); afterward, isoprene fluxes decreased gradually to nearly zero at the end of October when our VOC measurements stopped (Figs 1 and 2). Monoterpene fluxes closely followed isoprene seasonal trends but with lower magnitudes: their half-hour and daytime average maxima were 4.2 and $1.9 \text{ mg m}^{-2} \text{h}^{-1}$, respectively. Methanol diurnal fluxes revealed that, on average, the prevailing ecosystem exchange around sunrise (5:00–7:00 h) was characterized by deposition, reaching hourly average fluxes of -0.16 , and half-hour fluxes of $-1.36 \text{ mg m}^{-2} \text{h}^{-1}$. Later in the day, emissions were predominant and, on average, were within the range of total monoterpenes during the central part of the day (Fig. 2). In contrast to isoprenoid fluxes, daytime methanol emissions varied less throughout the measurement campaign. Hourly average methanol peak emissions ranged between 0.32 and $0.5 \text{ mg m}^{-2} \text{h}^{-1}$ in all episodes (peaking during *MaxVOC*) except *Recovery*, when the morning deposition period lasted longer and the hourly maximum average emission dropped to only $0.11 \text{ mg m}^{-2} \text{h}^{-1}$ (Fig. 2). Half-hour emission peaks for methanol were as high as $1.78 \text{ mg m}^{-2} \text{h}^{-1}$.

The carbon fraction from GPP and NEE released back to the atmosphere in the form of BVOCs is shown in Fig. 3. The fraction of daytime (7–17 h) carbon lost combining the three measured BVOCs was approximately 2% of GPP and 4.9% of NEE on average for our whole measurement campaign. For all three VOCs, the percent of carbon loss through emission was highest from the end of June until the end of August. During this period, when VPD was also highest, CO_2 net flux was greatly reduced, and VOC fluxes peaked and started declining. Isoprene was obviously contributing the most to the loss of assimilated carbon (98% among the three BVOCs), being highest from mid-July to beginning of August, with daytime peaks of 5–9% and 12–20%, respectively, for GPP and NEE. Monoterpenes had timing similar to isoprene, with peaks up to 0.5–0.8% for GPP and 3–5% for NEE. Finally, the contribution of methanol reached approximately 0.3% of GPP and 3% of NEE (Fig. 3).

Modeled VOC fluxes

Figure 4 shows the response of canopy-level isoprene and monoterpene emissions to incident light (PAR) by fitting the observations to the leaf-level algorithm of Eqn 1. Isoprene fluxes increased with PAR—as expected—and even though the combination of all the available isoprene data (measured at 23–27 °C) did not

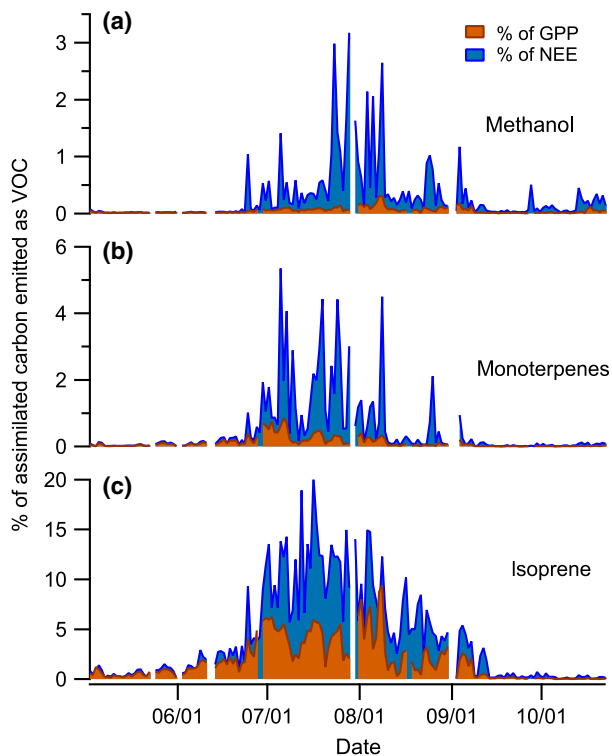


Fig. 3 Carbon (expressed as % of GPP and NEE) emitted daily in the form of (a) methanol, (b) monoterpenes, and (c) isoprene along the 2012 season during daytime hours (7:00–17:00 h CST). Areas representing the percent start from the bottom of the *y*-axis (i.e. they are not stacked on top of each other). Note the different scaling of the *y*-axis for each compound. Date labels indicate 00:00 h CST.

achieve a fit to the algorithm, the algorithm fit the data of each of the episodes individually with good agreement ($r^2 > 0.61$, see Table S1). Monoterpene fluxes also increased with PAR, and the algorithm performed well in describing both the entire dataset and also each of the first four episodes with acceptable agreement ($r^2 > 0.53$, see Table S2). The model fit during the *Drought* and *Recovery* episodes was poor due to higher variability and lower fluxes present in the monoterpene flux data of those episodes.

