


Differential controls by climate and physiology over the emission rates of biogenic volatile organic compounds from mature trees in a semi-arid pine forest

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Abstract Drought has the potential to influence the emission of biogenic volatile organic compounds (BVOCs) from forests and thus affect the oxidative capacity of the atmosphere. Our understanding of these influences is limited, in part, by a lack of field observations on mature trees and the small number of BVOCs monitored. We studied 50- to 60-year-old *Pinus ponderosa* trees in a semi-arid forest that experience early summer drought followed by late-summer monsoon rains, and observed emissions for five BVOCs—monoterpenes, methylbutenol, methanol, acetaldehyde and acetone. We also constructed a throughfall-interception experiment to create “wetter” and “drier” plots. Generally, trees in drier plots exhibited reduced sap flow, photosynthesis, and stomatal conductances, while BVOC emission rates were unaffected by the artificial drought treatments.

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During the natural, early summer drought, a physiological threshold appeared to be crossed when photosynthesis $\cong 2 \mu\text{mol m}^{-2} \text{s}^{-1}$ and conductance $\cong 0.02 \text{ mol m}^{-2} \text{s}^{-1}$. Below this threshold, BVOC emissions are correlated with leaf physiology (photosynthesis and conductance) while BVOC emissions are not correlated with other physicochemical factors (e.g., compound volatility and tissue BVOC concentration) that have been shown in past studies to influence emissions. The proportional loss of C to BVOC emission was highest during the drought primarily due to reduced CO_2 assimilation. It appears that seasonal drought changes the relations among BVOC emissions, photosynthesis and conductance. When drought is relaxed, BVOC emission rates are explained mostly by seasonal temperature, but when seasonal drought is maximal, photosynthesis and conductance—the physiological processes which best explain BVOC emission rates—decline, possibly indicating a more direct role of physiology in controlling BVOC emission.

Keywords Terpenoid · Drought · Atmospheric chemistry · Cloud-condensation nuclei · Climate change

Introduction

Trees produce a variety of biogenic volatile organic compounds (BVOCs), including isoprene, non-oxygenated and oxygenated terpenes, and short-chain BVOCs, such as methanol and acetone (Harley et al. 1998; Schade et al. 2000; Gray et al. 2003; Seco et al. 2007). Once these compounds are emitted to the atmosphere, they participate in the chemistry that leads to the formation of tropospheric ozone and secondary organic aerosols and can have significant effects on regional

air quality (Litvak et al. 1999; Monson 2002; Atkinson and Arey 2003; Park et al. 2013) and climate (Goldstein et al. 2009; Laothawornkitkul et al. 2009; Ortega et al. 2014). Numerous studies have been conducted on the responses of BVOC emissions to various biotic and abiotic stresses (Niinemets 2010). Most of these studies have been conducted with the aim of elucidating physiological responses to stress under highly controlled growth conditions and on tree saplings growing in pots or gardens (e.g., Sharkey and Loreto 1993; Bertin and Staudt 1996; Fang et al. 1996; Hansen and Seufert 1999; Pegoraro et al. 2004; Brilli et al. 2007; Staudt et al. 2008; Peñuelas et al. 2009; Copolovici et al. 2014; Boursoukidis et al. 2014). Only a few have been conducted within the natural ecological settings of the plants and in response to natural stresses (see Lavoit et al. 2009; Llusà et al. 2011, 2013), and all of these field-oriented studies focused on broad-leaved trees with limited study of emissions during the entire seasonal climate cycle and/or on one or two limited types of BVOCs. Despite all of these studies, we still do not understand the general controls over BVOC emission rates during natural drought.

BVOC emissions from the leaves of potted tree saplings have been shown to respond to changes in both climate and physiological factors, such as photosynthesis rate and stomatal conductance (g_s). Most past studies have focused on isoprene emissions from leaves, and this type of emission has been linked to the physiological protection of the photosynthetic apparatus in chloroplasts during abiotic and biotic stress (Sharkey and Yeh 2001; Loreto and Schnitzler 2010). We will not consider isoprene emissions further in this analysis, because *Pinus ponderosa* exhibits non-measurable emissions of this compound. However, other BVOC emissions, such as those for methylbutenol and the light-dependent monoterpenes, are related to isoprene emissions, and likely serve a similar role in protecting photosynthesis against stress in *P. ponderosa* (Harley et al. 1998; Schade and Goldstein 2002; Harley et al. 2014). Given the physiological connections between BVOC emissions and abiotic stress in trees, it is not entirely surprising that changes in the levels of abiotic stress will also change rates of BVOC emissions. In this study, we have focused on the effects of changes in climate on emissions, while recognizing that there exist connections in the other direction, from emissions toward plant tolerance of stress.

Many of the environmental factors that are expected to contribute to future global change are likely to influence the emission of BVOCs (Peñuelas and Staudt 2009; Sharkey and Monson 2014). There is high uncertainty in the magnitude, and even direction, of this influence, however. For example, some studies have shown increased

BVOC emission under drought and others have shown a decrease (Niinemets 2010). Niinemets (2010) proposed that these differing observations may be due to differences in the severity of drought, and hypothesized that though emissions are not affected by mild drought, they tend to decrease during severe drought and can increase to values even higher than those initially observed during recovery from drought. One limitation that has prevented us from understanding these relations within a more accurate ecological and climatic context, is that most past studies have been conducted on young tree saplings grown in pots and exposed to highly controlled drought regimes. Furthermore, most studies have been conducted with regard to isoprene or light-dependent monoterpene emissions from broad-leaved trees, both of which are tightly coupled to instantaneous rates of leaf photosynthesis. Studies of a broader set of BVOC emissions from mature trees, including coniferous trees, during natural seasonal patterns of temperature and drought, are lacking.

In many coniferous forests across the globe, isoprene emissions or light-dependent monoterpene emissions are not the most significant BVOC. In fact, many of the BVOCs emitted from coniferous forests are controlled by different physiological relations to photosynthesis rate and g_s than those for emissions from broad-leaved species. Some coniferous species, such as some pines, emit a BVOC that is related to isoprene, called methylbutenol (MBO). The types of monoterpene emissions from coniferous trees are of a much broader range than those emitted from broad-leaved species; some are light dependent, but many are not. Our ability to evaluate hypotheses such as Niinemets' (2010), in which rates of BVOC emissions are affected by differing levels of stress, is highly limited by a lack of studies on trees exposed to natural stresses, at mature life cycle stages, and for the broad range of different types of BVOCs. In fact, in Niinemets' (2010) analysis, few coniferous tree studies, even for potted plants, were available to provide insight into the effects of drought stress.

The goal of this study was to determine how the emissions of several BVOCs from mature *P. ponderosa* trees are influenced simultaneously by changes in seasonal temperature and drought. To accomplish this goal, we took advantage of the seasonal climate system found in many montane forests in the Western USA in which an early summer drought is followed by later summer monsoon rains. We set up a throughfall-interception and redirection experiment to manipulate the precipitation experienced by individual mature trees. We used combined measurements of photosynthesis, whole-tree transpiration, needle g_s , and emission rates of several BVOCs to gain a mechanistic

understanding of emission responses to intensification or relaxation of seasonal drought.

