

## Contributions of biogenic volatile organic compounds to net ecosystem carbon flux in a ponderosa pine plantation

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### H I G H L I G H T S

- ▶ We quantified the carbon lost as BVOCs from a ponderosa pine plantation.
- ▶ We found that BVOCs contribute to 4.0 (2.0–7.9) % of annual NEE.
- ▶ Neglecting BVOC carbon loss causes an overestimation of carbon storage.

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### A B S T R A C T

When assessing net ecosystem exchange (NEE) and net ecosystem carbon balance (NECB), respiration is generally assumed to be the only significant loss of carbon to the atmosphere. However, carbon is also emitted from ecosystems in the form of biogenic volatile organic compounds (BVOCs). Here we consider the magnitude of systematic difference caused by omitting this additional carbon loss from the net ecosystem carbon balance, as compared to the NEE term, of the ponderosa pine plantation at Blodgett Forest. We find that 9.4 (range 6.2–12.5)  $\text{g C m}^{-2} \text{ yr}^{-1}$  were emitted from this ecosystem as BVOCs. This is 4.0 (2.0–7.9) % of annual NEE, and neglecting this additional loss of carbon causes an overestimation of carbon storage for this rapidly growing commercial forest plantation. For ecosystems that are not storing carbon as rapidly, where photosynthesis and respiration are more closely balanced, ignoring BVOC emission may cause a larger error in the estimation of NECB.

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## 1. Introduction

Understanding the complexities of the carbon budget on local, regional, and global scales is important for addressing the rising concentrations of carbon dioxide in Earth's atmosphere and the

implications for climate change. The overall amount of carbon assimilated by an ecosystem is defined as the gross primary productivity (GPP). Much of this carbon is later released by (auto-trophic and heterotrophic) respiration throughout the ecosystem ( $R_e$ ). The carbon dioxide ( $\text{CO}_2$ ) flux, called net ecosystem exchange (NEE), between the terrestrial ecosystem and the atmosphere can be measured using the eddy covariance method (e.g. Baldocchi and Meyers, 1998). It is the sum of the GPP and  $R_e$  flux components where, by convention, fluxes into the ecosystem are negative and fluxes out of the ecosystem, into the atmosphere, are considered positive. The eddy covariance technique is being used by FLUXNET sites across the world to quantify and compare ecosystem carbon balance and the influence of biotic and abiotic factors on carbon fluxes (Baldocchi et al., 2001).

Errors in eddy covariance NEE measurements can be classified as systematic or random. Random errors have inconsistent effects on the measurements and result in data scatter. Using eddy covariance methods, random errors range from instrument electronic noise (10–20%) to filling the gaps in datasets (1.5–20%)

*Abbreviations:* BVOC, biogenic volatile organic compound; NEE, net ecosystem exchange; NECB, net ecosystem carbon balance; GPP, gross primary productivity; MBO, 2-methyl-3-buten-2-ol.

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(Loescher et al., 2006). These uncertainty value ranges correspond to the typical 30-min measurement interval used. Systematic errors, on the other hand, are biases in the measurement that consistently shift the data in one direction away from the true value. Sources of systematic error in eddy covariance measurements include the sonic anemometer coordinate rotation and averaging intervals (0–25%), instrument response time (0–2%), and systematic exclusion of high or low frequency turbulence (0–16%) (Loescher et al., 2006). In contrast to random errors, systematic errors, once quantified, can be corrected for.