The responses of VOC emissions to air temperature are summarized in Fig. 5. The *Recovery* episode featured cooler temperatures and did not have enough VOC flux data at 303 K (used for flux normalization in Eqn 2 and as a reference flux in Eqn 3) to allow the computation of the fitting parameters for that episode. Normalized fluxes of both isoprene and monoterpenes were fitted to Eqn 2 with very good agreement ($r^2 > 0.88$, see Tables S3 and S4) except for the monoterpene *Drought* episode ($r^2 = 0.44$). The fit of all data together for each isoprenoid revealed an optimal air temperature (T_{opt}) for isoprene emission of 311 K

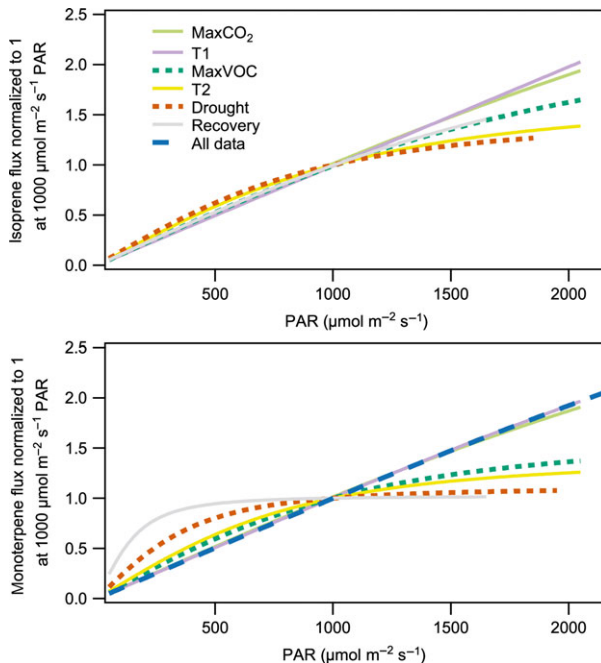


Fig. 4 Response of canopy-level isoprene and monoterpene emissions to light (big-leaf model) calculated by fitting the leaf-level emission algorithm of Eqn 1 (see main text). Note that 'all data' for isoprene did not achieve a fit to the algorithm although isoprene flux increased with increasing PAR (data not shown).

(38 °C) while for monoterpenes, T_{opt} was above the measured range, which means that no temperature optima were obtained for monoterpenes according to Eqn 2. Interestingly, both isoprene and monoterpenes had a lower T_{opt} around 305 K (32 °C) during *T1*. Temperatures during the previous episode (*MaxCO₂*) were never higher than 304 K, so it was impossible to compare whether T_{opt} was also around 305 K for *MaxCO₂*. But air temperatures were higher than 304 K for the period between *MaxCO₂* and *T1*, and the same analysis for that period (data not shown) showed that fluxes of isoprene declined above 306 K at the beginning of the season. Monoterpenes, on the other hand, showed T_{opt} at 311 K for that interepisode period, a value lower than that found with all the monoterpene data but again is not meaningful because it is well above the temperature range measured during that period. Monoterpene and methanol fluxes were also fitted to the exponential equation of Eqn 3 (Fig. 5). The fit of all available monoterpene data showed as good an agreement ($r^2 = 0.97$; Table S5) as it did with Eqn 2 which is used for light-dependent emissions including isoprene and a fraction of monoterpene emissions. Likewise, individual monoterpene episodes showed a very good agreement ($r^2 > 0.87$) except for the *Drought* episode ($r^2 = 0.47$). In the case of methanol, the fit

agreement was generally lower ($r^2 = 0.75$ for all data; see Table S6) with more scatter of the 1K-binned data averages, but all episodes showed $r^2 > 0.5$ except for T2 ($r^2 = 0.38$).

The daily courses of the observed and the MEGAN model calculated VOC fluxes for each episode are compared in Fig. 6. MEGAN did not capture the observed morning methanol deposition, and predicted methanol fluxes were in all cases higher than the measured values by up to a factor of three in midsummer. During midday, the maximum hourly average model positive bias ranged from 0.2 to 0.3 $\text{mg m}^{-2} \text{h}^{-1}$ (50–100% of the measured fluxes) except for the *MaxVOC* and T2 episodes, when this bias reached 0.8–1.2 $\text{mg m}^{-2} \text{h}^{-1}$ (170–300% of the measured fluxes). MEGAN monoterpene average flux values were higher than measurements during nighttime in all cases (Fig. 6). During daytime, modeled fluxes adequately reflected the actual afternoon emissions during T1 and *MaxVOC*, but the modeled fluxes were higher for the remaining episodes, especially in the case of T2 (1 $\text{mg m}^{-2} \text{h}^{-1}$ or 175% more) and *Drought* (0.5 $\text{mg m}^{-2} \text{h}^{-1}$ or 475% higher).

MEGAN midday isoprene flux estimates without a drought algorithm correction were 27% and 15% (1.5 and 2.5 $\text{mg m}^{-2} \text{h}^{-1}$) higher than measurements during *MaxCO*₂ and *MaxVOC* (Fig. 6). During T1, in

contrast, maximum hourly modeled values were approximately 32% less than the 12.5 $\text{mg m}^{-2} \text{h}^{-1}$ measured. The largest differences were found during T2, when MEGAN's isoprene predictions were 166% more than measured fluxes (22.9 vs. 8.6 $\text{mg m}^{-2} \text{h}^{-1}$) during the peak of the day. During *Drought*, the highest hourly modeled fluxes were also higher by 118% (8.3 vs. 3.8 $\text{mg m}^{-2} \text{h}^{-1}$), and the same happened for *Recovery* with a 210% increase, although the magnitudes were lower (3.1 vs. 1 $\text{mg m}^{-2} \text{h}^{-1}$) than in previous episodes (Fig. 6).