Materials and methods

Study site

The study was conducted at the US Forest Service Manitou Experimental Forest (36°6′0″N, 105°5′30″W) in Colorado, USA. The site is an open woodland dominated by 50- to 60-year-old trees of *Pinus ponderosa* var. *scopulorum* Engel. with a sparse understory of grasses. We selected 24 trees with diameter at breast height between 25 and 40 cm that had no neighboring trees within a 10-m radius. We grouped these trees into four blocks. Each of the six trees within a block was randomly assigned to one of the following treatments, which were applied using rain-collection conduits:

1. Control, without conduits and ambient precipitation.
2. Ambient, with perforated conduits and ambient precipitation.
3. Treatment, with conduits removing 50 % of the ambient precipitation.
4. Treatment, with conduits removing 25 % of the ambient precipitation.
5. Treatment, with perforated conduits and redirection adding 25 % of the ambient precipitation.
6. Treatment, with perforated conduits and redirection adding 50 % of the ambient precipitation.

The blocks of plots were randomly located in a 500 × 500-m area of the forest.

Meteorological variables were measured as part of a larger campaign at the site [the BEACHON project; described in an overview by Ortega et al. (2014)]. We made measurements during four periods in 2011: 13 May–1 June, Julian days 133–152 (hereafter “May”); 25 June–7 July 7, Julian days 176–188 (hereafter “June/July”), 15–22 August, Julian days 227–234 (hereafter “August”), and 16–24 September, Julian days 259–267 (hereafter “September”). The mean temperatures during the measurements in May and September were not significantly different from each other (means of 17 ± 4 and 18 ± 3 °C, respectively) and were both significantly different from June/July and August (means of 26 ± 3 and 25 ± 2 °C, respectively), which were not significantly different from each other. The cumulative precipitation was 11, 1, 77, and 29 mm for the 2 weeks preceding the May, June/July, August, and September periods, respectively, i.e., there were two cool periods with moderate rainfall (May and September) and two warm periods, one with high rainfall (August) and one with low rainfall (June/July).

Manipulation of precipitation

We analyzed results from five different experimental treatments that were applied by erecting a grid of evenly spaced polyvinylchloride rain conduits in a 10-m × 10-m square ~1 m above the ground with the target tree in the middle of the square (photograph in Electronic Supplementary Materials, Fig S1). In the water-removal treatments the conduits covered 50 or 25 % of the ground area and intercepted all precipitation falling on the covered area. The conduits were slightly elevated at one end so that the intercepted precipitation ran toward the lower end of the conduits where it was collected in covered barrels, and subsequently redistributed to the water-addition plots. Thus, all water additions to the water-amended plots were conducted with throughfall water collected from the water-removal plots. Similar to the water-removal treatments, the water-addition treatments had conduits covering 50 and 25 % of the ground area, respectively, but these conduits were perforated with 2-mm holes every 5 cm along the conduit length to allow precipitation to pass through and be delivered to the ground. Trees in natural (control) plots had no conduits. We established a sixth type of treatment plot in an effort to control for the presence of gutters, but with no alteration of rainfall, i.e., we tried to control for the presence of gutters independently of reduced rainfall. However, we found this not to be possible. Perforated gutters placed on the plots to cover 25 % of their surface area significantly impeded water throughfall to the ground, even when they were well perforated. Thus, we were not able to determine if the presence of gutters had any effects on tree water use, beyond that due to rain interception. We decided to not include this sixth type of plot in the analysis, and accepted the assumption that the principal effect of the elevated gutters on tree physiology was due to water interception, and not other factors (such as the amount of light falling on the forest floor, or influences on soil surface temperature). Over the course of the experiment, an average of 4015 L of water (± 440 , $n = 4$ plots) was moved from the water-removal plots to the water-addition plots in the 25 % treatments, and 7135 L (± 810 , $n = 4$) was moved from the water-removal plots to the water-addition plots in the 50 % treatments. Water was moved from the removal to the addition plots within 48 h of each precipitation event. These values correspond to approximately 40 and 70 mm of additional rain per plot, respectively, which, given observed rainfall amounts, translates to an effective average enhancement of 36 % for the intended 25 % treatment and 59 % for the intended 50 % treatment. The conduits were completely installed by 1 July 2013 (the summer prior to the measurements periods), and the first water transfers were made on 30 July 2013. The conduits on all treated plots were left in place during the winter when they intercepted snowfall that remained

in the conduits until one of the many brief thawing events that occurred throughout the winter. We could not quantify the amount of snow that was blown out of the conduits or was sublimated before it could melt. We transferred melted snow water from water-removal plots to water-addition plots during thaw periods. Although we know that snow water was removed or added, we could not quantify this effect accurately.

Sap flow measurements

We installed stem sap-flow sensors in all experimental trees. The heat ratio method was used with sensors designed following Burgess et al. (2001) and deployed as described in Moore et al. (2008). On 1 April 2011, one sensor was installed on the east-facing side of each tree at a height of 1.3 m and sap flow was measured and recorded every 30 min until 1 October 2011.

Photosynthesis and g_s measurements

Needle gas exchange was measured with a portable gas exchange system (LI-6400; LI-COR Biosciences, Lincoln, NE) using a broad-leaf cuvette with internal light source. For each measurement, five to nine needles were placed side-by-side within the cuvette and the light source was used to illuminate one side of the needles (photosynthetic photon flux density of $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$). All measurements were made on branches on the east side of the trees in the upper third of the canopy, which was accessed by an electric Z-lift elevator (commonly called a “cherry picker”). During each observation period, needles were measured at a similar temperature: 15°C in May, 25°C in July and August, and 20°C in September, each of which corresponded to the approximate average temperature of midday foliage during that period. Occasional extremely hot or cool days made it impossible to reach the target temperature for every sample, but 95 % of the measurements were within 5°C of the target temperature. Monoterpene and MBO emissions were mathematically adjusted to the target measurement temperature during each period using the temperature-correction equations from Guenther et al. (1993) and Harley et al. (1998), respectively. During all the measurement periods “mature” needles were measured. New (i.e., current-year) needles emerged in late June, but were not long enough for measurement until August. Fluxes are based on total needle area (not projected; see Table S3 for monthly specific leaf area values). Total needle area was determined using measurements of the length, width, and circumference of needle fascicles and applying calculations based on the geometry of needles from two-needle and three-needle fascicles as described in Eller et al. (2013).