When assessing the net carbon balance, respiration is generally assumed to be the only significant loss of ecosystem carbon into the atmosphere, but carbon is also lost in particulate, aqueous, and gaseous forms other than CO<sub>2</sub>. The net ecosystem carbon balance (NECB), by definition, considers all fluxes of carbon – CO<sub>2</sub> (from NEE), carbon monoxide, methane, dissolved inorganic carbon, dissolved organic carbon, particulate carbon, and volatile organic compound fluxes – into or out of the ecosystem (Chapin et al., 2006). Here, our focus is on the emission of biogenic volatile organic compounds (BVOCs) from vegetation. We argue that this additional loss of carbon is a significant contributor to any NECB calculation. Most emissions of volatile organic compounds to the atmosphere are biogenic in origin, and on a global scale, vegetation is estimated to emit 1150 Tg of BVOC carbon per year (Guenther et al., 1995). In recent years, a wider suite of BVOC emissions have been measured or inferred (e.g. Goldan et al., 1993; Kurpius and Goldstein, 2003; Goldstein et al., 2004; Holzinger et al., 2005; Goldstein and Galbally, 2007; Helmig et al., 2007; Bouvier-Brown et al., 2009a), in part due to continuing improvements in analytical instrumentation allowing for the detection of less volatile and more reactive compounds.

Volatile organic compounds have already been mentioned as a potential addition to the estimate of forest productivity (e.g. Clark et al., 2001), but to our knowledge, this additional loss of carbon has not quantitatively been taken into account. Kesselmeier et al. (2002) and Guenther (2002) have estimated that BVOC emissions are significant to the carbon balance on a global scale, and in this analysis we quantify the total BVOC emission contribution at one particular site.

Blodgett Forest, as one of the Ameriflux (part of FLUXNET) sites, has produced extensive BVOC emission data over a 10-year period allowing us to quantitatively explore the impact of BVOC carbon emission. In this study, we will compare the magnitude of each BVOC, or class of BVOCs, to total ecosystem GPP and NEE as well as estimate the annual mass of carbon lost from Blodgett Forest through the emission of BVOCs. The purpose of this analysis is to consider the magnitude of systematic error due to omitting this carbon loss from the net ecosystem carbon balance when considering only measured NEE fluxes in annual NECB calculations.

## 2. Field site

The study site near Blodgett Forest Research Station is a part of the Ameriflux and FLUXNET networks. It is located on the western slope of the Sierra Nevada Mountains of California at 38°53'42.9N, 120°37'57.9W and 1315 m in elevation. The plantation (~20 ha) is dominated by an overstory of ponderosa pine (*Pinus ponderosa* L.) trees with an understory of manzanita (*Arctostaphylos* spp.) and whitethorn ceanothus (*Ceanothus cordulatus*) shrubs. In 1999, the nine-year-old trees averaged 2.6 m in height. Blodgett Forest is characterized by a Mediterranean climate with a hot and dry summer, and a cold, wet winter with most precipitation between September and May. The ponderosa pine growing season begins as soon as the spring weather permits and lasts ~80 days (Misson et al., 2006). Because the ecosystem is drought-stressed in the

summertime, revitalization of soil moisture with the onset of precipitation in the fall considerably changes the ecosystem photosynthetic rates (Misson et al., 2006), and therefore some ecosystem biogenic emissions (e.g. Bouvier-Brown et al., 2009a).

## 3. Measurements

Mixing ratios and fluxes of carbon dioxide (CO<sub>2</sub>), water vapor (H<sub>2</sub>O), and ozone (O<sub>3</sub>), along with meteorological parameters, such as air temperature and photosynthetically active radiation (PAR), have been measured at the site from 1997 through 2009. Annual trends are reported in detail elsewhere (e.g. Goldstein et al., 2000; Bauer et al., 2000).

### 3.1. Ecosystem productivity

Calculations of gross ecosystem productivity are described by Misson et al. (2005) and summarized here. Daytime net ecosystem exchange (NEE) was measured using eddy covariance CO<sub>2</sub> flux measurements, while nighttime NEE data was modeled based on field measurements of leaf, bole, and soil respiration. Gross primary productivity (GPP) was calculated by adding ecosystem respiration ( $R_e$ ), where  $R_e = R_{\text{leaf}} + R_{\text{bole}} + R_{\text{soil}} + R_{\text{wooddecay}}$ , to the NEE. To examine a continuous annual dataset in detail which overlaps with BVOC fluxes (see Section 3.2.), we focus on spring 1999 (starting 22 May, day of year 142) through spring 2000.