When the drought algorithm for isoprene included in MEGAN was used (with a wilting point of 0.23 $\text{m}^3 \text{m}^{-3}$), the modeled isoprene fluxes changed for all episodes except for *MaxCO*₂ as there was no drought at that time of the season (Fig. 6). During T1 (when the original modeled fluxes were already 32% lower than measurements), the new maximum hourly modeled values became even lower, reaching 50% of those measured. During *MaxVOC*, modeled fluxes went from being 15% higher to 25% lower than measurements. The big discrepancy between model and measurements registered during T2 and *Drought* was moderated by the drought algorithm by lowering the model outputs by approximately 39%, with new modeled maximum hourly fluxes at 63% and 34% more than those measured (instead of the original 166% and 118%) for T2 and

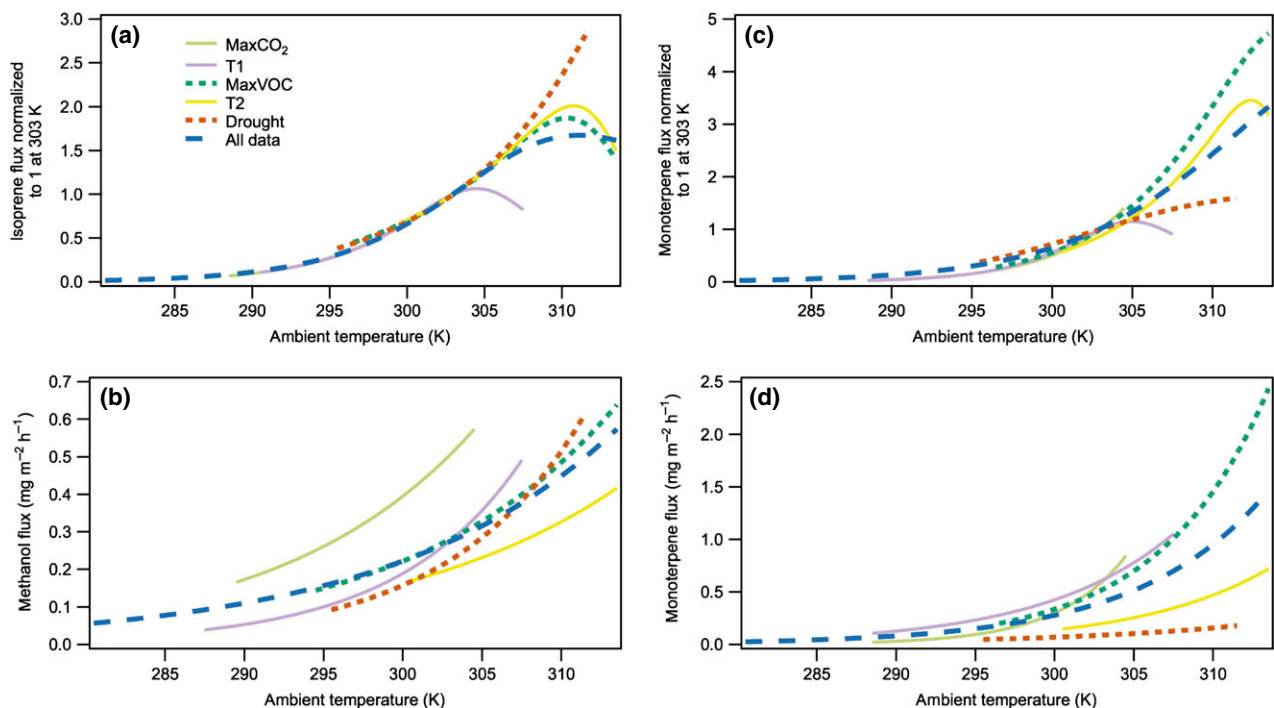


Fig. 5 Response of VOC emissions to air temperature (big-leaf model) calculated by fitting the leaf-level emission algorithms of Eqs. 2 and 3 (see main text). Isoprene (a) data were fitted to Eqn 2; methanol (b) to Eqn 3; and monoterpenes (c, d) to both equations.