Measurement of BVOC emission rates

BVOC concentrations in the needle chamber air were measured using proton-transfer reaction mass spectrometry (PTR-MS) (for details on PTR-MS see de Gouw and Warneke 2007). The PTR-MS was placed in the cherry-picker basket, so that it was near each experimental branch. Ambient air was pulled into the needle chamber from a 2.5-L-glass mixing volume. A platinum catalyst heated to 350°C was placed in-line before the leaf chamber to remove ambient BVOCs. A Teflon T-connector was used to route sample air from the cuvette to the inlet of the PTR-MS. We measured each mass for 1 s approximately once a minute and we calibrated the PTR-MS using sequential dilutions of a gas standard (Apel-Riemer Environmental) that included each of the following compounds at an undiluted concentration of 1 p.p.m.: 2-methyl-3-buten-2-ol, methanol, acetone, acetaldehyde, and α -pinene (used as the standard for monoterpenes). The charged atomic masses (m/z) we measured were: 33 (methanol), 45 (acetaldehyde), 59 (acetone), 87 (MBO), and 137 (sum of monoterpenes because only the total pool of emitted monoterpenes is measured with the PTR-MS.) We also monitored several masses associated with wound compounds (83, 99, and 101), but did not observe substantive emissions at these masses. We monitored masses in the empty cuvette before and after each sample and “background concentrations” were subtracted from sample values. BVOC emission rates were calculated as described in Eller et al. (2012). The proportion of photosynthetic C lost via the emission of BVOC was determined at each month’s target temperature by adding the molar C fluxes of all BVOCs and dividing by the molar flux of CO_2 .

In July and August, we collected samples to determine the fractional representation of specific emitted monoterpenes. Air exiting the leaf chamber was pulled through a two-stage solid adsorbent cartridge (~ 350 mg Tenax GR and Carbograph 5TD; Markes International, Llantrisant, UK) at a rate of 100 mL min^{-1} for 20 min. The cartridges were refrigerated until analysis (2–6 weeks later). Cartridge samples were thermally desorbed and analyzed using gas chromatography–mass spectrometry as described in Eller et al. (2013).

Foliar samples and monoterpene chemical analysis

After each BVOC flux measurement, five to nine needles from the same branch were flash frozen in liquid N_2 and placed in a -80°C freezer. Frozen needles were ground in liquid N_2 using a chilled mortar and pestle. Approximately 0.5 g of frozen needle powder was weighed into 2-dram glass vials and 4 mL of gas chromatography-grade n-hexane (Fisher Scientific) containing $0.1 \mu\text{L mL}^{-1}$

(+)-fenchone (Sigma-Aldrich) was added as an internal standard. After a 7-day extraction period, 100 μL of the extract was injected into micro-inserts in clear vials and capped with polytetrafluoroethylene liners (Alltech Associates, Deerfield, IL). Gas chromatography was used to determine extract monoterpene concentrations following Trowbridge et al. (2014), including the use of a chiral column to determine the difference between (+)- α -pinene and (–)- α -pinene.

Statistical analyses

Statistical analyses were performed using R statistical software. Linear regressions and ANOVAs were performed using the `lm` and `aov` functions, respectively. Post hoc Tukey pairwise comparisons were made using Tukey honestly significant difference; an α of 0.05 was used.

Results

Manipulated and seasonal drought effects

When averaged across the entire growing season, sap flow in trees from the 50 % water-removal treatment was reduced relative to trees in the control plots (without conduits) and the 25 % water-removal treatment plots (Fig. 1a). Both the 50 and 25 % water-removal treatments reduced sap flow velocities relative to the 25 % water-addition treatment. For the 50 % water-addition treatment, the perforated conduits were at a higher density and likely caused some interception and draining of water (off the plot) such that trees in the 25 % water-addition treatment exhibited higher sap flow velocities than trees in the 50 % water-addition treatment. During the May, August, and September measurement periods (i.e., every period that had significant amounts of rainfall), individuals in the 50 % water-interception treatment had significantly lower sap flow than those in the 25 % water-addition treatment (generally the difference was about 15 cm h^{-1} ; Fig. 1b). Only 1 mm of rain fell in the 2 weeks before the June/July measurements, which meant there was no significant rainfall to capture and redistribute. The dry June/July conditions resulted in low sap flow velocities in all individuals (mean sap flow = 26 cm h^{-1}).

When the six drought treatments were considered separately, there was no significant impact of any of them across the growing season on needle g_s , photosynthesis, or BVOC emission rate (all p -values >0.05). However, when we combined the 50 % water-removal and the 25 % water-removal plots to form a single bin (dry treatment), the 50 % water-addition and 25 % water-addition to form a single treatment (wet treatment), and the control (without conduits) plots to

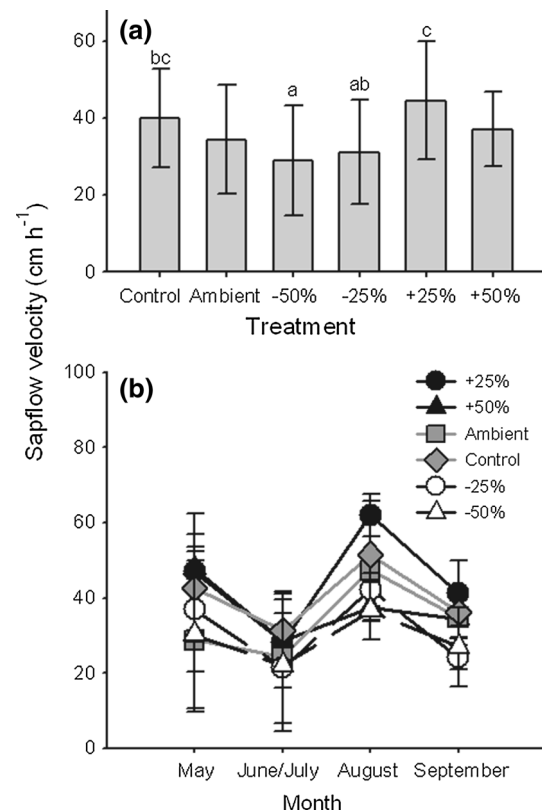


Fig. 1 Mean sap flow velocity in **a** each treatment when averaged across the entire growing season, and **b** in each treatment during each month. Bars are mean \pm SD. Different letters indicate statistically significant differences

form a single treatment (control), we observed a significant impact of the imposed drought treatments on water fluxes (p -values <0.05). Overall, trees in the dry treatment exhibited significantly lower sap flow velocities, photosynthesis rates (only lower than those in the wet treatment), and g_s , relative to trees in the wet and control treatments (means in Table 1 and S2; ANOVA results in Table 2), but VOC emission rates including those of monoterpenes, MBO, methanol, acetaldehyde and acetone across the whole growing season were not significantly affected by the treatments, even when plots were combined into wet, dry, and control bins. During the June/July measurement period there was a marginal reduction in the emission of monoterpenes from the dry group relative to the control ($p = 0.08$), but no other BVOC emissions were altered. We observed that neither the composition of the BVOC emissions nor percentage of instantaneously fixed C emitted as BVOCs changed in response to manipulated precipitation.