### 3.2. Measuring ambient biogenic volatile organic compounds

Volatile organic compounds (VOCs) have been measured at Blodgett Forest for more than 10 years. Assessing the biogenic VOC (BVOC) carbon loss in relation to NEE requires an extensive dataset of above-canopy VOC fluxes which overlaps with CO<sub>2</sub> flux measurements. The most complete set of VOC fluxes that fit these criteria were measured in 1999–2000. As a part of routine management of the Blodgett Forest plantation, understory shrubs were selectively removed over several weeks in early summer 1999 and pre-commercial thinning and mastication was carried out from 11 May to 15 June 2000 (see Schade and Goldstein (2003) and Misson et al. (2005) for more information). The shrubs, cut at the base of their trunks, were left on site to decompose; Schade and Goldstein (2001) demonstrated that on site soil and litter contributed to measured emissions of methanol, and to a lesser extent ethanol, acetaldehyde, and acetone. The mastication process in 2000 also enhanced BVOC emissions at the site, particularly monoterpenes (Schade and Goldstein, 2003), and likely sesquiterpenes (Goldstein et al., 2004). We focus on the most complete set of less-disturbed speciated BVOC fluxes obtained 9 July–8 September 1999.

During 1999 and 2000, volatile organic compound fluxes were measured ~6 m above the average tree height giving a footprint extension of ~200 m in the daytime. Hourly fluxes of methanol, ethanol, acetaldehyde, acetone, 2-methyl-3-buten-2-ol (MBO),  $\alpha$ -pinene,  $\beta$ -pinene, and 3-carene were measured using a relaxed eddy accumulation (REA) approach coupled to a dual-channel in-situ gas chromatograph with flame ionization detectors (GC-FID). This analytical procedure is fully described by Schade and Goldstein (2001), but briefly summarized here. For REA measurements, updrafts and downdrafts were subsampled from within a turbulent ambient air sample stream (10 L min<sup>-1</sup>) using Teflon segregator valves. Following identical parallel channels, these two subsamples were pre-concentrated for 30 min onto an adsorbent bed made up of Carboxpack B, Carbosieve SIII, and glass beads. Each sample was subsequently thermally desorbed onto a Rtx-WAX column and detected by a FID.

#### 4. Modeling BVOC emissions

BVOC emissions are typically modeled with either temperature-dependent or temperature- and light-dependent algorithms (e.g. Guenther et al., 1993). The temperature-dependent emission model explains the emission of BVOCs that are stored within the plant and emitted based on chemical vaporization and diffusion characteristics. This model is defined as:

$$E(T) = E_{\text{ref}} \exp(\beta(T - 303)) \quad (1)$$

where  $E_{\text{ref}}$  is the basal emission rate at 303 K normalized by dried needle or leaf mass,  $T$  is the temperature, and  $\beta$  is the temperature response factor. Additionally, light-dependent BVOC emissions, generally occurring immediately after synthesis can be modeled by

$$E = E_{\text{ref}} C_L C_T. \quad (2)$$

Here,  $E_{\text{ref}}$  is the emission rate at a standard temperature ( $T_s$  (303 K)) and a standard PAR flux ( $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ ).  $C_L$  describes the light-dependence and  $C_T$  describes the temperature dependence as defined by Guenther et al. (1993). The temperature-dependent emission model has been used to describe emissions of methanol, ethanol, acetaldehyde, acetone (Schade and Goldstein, 2001), monoterpenes (Schade and Goldstein, 2001, 2003; Lee et al., 2005; Holzinger et al., 2006; Bouvier-Brown et al., 2009c), and sesquiterpenes (Bouvier-Brown et al., 2009c) at Blodgett Forest, whereas the temperature- and light-dependent model has been used to analyze MBO (Harley et al., 1998; Baker et al., 1999; Schade et al., 2000; Gray et al., 2005, 2006) and methyl chavicol (Bouvier-Brown et al., 2009a) emissions at the site. Table 1 shows the best-fit modeling parameters for canopy-scale BVOC fluxes at Blodgett Forest that were used in the current analysis. Schade and Goldstein (2001) determined the parameters for methanol, ethanol, acetaldehyde, acetone, and MBO. Modeling parameters for total monoterpenes ( $E_{\text{ref}} = 1.1 \text{ mg C m}^{-2} \text{ h}^{-1}$ ,  $\beta = 0.12$ ) were calculated from the summer 1999 data, and they are very similar to values calculated by Lee et al. (2005) and Holzinger et al. (2006) for total monoterpene summertime fluxes in this ecosystem. Parameters for sesquiterpenes were extrapolated from the chamber data of Bouvier-Brown et al. (2009c) (Section 4.1.2).