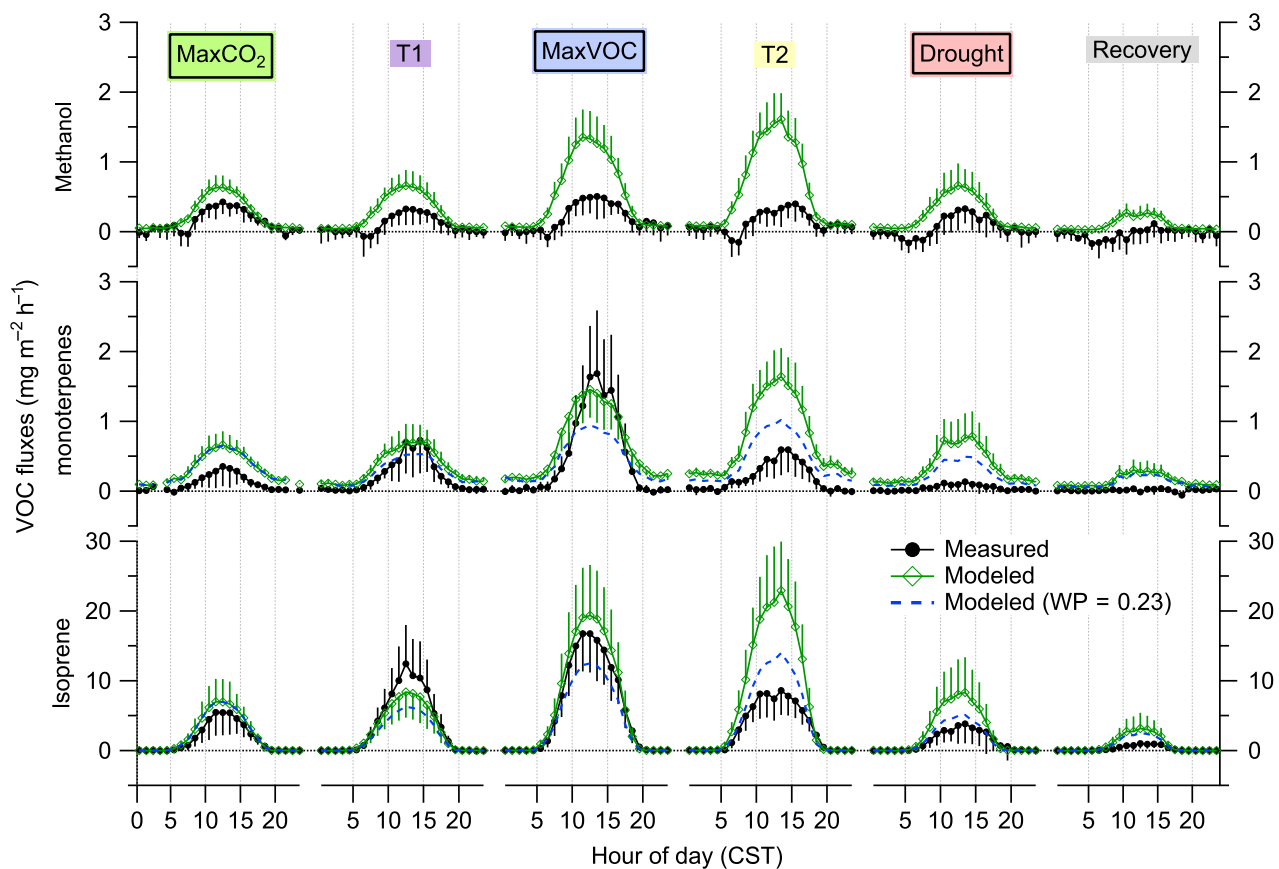


Fig. 6 Comparison of hourly averaged diel cycles of canopy-level VOC fluxes between the measurements (closed circles) and the MEGAN model results (no drought algorithm used; open diamonds) for each episode. For monoterpenes (middle panel) and isoprene (lower panel), the dashed line shows the MEGAN output using the model's built-in isoprene drought algorithm using a wilting point of $0.23 \text{ m}^3 \text{ m}^{-3}$. Error bars indicate plus or minus one standard deviation for each hourly average. Note that the axis of isoprene is one order of magnitude higher than the others.

Drought, respectively. In the case of *Recovery*, maximum hourly isoprene fluxes were lowered by 19%, becoming 150% higher than measurements instead of the original 210% (Fig. 6).

The direct comparison of all available individual half-hour flux measurements with MEGAN predictions clearly showed that MEGAN overpredicted isoprene fluxes by approximately 40% on average when no drought algorithm was included (Fig. 7). When MEGAN's drought algorithm was used (with a wilting point of $0.23 \text{ m}^3 \text{ m}^{-3}$), the overall model results became closer to the observations with an underprediction of approximately 10% (Fig. 7). Both estimates by MEGAN had a very similar coefficient of correlation with measured isoprene fluxes (approximately $r = 0.82$), but the use of the drought algorithm improved the prediction of the model (root mean square error (RMSE) = $3.88 \text{ mg m}^{-2} \text{ h}^{-1}$ without drought algorithm vs. RMSE = $2.66 \text{ mg m}^{-2} \text{ h}^{-1}$ with drought algorithm). Comparing MEGAN's results for monoterpenes with all

half-hour flux measurements and also applying the same drought correction as was applied to isoprene (viz. using isoprene's drought activity algorithm with a wilting point value of $0.23 \text{ m}^3 \text{ m}^{-3}$) resulted in results virtually identical to those obtained for isoprene: without drought correction, MEGAN overpredicted monoterpene fluxes by 40% and with drought correction, the model under predicted fluxes by 11% (Figs 6 and 7).

Discussion

VOC measurements in context

Measurements presented in this study covered most of the vegetation growing season at the Missouri Ozarks site. However, it is likely that we missed a strong emission of methanol during bud break (around the beginning of April, see LAI in Fig. 1) and early stages of leaf development. Pectin demethylation during cell wall