Sap flow, photosynthesis, g_s , and BVOC emissions differed among measurement periods (Tables 1, 2; S2). Monoterpene and MBO emissions were highest during the warmer measurement periods (June/July and August), compared to the cooler measurement periods (May and

Table 1 Mean mature needle values for each variable, including photosynthesis (*A*), stomatal conductance (g_s), sap flow, the emissions of total biogenic volatile organic compounds (BVOCs; monoterpenes (*MT*), methylbutenol (*MBO*), methanol, acetaldehyde, and acetone), the percentage photosynthesis lost to BVOC emissions, and the ratios of *MT* and *MBO* to the total emission of BVOCs

Variable	Drought treatment			Month			
	Dry ($n = 48$)	Control ($n = 16$)	Wet ($n = 32$)	May ($n = 16$)	June/July ($n = 16$)	August ($n = 16$)	September ($n = 16$)
Total BVOC emission ($\text{nmol m}^{-2} \text{s}^{-1}$)	3.28 a \pm 0.43	4.46 a \pm 0.8	3.99 a \pm 0.53	1.16 a \pm 0.12	6.56 b \pm 0.92	5.64 b \pm 0.39	1.79 a \pm 0.15
<i>MT</i> emission ($\text{nmol m}^{-2} \text{s}^{-1}$)	0.12 a \pm 0.02	0.19 a \pm 0.1	0.13 a \pm 0.03	0.03 a \pm 0.01	0.30 c \pm 0.06	0.18 b \pm 0.03	0.04 a \pm 0.01
<i>MBO</i> emission ($\text{nmol m}^{-2} \text{s}^{-1}$)	2.94 a \pm 0.41	3.99 a \pm 0.8	3.60 a \pm 0.50	0.87 a \pm 0.11	6.02 b \pm 0.86	5.17 b \pm 0.39	1.53 a \pm 0.14
Methanol emission ($\text{nmol m}^{-2} \text{s}^{-1}$)	0.16 a \pm 0.01	0.21 a \pm 0.0	0.19 a \pm 0.02	0.15 a \pm 0.02	0.19 a \pm 0.04	0.21 a \pm 0.01	0.18 a \pm 0.02
Acetaldehyde emission ($\text{nmol m}^{-2} \text{s}^{-1}$)	0.19 a \pm 0.04	0.30 a \pm 0.1	0.20 a \pm 0.04	0.25 a \pm 0.09	0.15 a \pm 0.04	0.29 a \pm 0.09	0.17 a \pm 0.06
Acetone emission ($\text{nmol m}^{-2} \text{s}^{-1}$)	0.06 a \pm 0.01	0.09 a \pm 0.01	0.07 a \pm 0.01	0.10 a \pm 0.02	0.07 ab \pm 0.02	0.08 ab \pm 0.02	0.04 b \pm 0.01
% C devoted to VOCs	2.9 a \pm 0.62	3.2 a \pm 1.4	2.3 a \pm 0.60	0.3 a \pm 0.08	9.1 b \pm 0.93	1.0 a \pm 0.13	0.3 a \pm 0.03
<i>MT</i> :total VOCs	8.9 a \pm 1.27	6.4 a \pm 1.2	5.6 a \pm 0.88	5.3 a \pm 1.83	10.6 b \pm 1.93	7.4 ab \pm 1.88	5.1 a \pm 1.03
<i>MBO</i> :total VOCs	83.4 a \pm 1.76	83.4 a \pm 3.3	88.4 a \pm 1.07	79.8 a \pm 3.78	86.8 ab \pm 2.25	88.2 b \pm 2.00	87.7 ab \pm 1.48
Sap flow (cm h^{-1})	30 a \pm 2.02	40 b \pm 3.3	41 b \pm 2.17	41 ab \pm 3.75	26 c \pm 3.00	46 a \pm 3.00	32 bc \pm 2.25
<i>A</i> ($\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$)	2.3 a \pm 0.19	2.5 ab \pm 0.3	2.7 b \pm 0.22	2.7 b \pm 0.23	0.7 c \pm 0.13	3.4 a \pm 0.20	3.2 ab \pm 0.18
g_s ($\text{mmol H}_2\text{O m}^{-2} \text{ s}^{-1}$)	20 a \pm 2.17	23 b \pm 3.3	26 b \pm 2.83	24 b \pm 3.25	5 c \pm 1.00	33 a \pm 3.00	32 a \pm 3.00

Total leaf area was used for all area-based measurements. Treatment means (\pm SE) presented in the same format as the ANOVA analyses presented in Table 2. Data are provided for dry and wet drought treatments and control (all time periods combined), and for May, June/July, August, and September treatments (all drought treatments combined). For the means of each treatment during each month (the drought \times month interaction in the ANOVA) see Supplementary material Table S2. Different letters indicate statistically significant differences between the means of each variable within each group of treatments (e.g., dry vs. wet vs. control, and May vs. June/July vs. August vs. September), based on ANOVA post hoc tests using Tukey pairwise comparisons

September). Despite similar temperatures during the June/July and August measurement periods, monoterpene emissions were significantly higher in June/July than August. Sap flow was highest in August, significantly higher than in June/July or September, and sap flow in May was significantly higher than in June/July. Photosynthesis and g_s were significantly lower in June/July than in any other measurement period and significantly higher in August than in May or June/July. Acetone emissions were highest in May, with a significant difference between May (cool) and September (cool). Acetone and acetaldehyde emissions did not differ among measurement periods.

The compound composition of the emitted monoterpenes did not change in a statistically significant manner between June/July and August and was not influenced by drought treatment (data not shown). Monoterpene emissions were composed of 30–35 % β -pinene (this value may also include myrcene), 20–30 % limonene plus β -phellandrene

(these peaks were not differentiated), 15–18 % α -pinene, and 5–8 % carene. The only exception was camphene, which rose from 3 to 5 % between June/July and August. (Note that the values do not add up to 100 % because we are reporting mean values and did not include compounds present as <1 % of the total.)

The percentage of photosynthetic C lost from the needles through BVOC emission was highest in June/July (Fig. 2), significantly higher than during any other measurement period, and was unaffected by drought manipulation. In the May, August, and September measurement periods mature needles lost an average 0.3, 1.0, and 0.3 % of their instantaneously fixed C as BVOCs (in this case monoterpenes plus *MBO* plus methanol plus acetaldehyde plus acetone), respectively. In July, plants lost an average of 9.3 % of the instantaneously fixed C through BVOC emissions, with 1.1 % lost as monoterpenes, 8.1 % as *MBO*, and <0.1 % each as methanol, acetaldehyde, and

Table 2 Results of ANOVA for the effects of drought treatment, month, and their interaction on the emission rate of indicated BVOCs and for selected physiological measurements