##### 4.1. Inferred BVOC fluxes

Using the BVOC fluxes measured 9 July–8 September 1999 (see Section 3.2), we inferred the fluxes for additional known biogenic emissions at Blodgett Forest.

##### 4.1.1. Total monoterpenes

Recent studies at Blodgett Forest have focused on quantifying monoterpene and sesquiterpene fluxes. When using a Rtx-5 chromatography column, 8 (Lee et al., 2005) and 9 (Bouvier-Brown et al., 2009b, 2009c) specific monoterpene species have been identified. Because the GC-FID system resolved  $\beta$ -pinene best, Lee et al. (2005) calculated the sum of speciated monoterpene fluxes by scaling the  $\beta$ -pinene flux. This process showed that total monoterpene flux at the site was equivalent to the  $\beta$ -pinene flux scaled by a factor of 2.498 ( $R^2 = 0.6$ ) (Fig. A1). This scaling factor of  $\sim 2.5$  is corroborated by re-analysis of the average total monoterpene-to- $\beta$ -pinene response from the ponderosa pine branches studied in the branch enclosures described by Bouvier-Brown et al. (2009c). To account for all monoterpenes at Blodgett Forest in 1999, many of which were not measured directly at that time, we therefore multiplied the  $\beta$ -pinene flux by 2.5.

##### 4.1.2. Total sesquiterpenes

The total sesquiterpene canopy flux was inferred from the branch enclosure system data. Emissions from each prominent species – ponderosa pine, manzanita, and ceanothus – at Blodgett Forest, compiled by Bouvier-Brown et al. (2009c), were upscaled to the entire ecosystem using leaf area indexes and plant density. An average basal emission rate of  $0.29 \text{ mg C m}^{-2} \text{ h}^{-1}$  was calculated for total sesquiterpenes in summer 1999, with an average temperature response ( $\beta$ ) of  $0.1 \pm 0.05$  ( $1 \sigma$ ) (Table 1). Thus, similar to the other BVOCs, sesquiterpene emissions will be modeled with an uncertainty factor of 2.

##### 4.1.3. Methyl chavicol

Bouvier-Brown et al. (2009a) recently characterized methyl chavicol (estragole), a biogenic oxygenated aromatic compound. Its emissions can often be a significant contribution to total BVOC at Blodgett Forest; in fact, methyl chavicol fluxes can be 4–68% of MBO fluxes, by mass of carbon, depending on the season (Bouvier-Brown et al., 2009a). For this analysis, we assumed that methyl chavicol is 16% of the MBO flux, with a range of 4–24%. These values are representative of what has been observed during warm and dry conditions, like that in the summer study period. The larger 68% value was observed during cool and wet conditions.