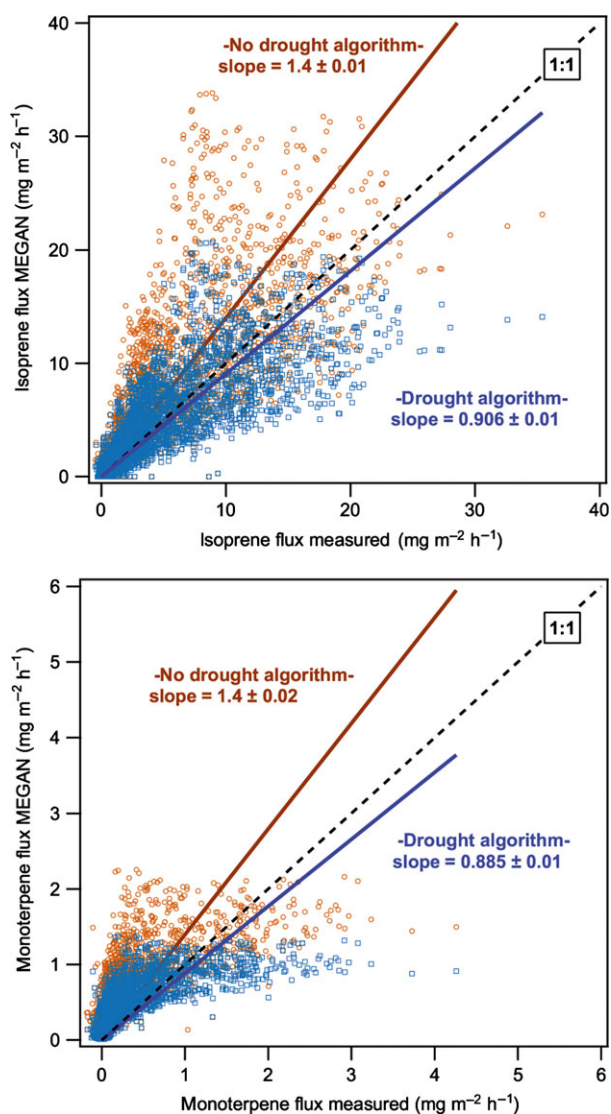


Fig. 7 MEGAN model results of isoprene and monoterpene fluxes (*y*-axis) plotted vs. actual measured fluxes (*x*-axis). MEGAN results are shown without drought algorithm (red circles) and with drought algorithm (blue squares; $WP = 0.23 \text{ m}^3 \text{ m}^{-3}$). Slopes were calculated by orthogonal distance regression and forcing the regression lines through the origin.

expansion is a major source of methanol emission from growing leaves (Nemecek-Marshall *et al.*, 1995; Hüve *et al.*, 2007) and methanol emission rates typically decline as leaves mature. In contrast, isoprene emissions from new, developing leaves are usually very low (e.g. Monson *et al.*, 1994), and considering lower temperatures and solar radiation during April, we expect that isoprene (and likewise monoterpene) fluxes prior to our measurements were low.

The high abundance of methanol in the air was expected because methanol is the second most abundant organic gas in the atmosphere after methane

(Jacob *et al.*, 2005), and it has been reported as one of the dominant VOCs in urban, rural, and forest environments (Seco *et al.*, 2007, 2011b). Despite its relatively low emission rate, methanol's higher atmospheric abundance can be explained by its relatively long atmospheric lifetime (~ 10 days; Jacob *et al.*, 2005); therefore, the high measured mixing ratios are not only a product of local emissions but also a result of long-range atmospheric oxidation and transport processes. Biogenic fluxes of methanol reported here fall within published ranges from various types of vegetation (see Wohlfahrt *et al.*, 2015, for a review on ecosystem-scale methanol fluxes).

High isoprene emission fluxes and mixing ratios during most of the measurement campaign played a potentially major role in atmospheric chemistry at this site. Monoterpenes, which had lower emission fluxes but have higher aerosol yields, contributed to atmospheric particle growth along with isoprene (Yu *et al.*, 2014). Maximum isoprene fluxes measured at this Missouri forest during this study in 2012 ($35.4 \text{ mg m}^{-2} \text{ h}^{-1}$) and in 2011 by Potosnak *et al.* (2014; $53.3 \text{ mg m}^{-2} \text{ h}^{-1}$) are the highest ever reported for a forest canopy, surpassing fluxes of up to $30 \text{ mg m}^{-2} \text{ h}^{-1}$ previously reported from an oil palm plantation in Borneo (Misztal *et al.*, 2011). Other North American temperate forests with large components of isoprene-emitting tree species showed lower fluxes, with maxima on the order of $13 \text{ mg m}^{-2} \text{ h}^{-1}$ (Baldocchi *et al.*, 1999; Fuentes *et al.*, 2007; McKinney *et al.*, 2011; see Potosnak *et al.*, 2014 for a discussion). The higher values at the MOFLUX site compared to other North American temperate forests are expected due to a higher fraction of isoprene emitters and higher temperatures. European forests dominated by isoprene-emitting oaks also showed lower maximum fluxes ($10 \text{ mg m}^{-2} \text{ h}^{-1}$; Kalogridis *et al.*, 2014), as did tropical forests (Langford *et al.*, 2010) including Amazonia and Costa Rica (up to $12 \text{ mg m}^{-2} \text{ h}^{-1}$; Karl *et al.*, 2004, 2007). Isoprene mixing ratios in all these studies were also lower than the values reported here, except in the cases of Amazonia and Borneo with up to 12 and 26 ppbv, respectively.

Monoterpene mixing ratios reported in the literature from forests where isoprene is the dominant isoprenoid emitted were generally < 1 ppbv, somewhat lower than average mixing ratios described here. Maximum fluxes were also on the lower side of those at MOFLUX, approximately $0.5 \text{ mg m}^{-2} \text{ h}^{-1}$ (Karl *et al.*, 2004; Langford *et al.*, 2010; McKinney *et al.*, 2011; Misztal *et al.*, 2011), except for the Amazon (similar with up to $1.2 \text{ mg m}^{-2} \text{ h}^{-1}$; Karl *et al.*, 2007) and for an oak-dominated forest in France that featured monoterpene fluxes below the detection limit (Kalogridis *et al.*, 2014). In European forests dominated by monoterpene emitters,

monoterpene fluxes were in a range similar to the values in Missouri (maxima of $1 \text{ mg m}^{-2} \text{ h}^{-1}$; Rinne *et al.*, 2007; Davison *et al.*, 2009), while mixing ratios were either lower (0.3 ppbv; Davison *et al.*, 2009) or above (daytime mean of 2.1 ppbv and maxima around 2.5 ppbv; Seco *et al.*, 2011b) the values reported in this work.