Variable	Effect	df	F	p
Total BVOC emission (nmol m ⁻² s ⁻¹)	Drought	2, 63	2.314	0.11
	Month	3, 63	41.561	<0.001
	Drought × month	6, 63	1.011	0.43
Monoterpenes (nmol m ⁻² s ⁻¹)	Drought	2, 63	1.563	0.22
	Month	3, 63	22.654	<0.001
	Drought × month	6, 63	2.401	0.04
Methylbutenol (nmol m ⁻² s ⁻¹)	Drought	2, 63	2.083	0.13
	Month	3, 63	41.556	<0.001
	Drought × month	6, 63	0.811	0.57
Methanol (nmol m ⁻² s ⁻¹)	Drought	2, 62	1.812	0.17
	Month	3, 62	1.549	0.21
	Drought × month	6, 62	0.976	0.45
Acetaldehyde (nmol m ⁻² s ⁻¹)	Drought	2, 57	0.964	0.39
	Month	3, 57	1.132	0.34
	Drought × month	6, 57	0.655	0.6857
Acetone (nmol m ⁻² s ⁻¹)	Drought	2, 62	1.124	0.33
	Month	3, 62	3.082	0.03
	Drought × month	6, 62	1.520	0.1865
% C of VOCs	Drought	2, 63	1.379	0.26
	Month	3, 63	98.658	<0.001
	Drought × month	6, 63	0.751	0.611
Sap flow (cm h ⁻¹)	Drought	2, 63	8.293	<0.001
	Month	3, 63	11.728	<0.001
	Drought × month	6, 63	0.206	0.97
A (μmol m ⁻² s ⁻¹)	Drought	2, 63	2.919	0.06
	Month	3, 63	68.368	<0.001
	Drought × month	6, 63	0.814	0.56
g _s (mol m ⁻² s ⁻¹)	Drought	2, 63	3.871	0.03
	Month	3, 63	37.45	<0.001
	Drought × month	6, 63	1.232	0.30

See Table 1 for definition of variables and abbreviations

acetone (for correlations between emission rates of different BVOCs, see Table S5).

Relationship between needle physiology and BVOC emission

Photosynthesis rates and g_s were correlated (R² = 0.94) in all four measurement periods for both new and mature needles (Fig. 3a). While the correlation between photosynthesis and g_s was expected, in this case the correlation was so strong that it is difficult to determine any independent effects of the two processes on BVOC emissions. Needle transpiration rates were positively correlated with both g_s (R² = 0.87; Fig. 3b) and photosynthesis (R² = 0.85). Across the season, sap flow velocity was positively correlated with photosynthesis (log–log

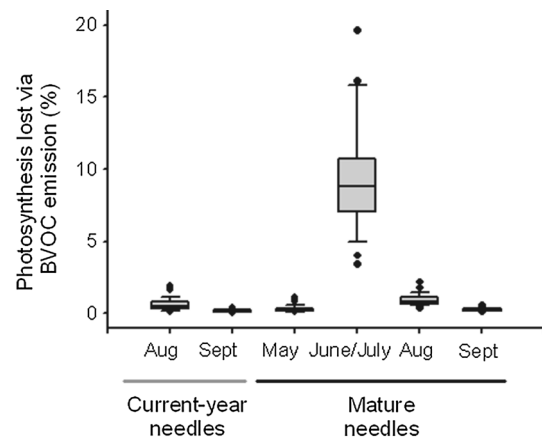


Fig. 2 C lost via biogenic volatile organic compounds (BVOCs) as a percentage of the C instantaneously fixed via photosynthesis for each month and needle age. Bars are mean ± SD (n = 24)

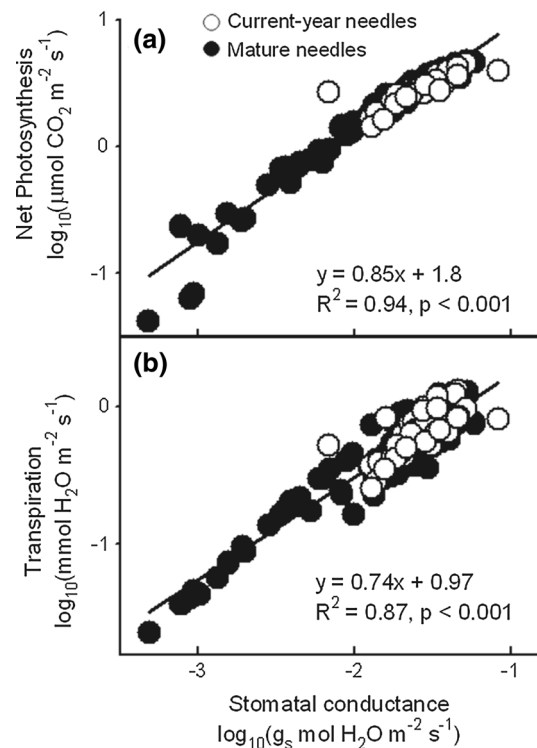


Fig. 3 Relationship between net photosynthesis (A) and **a** stomatal conductance (g_s) and **b** transpiration for mature needles (solid circles) and current-year needles (open circles). **a, b** Trend lines and regression statistics show the relationship of the variables across all needles. Note that A, g_s, and transpiration have been calculated based on total leaf area and have been log transformed

relationship, R² = 0.28), needle transpiration rate (R² = 0.29), and g_s (R² = 0.15). On a seasonal basis, the positive relationships of sap flow with g_s and transpiration were only significant during the summer (June/July and August) (Fig. 4a, b).

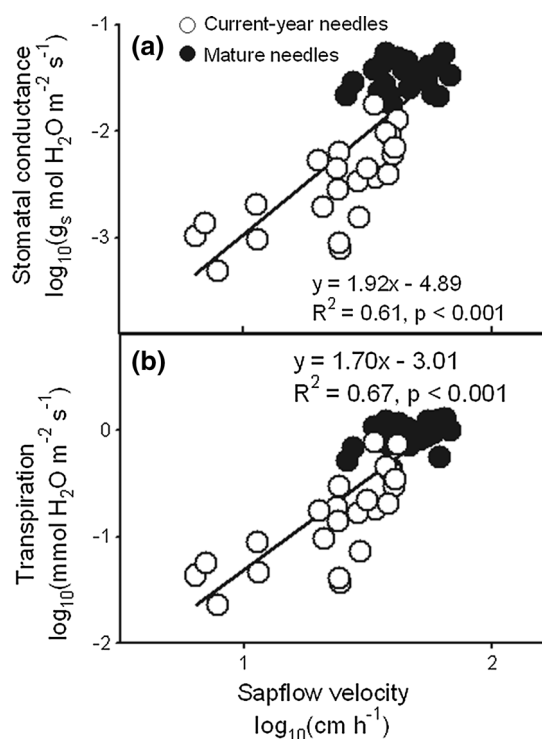


Fig. 4 g_s (a) and transpiration (b) vs. sap flow velocity during July (open circles) and August (solid circles). Trend line and regression statistics show the correlation for the combined July and August data. Note that g_s and sap flow are calculated based on total leaf area and have been log transformed

When significant correlations were present, BVOC emissions were positively related to photosynthesis rate and g_s (and to transpiration rate to a lesser extent) (Fig. 5; Table S4 in Electronic Supplementary Material). Across the season, photosynthesis rate and g_s separately explained ~10 % of the variation in monoterpene, methanol, and acetaldehyde emission, and transpiration rate explained ~10 % of the variation in methanol emissions (data not shown). Separating the data into individual measurement periods revealed that most of the explanatory power of photosynthesis, g_s , and transpiration on BVOC emissions came from the relationships during the June/July measurement period (Fig. 5a–r; Table S4 in Electronic Supplementary Material). In June/July, emissions of all BVOCs were positively correlated with g_s , transpiration, and photosynthesis. Positive correlations were also observed in August for MBO emission. The only case where we observed a negative correlation was for monoterpene emissions in August.