##### 4.1.4. Annual emissions

While summertime has the highest temperatures, and therefore typically the largest BVOC emissions, emissions can occur throughout the year; some are even sensitive to rain, snow, and spring growth events. In terms of their response to the phenological cycle and weather at Blodgett Forest, we have the most

**Table 1**

Best-fit emission modeling parameters for canopy-scale fluxes at Blodgett Forest.  $E_{\text{ref}}$  is the emission rate at 303 K;  $\beta$ ,  $\alpha$ , and  $C_{L1}$  are empirical coefficients from the best fit curve;  $T_{\text{opt}}$  is the temperature (K) at which  $E_{\text{opt}}$  occurs;  $C_{T2}$  and  $C_{T1}$  are activation and deactivation energies, respectively.  $\beta$  is used in Eq (1),  $\alpha$  and  $C_{L1}$  are used to find  $C_L$  in Eq (2), and  $E_{\text{opt}}$ ,  $C_{T2}$ , and  $C_{T1}$  are used to find  $C_T$  in Eq (2). (For further discussion of models, please see: Guenther et al., 1993; Harley et al., 1998; Schade and Goldstein, 2001.)

Compound	$E_{\text{ref}}^a$	$\beta$	$\alpha$	$C_{L1}$	$E_{\text{opt}}$	$C_{T2}^b$	$C_{T1}^b$	$T_{\text{opt}}^c$	$E$ range <sup>e</sup>
Methanol	2.87 <sup>d</sup>	0.11 <sup>d</sup>							0.96–5.74
Ethanol	0.64 <sup>d</sup>	0.14 <sup>d</sup>							0.32–1.28
Acetone	0.37 <sup>d</sup>	0.11 <sup>d</sup>							0.19–0.74
Acetaldehyde	0.20 <sup>d</sup>	0.13 <sup>d</sup>							0.10–0.40
MBO	2.5		0.0011 <sup>d</sup>	1.37 <sup>d</sup>	1.45 <sup>d</sup>	154 <sup>d</sup>	131 <sup>d</sup>	312 <sup>d</sup>	2.62–3.93
Monoterpenes	1.1	0.12							0.55–1.65
Sesquiterpenes	0.29	0.1							0.15–0.58

<sup>a</sup> In  $\text{mg C m}^{-2} \text{ h}^{-1}$ .

<sup>b</sup> In  $\text{kJ mol}^{-1}$ .

<sup>c</sup> In Kelvin.

<sup>d</sup> Parameters calculated by Schade and Goldstein (2001).

<sup>e</sup> At 30 °C; uncertainty factor  $\pm 2$  for all except:  $\pm 1.5$  for monoterpenes,  $\pm 1.2$  for MBO, and  $1/3 - 2$  for methanol.

**Table 2**

Modeling parameters ( $E_{ref}$ , the emission at 303 K, and  $\beta$ , the temperature dependence coefficient) observed by Holzinger et al. (2006) for monoterpenes in different seasons. Using summer as the baseline period, new parameters were calculated for the May 1999–May 2000 year. Significantly higher values were observed at the first rain and snow events, so unique parameters were assigned for those time periods.

	Holzinger et al. (2006)		Scaled using summer 1999	
	$E_{ref}^a$	$\beta$	$E_{ref}^b$	$\beta$
Summer	1.25	0.13	1.1	0.12
Winter	2	0.12	1.8	0.11
Spring	3.4 <sup>c</sup>	0.165 <sup>c</sup>	3	0.15
1st rain	8.9	0.27	7.8	0.25
1st snow	48.5	0.24	42.5	0.22