Responses to drought

Drought stress endured by the vegetation of the Ozarks during the 2012 season was apparent not only in Ψ_{pd} measurements but also in the diel ecophysiological data (Fig. 2). A shift to an earlier diurnal peak in leaf photosynthesis during drought has been widely observed in other studies, and this shift is usually correlated with an increased stomatal closure after mid-morning (Pathre *et al.*, 1998; Haldimann *et al.*, 2008). Stomatal closure is one of the earliest responses to drought and the dominant limitation to photosynthesis during mild-to-moderate drought (Flexas & Medrano, 2002). This observation is consistent with the observed morning peak in the CO_2 flux diel cycle between episodes *T1* and *Drought* but not during *MaxCO2* or *Recovery* when significant water stress was not present (Fig. 2). H_2O flux did not show the same morning peak, but the H_2O flux did show a small decrease just before noon from *T1* through *Drought*. The closing of stomata had a bigger effect on CO_2 flux than on H_2O flux because although stomata did close significantly after mid-morning, gradual increases in VPD (the driving force for transpiration) through early evening tended to offset reduced leaf conductance and sustain transpiration (Turner *et al.*, 1984). Nevertheless, from a seasonal perspective, the 2012 drought greatly reduced both CO_2 and H_2O fluxes as the lack of water intensified until rains returned in late August (Fig. 1).

Most biogenic isoprenoid emissions are practically insensitive to stomatal closure due to their high gas to water partitioning coefficient (Niinemets & Reichstein, 2003). Consequently, their fluxes did not show a significant midday reduction due to stomatal closure under drought (Fig. 2). Conversely, as methanol is highly soluble in water, one would expect that drought-induced stomatal closure would strongly affect methanol flux (e.g. Harley *et al.*, 2007; Filella *et al.*, 2009), which was not the case (Fig. 2). As with transpired water, the flux of methanol dissolved in water inside the leaf may have been sustained during the afternoon by the increase in VPD together with a higher methanol volatility and enzymatic production due to increased temperature. In support of this possibility, VPD was found to be the main driver of methanol exchange in another temperate forest ecosystem (Laffineur *et al.*, 2012).

Under drought conditions, isoprenoid fluxes at the Missouri forest not only had a different diel pattern than CO_2 (due to stomatal closure; Fig. 2), but our measurements also show that CO_2 and isoprenoid fluxes were uncoupled in time. Thus, the peak of net CO_2 assimilation occurred approximately 35 days earlier than the isoprene emission peak (Fig. 1). Even though isoprenoids derive most of their carbon from newly photosynthetically fixed CO_2 (Delwiche & Sharkey, 1993; Loreto *et al.*, 1996), it has recently been shown that alternative metabolic sources can supply carbon for isoprenoid biosynthesis, in particular when photosynthesis is reduced, for example, during drought (Affek & Yakir, 2003; Funk *et al.*, 2004; Brill *et al.*, 2007). In addition, several studies have reported that isoprenoid emissions continue under drought when photosynthesis has already decreased substantially and even increases in isoprenoid emissions during the first stages of the drought stress can occur (e.g. Bertin & Staudt, 1996; Pegoraro *et al.*, 2004a,b; Fortunati *et al.*, 2008; Genard-Zielinski *et al.*, 2014; Potosnak *et al.*, 2014; Wu *et al.*, 2015). Similarly, our measurements show that isoprenoid emissions continued to increase concurrently with a decrease in photosynthetic CO_2 fixation at the beginning of the summer (Fig. 1). Furthermore, the higher measured isoprene emissions compared to the MEGAN simulations during the *T1* episode (Fig. 6), during the early phases of the drought, might be interpreted as a modest increase of emissions over the emissions expected due solely to light and temperature conditions, considering that all other episodes showed higher modeled than measured emissions. This transient increase in isoprenoid emissions under mild drought stress has been interpreted (Niinemets, 2010; Potosnak *et al.*, 2014) to be a possible result of the drought-induced stomatal closure, which causes a leaf temperature rise, and subsequent increase in emissions due to limited transpirational cooling, and a decrease in the internal CO_2 concentration of the leaf (Rosenstiel *et al.*, 2003). These effects of stomatal closure are reproduced by some recently published mechanistic models that link isoprenoid emission to the photosynthetic process by variably partitioning plant-captured energy from light between photosynthesis and isoprenoid synthesis (Morfopoulos *et al.*, 2013, 2014; Grote *et al.*, 2014). During this milder drought phase, the investment of carbon in BVOC emissions (only for the three BVOCs reported here) represented more than 10% of the net carbon assimilated and more than 5% of the total carbon assimilated by the ecosystem (Fig. 3). Given this high cost to the vegetation, the enhanced isoprenoid emissions during drought have been postulated to be a response of the plants to cope with high temperatures that usually

accompany drought episodes (Loreto *et al.*, 1998; Peñuelas *et al.*, 2005).