In every month except September the percentage of C lost through BVOC emission decreased with increasing g_s /transpiration/photosynthesis (Fig. 6). Photosynthesis

was the best predictor, resulting in R^2 -values of 0.16, 0.38, 0.40, and 0.32 for May (marginally significant $p = 0.06$), July ($p < 0.01$), August ($p < 0.01$), and current-year August ($p < 0.01$) needles, respectively. When the summer months were combined, the relationship was even stronger, with $R^2 = 0.72$ ($p < 0.001$).

Differences between new and mature needles

The drought treatments decreased photosynthesis and g_s in new needles, but had no influence on BVOC emissions. Needles sampled from the dry treatment had photosynthesis and g_s values that were 30–40 % lower than needles sampled from the control ($p < 0.05$ for both) and wet treatments (only g_s , $p < 0.05$). In new needles, photosynthesis and g_s were generally not good predictors of monoterpene, MBO, or methanol emissions. The exceptions were positive relationships of methanol emission with g_s and transpiration in August and of acetone emission with transpiration in September.

Total BVOC emission was 50 % lower from new needles than from mature needles in both August (approximately 1 month after emergence) and September. In August, mean emission rates of monoterpenes and methanol from new needles were 0.32 and 0.43 $\text{nmol m}^{-2} \text{s}^{-1}$, respectively. These rates were higher than in the needles' mature counterparts. Conversely, the mean new needle MBO emission rate of 1.88 $\text{nmol m}^{-2} \text{s}^{-1}$ was lower than the corresponding rate from mature needles. Emissions of acetone and acetaldehyde did not differ between new and mature needles in August or September. The proportion of photosynthesis going to emission of BVOC was lower in new needles than mature needles in August [0.6 (± 0.5) %; $p < 0.01$], but this difference disappeared by September [0.1 (± 0.09) %].

Needle concentrations of monoterpenes

The lowest concentrations of monoterpenes were observed in May and June/July, which had significantly lower total monoterpenes than any other month (Table 3). The reduced total concentrations were largely driven by low concentrations of (—)- α -pinene, β -myrcene and β -pinene. By September, new needles had monoterpene concentrations similar to mature needles, including similar percentages of each type of monoterpene. We found no significant correlations between monoterpene concentrations and needle emission rates for each of the four measurement periods or for the combined data from all four measurement periods (data not shown).

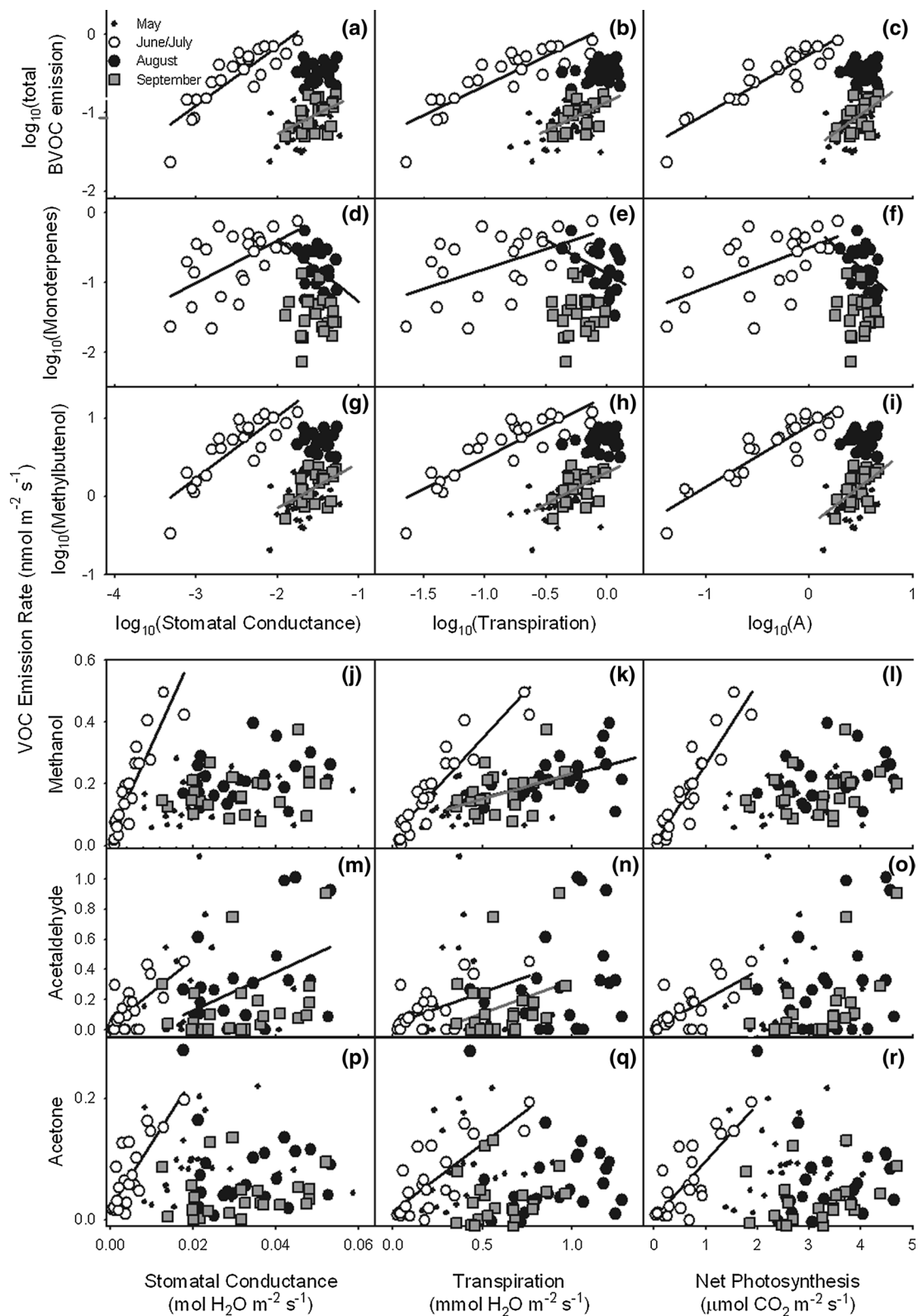


Fig. 5 Total BVOC emissions ($\text{nmol C m}^{-2} \text{s}^{-1}$) and emissions of individual VOC compounds ($\text{nmol m}^{-2} \text{s}^{-1}$) vs. g_s ($\text{mol H}_2\text{O m}^{-2} \text{s}^{-1}$), transpiration ($\text{mmol H}_2\text{O m}^{-2} \text{s}^{-1}$), and A ($\mu\text{mol m}^{-2} \text{s}^{-1}$) in mature needles. **a–c** Total BVOC emissions, **d–f** monoterpenes, **g–i** methylbutenol, **j–l** methanol, **m–o** acetaldehyde, and **p–r** acetone. Relationships are shown for each measurement

period: May (small crosses), June/July (open circles), August (filled circles), and September (gray squares). May data are omitted from the monoterpene figures due to the presence of emissions rates of zero that could not be log transformed. All variables were calculated using total leaf area. R^2 - and p -values are given in Table S4. For abbreviations, see Figs. 2 and 3