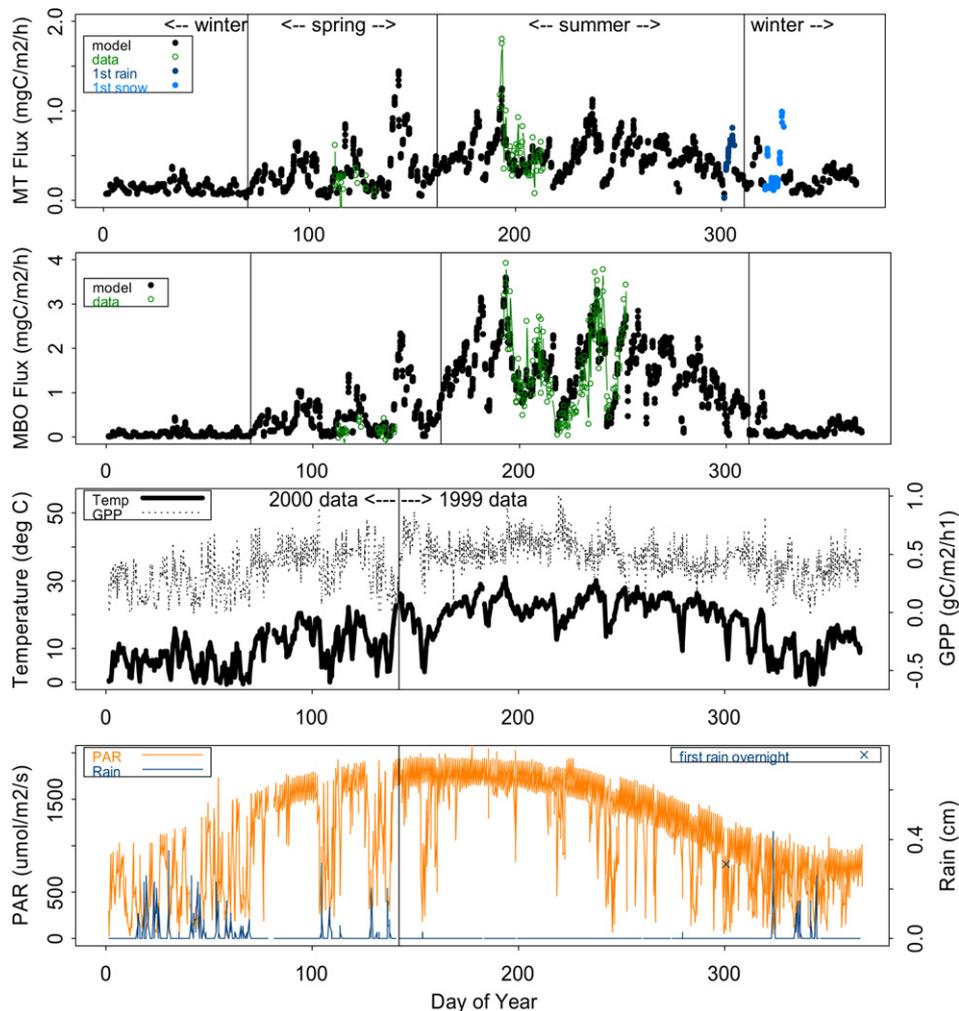
<sup>a</sup> Values reported in  $\mu\text{mol m}_{leaf}^{-2} \text{h}^{-1}$ .

<sup>b</sup> In  $\text{mgC m}^{-1} \text{h}^{-1}$ .

<sup>c</sup> 70% of spring 2004 values and 30% of spring 2003 values.

information about monoterpene fluxes. Using a year of data from Blodgett Forest, Holzinger et al. (2006) showed how the modeling parameters (i.e.  $E_{ref}$  and  $\beta$ ) changed dramatically over the course of the year, and that simply using the summertime values will underestimate the total annual monoterpene flux by up to 50%.

Using the site-specific summertime values reported by Holzinger et al. (2006) as the baseline period, we scaled the summer 1999 modeling parameters to attain  $E_{ref}$  and  $\beta$  values for winter, spring, the first rain event, and the first snow event (Table 2). The 'first' rain and snow events marked the end of dry periods; Holzinger et al. (2006) did not see any emission bursts during subsequent rain and snow events. Using these new modeling parameters and temperature data from 22 May (day of year 142) 1999 through 21 May 2000, we modeled the total monoterpene flux for one year, overlaid with real data when applicable (Fig. 1). The temperature dependence is apparent, but the time series also highlights the large pulses of monoterpene emissions driven by the first rain and first snow events. Fig. 1 also shows modeled MBO fluxes overlaid with data when applicable. The MBO flux is modeled over the 1999/2000 season using the parameters described in Section 4. This does not take into account the likely decrease in basal emission rate in the winter and early spring periods. No annual flux estimation was made for any of the oxygenated BVOCs (methanol, ethanol, acetone, acetaldehyde) because their emissions from vegetation are difficult to estimate and cannot be quantitatively accounted for with the available data. Many oxygenated VOCs are thought to be at least partially under stomatal control (e.g. Schade and Goldstein, 2001,