After mid-July, when the drought entered its stronger phase and long after photosynthesis was strongly inhibited, isoprenoid fluxes started to decrease (Fig. 1). *T2* was the period with the biggest difference between the actual isoprene fluxes and those modeled by MEGAN (Fig. 6). Modeled isoprene fluxes were the highest during this period because temperature and light were also among the highest of the entire campaign (Fig. 2) and (see discussion below) the plants would have acclimated to the hot weather of the preceding days. Nevertheless, measured isoprene fluxes during *T2* and *Drought*, although reduced, were still very similar to or higher than fluxes reported for many other forests in the world that were not subject to extreme drought (e.g. Karl *et al.*, 2004, 2007; Langford *et al.*, 2010; McKinney *et al.*, 2011; Kalogridis *et al.*, 2014). Monoterpenes showed a similar behavior with reduced emission fluxes compared with the model during the strongest phase of the drought (Fig. 6). Similarly, reductions in isoprenoid emissions under severe drought have been described on many occasions (Bertin & Staudt, 1996; Fang *et al.*, 1996; Brüggemann & Schnitzler, 2002; Funk, 2005; Brilli *et al.*, 2007; Fortunati *et al.*, 2008; Peñuelas *et al.*, 2009a).

Some authors have reported a return to emission levels comparable to prestress values when the plants were relieved from the drought stress, for example, after the plants were rewatered (e.g. Fang *et al.*, 1996; Brilli *et al.*, 2007; Peñuelas *et al.*, 2009a). We did not observe such a phenomenon in our measured isoprenoid fluxes after the rain that occurred at the end of August, even though CO₂ net fluxes did partially recover (Fig. 1). According to results using MEGAN, isoprenoid fluxes expected without any drought effects were already lower than the isoprenoid fluxes of summertime due to cooler weather (Fig. 6), with lower PAR and temperatures that favor a higher relative recovery of CO₂ assimilation compared to isoprenoid emission. In fact, the actual isoprenoid fluxes were clearly lower than the MEGAN predictions during the *Recovery* period (Fig. 6). This nonrecovery of isoprenoid emissions after late August rains could result partly from a likely reduction in isoprenoid emitting leaf area because we observed some leaf mortality during the drought. Furthermore, at that late point of the season, BVOC emissions could be decreased due to leaf senescence.

Overall, methanol emissions were not affected by drought to the extent of isoprenoids, which supports the idea that biosphere–atmosphere methanol exchange is governed by complex physiological and environmental drivers such as atmospheric concentration, rate of production and consumption/deposition either inside

the leaf or on the leaf surface (e.g. water films on leaves or epiphyllic bacteria), among others (Wohlfahrt *et al.*, 2015).

Modeled VOC fluxes

Canopy-level isoprene emissions responded to increases in ambient temperature with increases in fluxes up to 38 °C (Fig. 5). This behavior has been observed in many leaf-level studies (e.g. Harley *et al.*, 1996). Two features stood out in the response of isoprene to temperature. The first outstanding feature was the lower optimal temperature (T_{opt}) found at the beginning of the season until mid-June compared to later measurements. Possible explanations for this phenomenon are that the different species contributing to isoprene emissions throughout the season (i) were actively emitting during different periods, (ii) had varying leaf phenology, with younger leaves being subject to different temperature responses, and (iii) had different temperature optima. The latter explanation is consistent with measurements by C. Geron *et al.* (manuscript in preparation) that showed evidence at the leaf-level supporting higher basal emission rates and T_{opt} for drought-resistant oak species at this site. It is also consistent with the idea that the optimal temperature at a given time results from acclimation (see Niinemets *et al.*, 2010 and Monson *et al.*, 2012 for reviews), as assumed by the MEGANv2.1 model which has a T_{opt} that changes throughout the season based on the temperature of the past 10 days (Guenther *et al.*, 2012). The second feature is that the ecosystem-level isoprene response to temperature under severe drought conditions did not break down as was reported in a study on poplar leaves (Fortunati *et al.*, 2008). Equation 2 uses normalized fluxes and obviously the magnitude of emissions decreased with increasing drought (Fig. 2), but clearly isoprene emissions continued to rise with increasing temperature even during the *Drought* episode (Fig. 5). Nevertheless, the reported leaf-level breakdown in temperature response (Fortunati *et al.*, 2008) also occurs in the drought-sensitive species of the red oak subgenus (e.g. black oak) of the Ozark forest, while more drought-resistant species of the white oak section (e.g. white and post oaks) show a continued response to leaf temperature during drought similar to predrought conditions (C. Geron *et al.*, in preparation). Thus, the observed temperature response at the ecosystem level may be due to variation in rooting habit and cellular level drought tolerance mechanisms between oak species.

Fitting Eqn 2 to all available monoterpene fluxes did not show a valid optimal temperature for emission within the measured temperature range, and the