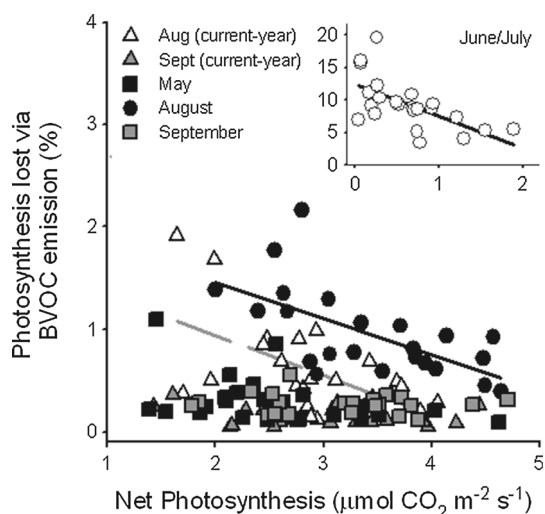


Fig. 6 Relationship between A ($\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$) calculated with total leaf area and the relative amount of C lost via BVOC emissions for mature needles in different months. For abbreviations, see Figs. 2 and 3

Discussion

Many ecosystems in the Southwestern USA are affected by seasonal drought, and the intensity and frequency of those droughts are likely to increase in the future (Cook and Seager 2013). The emission of BVOCs (in this case monoterpenes, MBO, methanol, acetaldehyde, and acetone) from the ponderosa pine forest studied were highest during the warmest part of the growing season, including the early season drought during June and July and the late-season monsoon during August. Monoterpene emissions were higher during the dry June/July period than the wet August, even though the temperatures during the two periods were similar. Within the dry June/July period,

trees receiving artificially reduced precipitation exhibited reduced monoterpene emissions, which although only marginally significant statistically ($p = 0.08$) is part of a larger pattern. Neither the naturally occurring June/July drought nor the artificial reduction in precipitation altered the emissions of MBO, methanol, acetaldehyde, or acetone during the summer.

The elevated and reduced emissions of monoterpenes observed in response to drought appeared to be caused by a general increase in monoterpene emissions as water stress increased, which was not explained by parallel changes in photosynthesis rate g_s , until photosynthesis and g_s dropped below a threshold value, after which the emissions became coupled with these components of leaf physiology. Previous studies on potted or very young trees have mixed findings regarding the response of monoterpene emissions to drought, but most commonly found an increase in monoterpene emissions in response to mild to moderate drought (Blanch et al. 2007) and a decrease in response to severe drought (Grote et al. 2009; Llusià and Peñuelas 1998), sometimes observed as an initial increase in monoterpene emission followed by a decrease as drought severity increases (Staudt et al. 2008; Bertin and Staudt 1996). Very few studies have been done on adult trees measured in situ and their findings are variable, with reports of drought increasing light-dependent monoterpene emissions (Llusià et al. 2008) and also decreasing them (Grote et al. 2009; Llusià et al. 2009). No studies to date have examined the effect of drought on the emissions of other BVOCs, including the light-independent monoterpenes, across the growing season in mature trees, and no studies have examined these relations in coniferous trees. Our data show that in August when the plants were not drought stressed, lower photosynthesis and g_s were weakly associated with higher monoterpene emissions; June/July data showed a positive relationship between monoterpene emissions and

Table 3 Monoterpene concentration (mg g^{-1} dry weight) of new and mature needles across the growing season

Monoterpene	New needles		Mature needles			
	August	September	May	June/July	August	September
(+)- α -Pinene	0.20 ± 0.05	0.29 ± 0.06	0.18 ± 0.04	0.18 ± 0.05	0.28 ± 0.06	0.33 ± 0.08
(-)- α -Pinene	$0.27 \text{ ab} \pm 0.03$	$0.31 \text{ a} \pm 0.03$	$0.18 \text{ b} \pm 0.02$	$0.19 \text{ b} \pm 0.03$	$0.27 \text{ ab} \pm 0.03$	$0.32 \text{ a} \pm 0.06$
Camphene	0.01 ± 0.003	0.01 ± 0.003	0.01 ± 0.003	0.01 ± 0.003	0.01 ± 0.003	0.01 ± 0.005
β -Myrcene	$1.34 \text{ ab} \pm 0.10$	$1.34 \text{ ab} \pm 0.14$	$1.00 \text{ a} \pm 0.09$	$1.01 \text{ a} \pm 0.09$	$1.41 \text{ b} \pm 0.13$	$1.23 \text{ ab} \pm 0.13$
β -Pinene	$0.95 \text{ ab} \pm 0.12$	$1.24 \text{ a} \pm 0.13$	$0.70 \text{ b} \pm 0.09$	$0.75 \text{ b} \pm 0.08$	$0.97 \text{ ab} \pm 0.10$	$1.02 \text{ ab} \pm 0.13$
Carene	$0.40 \text{ ab} \pm 0.07$	$0.45 \text{ a} \pm 0.08$	$0.26 \text{ ab} \pm 0.04$	$0.24 \text{ b} \pm 0.04$	$0.33 \text{ ab} \pm 0.05$	$0.41 \text{ ab} \pm 0.07$
Limonene	0.11 ± 0.02	0.12 ± 0.02	0.10 ± 0.02	0.09 ± 0.02	0.11 ± 0.02	0.11 ± 0.02
β -Phellandrene	0.14 ± 0.03	0.14 ± 0.03	0.09 ± 0.02	0.08 ± 0.02	0.11 ± 0.02	0.11 ± 0.02
Total MT	$3.40 \text{ a} \pm 0.25$	$3.90 \text{ a} \pm 0.25$	$2.51 \text{ b} \pm 0.20$	$2.54 \text{ b} \pm 0.20$	$3.49 \text{ a} \pm 0.23$	$3.54 \text{ a} \pm 0.36$

Values are mean (\pm SE). Different letters indicate significant differences between the means within each row, based on ANOVA post hoc tests using Tukey pairwise comparisons (for each mean, $n = 16$)

photosynthesis and/or g_s . Putting these data together we observe an inflection point at the level of drought stress where photosynthesis is reduced to $\sim 2 \mu\text{mol m}^{-2} \text{s}^{-1}$ and g_s is reduced to $0.02 \text{ mol m}^{-2} \text{s}^{-1}$ that appears to control the switch from increasing to decreasing monoterpene emissions. Others have found that when photosynthesis drops too low, the production of monoterpenes becomes substrate limited (Lavoie et al. 2009); we may have identified this point in ponderosa pine.