**Fig. 1.** Data from 22 May 1999–21 May 2000 but sorted by day of year (January–December); all data points occur during the daytime (10:00–16:00 PST) when the air in and above the canopy was vertically well mixed and eddy covariance fluxes are reliable. The top two panels show total monoterpene (MT) and MBO fluxes over one year. ● (closed solid black circle): model estimates using temperature data and the model parameters outlined in Table 1 (MBO) and Table 2 (MT). ○ (open green circle): actual flux data collected in summer 1999 and spring 2000 for comparison. The bottom two panels show calculated gross primary productivity (GPP, Misson et al., 2005) and measured temperature, photosynthetically active radiation (PAR), and rainfall for this time period. × denotes the first rain of the season that occurred overnight. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2002, 2006) and there is evidence of increased emissions as needles elongate in the spring (Schade and Goldstein, 2006).

## 5. Results and discussion

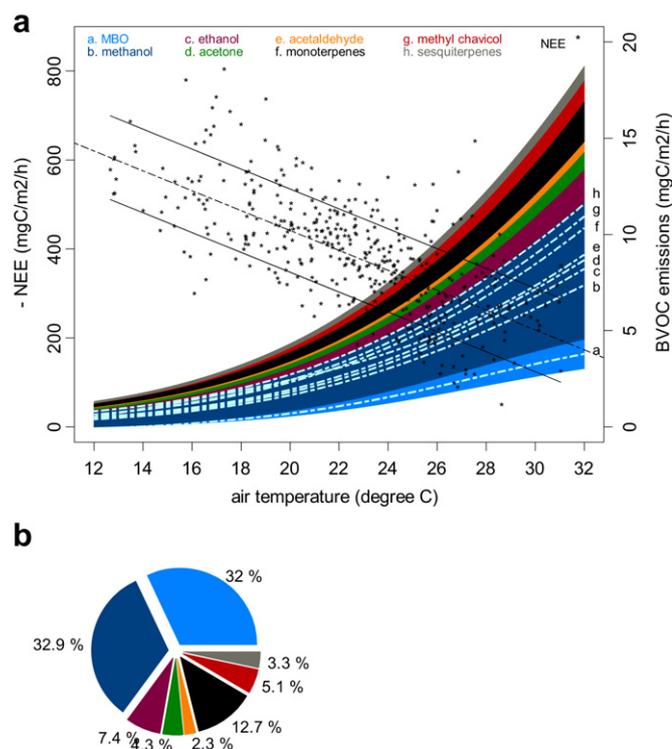
The emission models conservatively fit their respective BVOC data within a factor of 2, and such accuracy is generally achieved for BVOC modeling and considered a reasonably good agreement (Warneke et al., 2010). The exceptions are monoterpenes, which are within a factor of 1.5, MBO, which is within a factor of 1.2, and methanol. Ecosystem methanol emissions were likely high in the summer 1999 period due to left-over litter from the preceding understory brush clearing (section 3.2; Schade and Goldstein (2001)). Later measurements at the site suggest that ‘undisturbed’ methanol fluxes are lower by a factor of 2–3. Thus, we use an uncertainty ranging from one third to twice the measured summer 1999 emissions. We applied the resulting ranges (i.e.  $\pm$  generally a factor of 2) for each emission at 30 °C, as specified in Table 1, and propagated this uncertainty through the following calculations to assess the contribution of BVOC emissions to NEE. Values will be presented as “mean (range).”