response of monoterpenes to temperature was simulated well by the simpler exponential Eqn 3 (Fig. 5), as expected for emissions of monoterpenes from storage structures that are often considered exclusively temperature dependent (Tingey *et al.*, 1980; Guenther *et al.*, 1993). Temperature had an important role in driving monoterpene emissions, as exemplified by monoterpene daily flux peak occurring when temperatures were higher, in the afternoon, later than the noontime isoprene peak (Fig. 2). Nevertheless, fitting of monoterpene fluxes of individual episodes to Eqn 2 revealed that, as in the case of isoprene, the optimal temperature T_{opt} was lower at the beginning of the season possibly indicating that acclimation to the past temperatures is occurring for monoterpenes as well. In fact, this acclimation is already considered in the MEGANv2.1 model for monoterpene emission but only for the light-dependent fraction calculated with the same light and temperature algorithms as isoprene (modified versions of Eqns 1 and 2; Guenther *et al.*, 2012). This model assumes varying fractions of monoterpenes are light dependent by compound. For instance, ocimene is considered to be 80% light dependent, while α -pinene and β -pinene are 60% and 20% light dependent, respectively (Guenther *et al.*, 2012). In reality, these percentages vary largely with plant species, and it is likely that nearly 100% of monoterpene emissions from oak forests are light dependent. Our leaf-level data (C. Geron *et al.*, in preparation) also indicate that monoterpene emissions vary by rate and compound between oak species and that some compounds, such as ocimene, may become more abundant during drought and temperature stress conditions. Fig. 4 clearly demonstrates that light did also drive monoterpene emissions at this Ozarks deciduous forest, as previously reported for many plant species and particularly true for species, such as oaks, that lack specialized monoterpene storage organs (e.g. Staudt & Bertin, 1998; Owen *et al.*, 2002; Dindorf *et al.*, 2006). Indeed, the low nighttime monoterpene emissions, in particular compared with MEGAN results (Fig. 6), suggest a substantial control by light of newly synthesized monoterpene emissions in this ecosystem, at least more than assumed by the MEGANv2.1 model with the default parameterization used in this study. The fact that monoterpene mixing ratios were higher during daytime (Fig. 2) reinforces this point. In ecosystems where monoterpene emissions are mainly a temperature controlled release of stored monoterpenes, the nighttime mixing ratios will be higher due to lower planetary boundary layer heights and oxidation rates even though emissions are lower (e.g. Davison *et al.*, 2009; Seco *et al.*, 2013).

Version 2.1 of the MEGAN model already captures the diurnal variation in isoprenoid emission fluxes and the

short-term variations due to sudden changes in light or temperature with remarkable accuracy, demonstrated by the high degree of correlation between model results and measurements. However, significant variability remains (Fig. 7), especially during stress events when the vegetation physiological conditions are far from optimum, as we have shown in this study (Fig. 6). Simply using an alternative wilting point of $0.23 \text{ m}^3 \text{ m}^{-3}$ to drive MEGAN's drought algorithm substantially improved isoprene (and monoterpene) modeled fluxes, particularly when calculating a season average total emission (Fig. 7). An alternative approach would be to keep this wilting point and increase the threshold, below which isoprene emission is influenced by soil moisture, to a value of about $0.27 \text{ m}^3 \text{ m}^{-3}$. However, these approaches may be insufficient for providing the modeled BVOC emissions needed as input for high temporal resolution chemistry calculations where short-term variations are crucial. The main challenge remains in correctly assessing the threshold and the wilting point and relating them to available soil texture classes and moisture data. In this sense, the importance of choosing a suitable wilting point for the soil moisture available data has already been emphasized (Guenther *et al.*, 2012), and other modeling studies have highlighted the importance of soil moisture parameterization for improved BVOC flux modeling (Monson *et al.*, 2012; Tawfik *et al.*, 2012; Huang *et al.*, 2015). Furthermore, soil moisture averaged over longer time periods (e.g. the previous month) may yield better predictive power for drought periods, similar to effects currently incorporated into MEGAN for the influence of light and temperature of the past 24 and 240 h (Guenther *et al.*, 2012). Longer term soil moisture data may also have utility in determining actual wilting point values, as soil moisture values tend to asymptote at the wilting point even as drought continues.

Methanol and other oxygenated VOC bidirectional exchange (Seco *et al.*, 2007, 2008; Niinemets *et al.*, 2014) remains an issue to be addressed by MEGAN and other VOC emission models, even though some attempts have been made to improve the bidirectional exchange modeling of methanol (Laffineur *et al.*, 2012). In this study, net methanol exchange resulted in deposition around the time of sunrise. The magnitude and duration of this deposition period increased as the season progressed and also as the drought increased in severity. The responses to light and temperature also changed seasonally for the three VOCs studied here. Variability in emission capacity and in responses to light and temperature have been documented (Monson *et al.*, 1994; Keenan *et al.*, 2009; Niinemets *et al.*, 2010; Guenther *et al.*, 2012), but it remains a difficult task to discern the relative role of

ontogeny and acclimation from that of drought stress response in cases like our Ozarks measurements. An improved understanding of the involved ontological, physiological, and biochemical mechanisms must be elucidated and incorporated into the models to improve their realism and accuracy.

MEGANv2.1 model accurately simulated short-term variations of isoprenoid emissions; however, the bidirectional exchange of methanol, the response of isoprenoid fluxes to drought stress, and the speciation and environmental control of mono- and sesquiterpenes are areas still in need of improvement. More laboratory (e.g. Kleist *et al.*, 2012; Wu *et al.*, 2015) and field measurements (e.g. Peñuelas *et al.*, 2013; Greenberg *et al.*, 2014) and consequently improved emission models will be needed to explore the impact of global change on BVOC emissions and vice versa, the impact of changed BVOC emissions on biospheric functioning and feedback on atmospheric chemistry and climate (Jacob & Winner, 2009; Peñuelas *et al.*, 2009b; Arneth *et al.*, 2010b; Peñuelas & Staudt, 2010).

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1. Light dependence (Eqn 1) for isoprene (Fig. 4).

Table S2. Light dependence (Eqn 1) for monoterpenes (Fig. 4).

Table S3. Temperature dependence (Eqn 2) for isoprene (Fig. 5).

Table S4. Temperature dependence (Eqn 2) for monoterpenes (Fig. 5).

Table S5. Temperature dependence (Eqn 3) for monoterpenes (Fig. 5).

Table S6. Temperature dependence (Eqn 3) for methanol (Fig. 5).