During the June/July measurement period, trees in the dry treatment had marginally reduced monoterpene emissions. This was the period of the naturally occurring drought season in this region and also the period when the trees were at or below the apparent threshold physiology required to link leaf physiology with monoterpene emissions. Once below the threshold, anything that further reduces photosynthesis and g_s is expected to reduce monoterpene emissions. This is an important consideration when predicting the future monoterpene emissions from this system since June/July is not only the time period with the highest monoterpene emissions, but also the period when photosynthesis and g_s are low enough that they are positively related to monoterpene emissions.

Although MBO, methanol, acetaldehyde, and acetone emissions did not respond to the drought treatments, they did become coupled with g_s and photosynthesis during the dry period of June/July, but were not coupled during the wet August period. Methylbutenol emission rates were generally high, accounting for >80 % of the total BVOC emission rate, which is consistent with other reports of *P. ponderosa* (Harley et al. 1998; Shade et al. 2000; Gray et al. 2003). Gray et al. (2003) found no differences in MBO emissions from *P. ponderosa* needles in response to drought, even when photosynthesis and conductance were reduced, which is both consistent and inconsistent with our findings, depending on the context of the observations. Although MBO emissions were not significantly different in the dry and wet treatments of our study, the coupling of MBO emissions with g_s and photosynthesis in severely drought-stressed trees indicates that once drought becomes severe enough, trees with the greatest reductions in their g_s and photosynthesis rates (which are presumably the most drought stressed) have the lowest MBO emissions. Gray et al. (2003) note in their study that the drought was not severe enough to induce midday stomatal closure; the lowest value of g_s they observed was $\sim 0.03 \text{ mol m}^{-2} \text{s}^{-1}$. In our study, in the drought period of June/July, values for g_s of $0.03 \text{ mol m}^{-2} \text{s}^{-1}$ were among the highest values that we observed. So, it seems likely that the trees in Gray et al. (2003) did not experience the extreme levels of water stress required to influence BVOC emissions.

Methanol, acetaldehyde and acetone emissions were similar during the cooler and warmer measurement periods

(Table 1). We observed no significant change in the average methanol emission rate in response to the onset of the seasonal drought during June/July, or in response to experimental increases in the intensity of that drought. These results differ from the decrease in methanol emissions observed for potted saplings of *Pinus halpensis* during a drought treatment in a greenhouse experiment (Filella et al. 2009). Despite no change in overall emission rate, emissions of methanol, like those associated with MBO and monoterpenes, shifted to become correlated with needle gas exchanges during the June/July drought ($R^2 = 0.80\text{--}0.86$; Fig. 5; Table S4). Methanol is the only compound for which the emission rate was observed to be more correlated with needle transpiration rate than conductance or photosynthesis rate (Table S4). In fact, methanol emission was significantly correlated with needle transpiration rate during every measurement period except May (Table S4). The lower Henry's law coefficient of methanol compared with other compounds should favor greater stomatal control (Niinemets and Reichstein 2003), but this is not always observed (Fowler et al. 2009). Acetone and acetaldehyde emissions were also correlated with needle gas exchange rates during the early summer June/July drought (Fig. 5). Filella et al. (2009) observed a similar relationship for acetaldehyde, but not for acetone. Most other studies have not observed a relationship between acetone emission and gas exchange (Filella et al. 2009; Janson and de Serves 2001; Cojocariu et al. 2004). Only Filella et al. (2009) included a drought treatment, applied as an extreme, acute treatment, so perhaps the relationships we observed are due to longer-term seasonal drought.

During seasonal periods of drought, stressed *P. ponderosa* lose proportionally more C via BVOC emission than at other times of the year. Increases in the percentage of C lost as BVOC emissions were mostly due to decreases in the rate of CO_2 assimilation, with no proportional decrease in the rate of BVOC emissions. When comparing June/July with August (the two warm periods), the total emission of all BVOCs and of monoterpenes was higher in June/July than August, but the magnitude of the difference was smaller than the differences in conductance and photosynthesis. For monoterpenes, one could make the case that there was an increase in the fractional allocation to the emission of these compounds, as their rate of emission increased during the June/July drought, despite decreases in the rate of photosynthesis.

The concentration of monoterpenes inside needles was unrelated to the emission rate of monoterpenes from those needles. This contrasts with some past studies in which needle concentrations were shown to be correlated with emission rate (e.g., Lerdau et al. 1995, 1997). In the study by Lerdau et al. (1995), potted saplings of *Pseudotsuga menziesii* (Douglas fir) were grown with different amounts of N

fertilizer, which induced differences in needle monoterpene concentration and correlated differences in emission rate. In the study by Lerdau et al. (1997), mature trees of *Pinus banksiana* and *Picea mariana* in a boreal forest ecosystem were used, and needles exhibiting differences in monoterpene concentration were correlated to emission rate. Needles of *P. ponderosa* at the semi-arid site used in this study are subjected to greater extremes of seasonal drought and temperature than those of the boreal forest, and the controls on emissions are entirely different than for those in the greenhouse study on Douglas fir. It is possible that the reason we did not observe a correlation between monoterpene concentration and emission rate in this study is that control over emission by seasonal climate is so great as to mask control by needle concentration.

New needles emitted VOCs at a lower rate and in a different composition than mature needles. In August, the current-year needles emitted monoterpenes, MBO, and methanol at lesser rates than mature needles, in addition to having lower monoterpene concentrations. By late September, the total emission of BVOCs from current-year needles was still lower than that of mature needles, but only because of lower MBO emissions. This finding is in contrast to previous work showing that MBO emissions decline with needle age (Gray et al. 2003), although the trees in that study were considerably younger (7–15 years old) than those used in this study. Our results are also in contrast to those reported by Aalto et al. (2014), in which much larger rates of monoterpene emissions were attributed to newly emergent foliage in a boreal evergreen forest. However, Aalto et al. (2014) used a branch enclosure, so it is possible that some of the increased emissions they observed were due to exposed resin on the bud or base of the needles, which has been observed to be particularly prevalent during times of bud break and needle emergence (Eller et al. 2013). By September, current-year needles had become similar to mature needles in terms of photosynthesis, conductance, transpiration, concentration of monoterpenes, and the emission of monoterpenes, methanol, acetone, and acetaldehyde.

In conclusion, emissions of monoterpenes, MBO, methanol, acetaldehyde, and acetone all become coupled with photosynthesis and g_s when water stress causes these values to be very low and the C lost via BVOC during periods of drought is proportionally greater than what is lost during wet periods. Comparing the June/July and August periods it is clear that modeling efforts for dry periods (June/July) may need to include leaf physiology even when those for wet periods (August) at the same site do not. Since drought in this ecosystem occurs during the summer, when emissions are normally high as a result of high temperatures, the reductions in BVOC emissions that were coupled with the drought-induced reductions of needle gas exchange could

result in lower summertime emissions than predicted by current models. This has the potential to influence predictions of regional ozone production, especially during summer when stationary weather systems foster an active form of oxidative photochemistry.

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