All of the BVOC emission fluxes increased with increasing ambient temperature. Fig. 2a shows the modeled BVOC emissions  $\pm$  their uncertainty range. Stacked on top of each other, one can see that the total emission at 30 °C was 9.3 (4.9–15.2)  $\text{mg C m}^{-2} \text{h}^{-1}$ . Using these models, we calculated the relative contribution of each BVOC flux to the total at 30 °C (Fig. 2b). Methanol and MBO had equally large

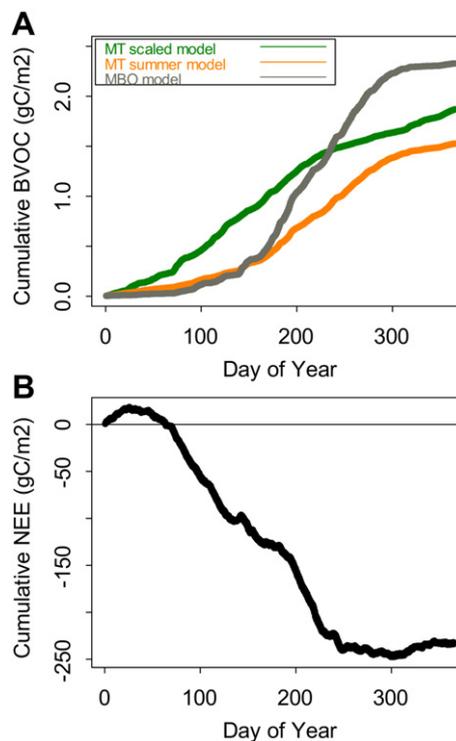
contributions; together they made up over 60% of the BVOC flux at Blodgett Forest in 1999. Sesquiterpenes and methyl chavicol, both semi-volatile compounds that have only been recently measured and quantified at the site (Bouvier-Brown et al., 2007, 2009a, 2009b, 2009c), contributed 3 and 5%, respectively.

To quantify the amount of carbon lost as BVOC emissions relative to the amount of carbon photosynthesized or the net amount of carbon exchanged by the ecosystem, we focused on daytime (10:00–16:00 PST) data when the air in and above the canopy was vertically well mixed and eddy covariance fluxes are reliable. NEE at Blodgett Forest was negative all summer (ecosystem carbon uptake), but the magnitude scaled negatively with temperature (Fig. 2a). Thus, in general, the ratio of BVOC emissions to NEE increases strongly with temperature; the same trend holds true for GPP (data not shown). At 30 °C, NEE was  $-218$  ( $-122$  to  $-310$ )  $\text{mg C m}^{-2} \text{h}^{-1}$  (the range reflects the  $1 \sigma$  prediction limit plotted in Fig. 2a). Hence, BVOCs were 4.3 (1.6–12) % of NEE at 30 °C in the summer. The calculated average GPP at 30 °C was  $-468$  ( $-370$  to  $-565$ )  $\text{mg C m}^{-2} \text{h}^{-1}$ , meaning BVOC emissions were 2.0 (0.9–4.1) % of GPP at 30 °C in the summer. Kesselmeier et al. (2002) calculated similar values – a 1% average contribution to GPP, with peak values between 2 and 3%, during summer over a temperate forest.

Using the modeled annual emissions of monoterpenes and MBO (Fig. 1), we calculated how much carbon is lost into the atmosphere through these BVOC emissions over the full year. Fig. 3a shows a cumulative sum of the BVOC emission for the 1999/2000 dataset: 1.86 (0.93–2.79)  $\text{g C m}^{-2}$  of monoterpenes were emitted over this one-year period from Blodgett Forest using the best-estimate annual model. When only considering the summer model (E<sub>ref</sub> = 1.1 and  $\beta$  = 0.12), we calculated a lower monoterpene emission of 1.52 (0.76–2.28)  $\text{g C m}^{-2}$ . Thus, over one year, there would have been an 18% underestimation of monoterpene flux out of the ecosystem when only the summer model parameters



**Fig. 2.** a: Modeled BVOC emissions  $\pm$  uncertainty for the daytime (10:00–16:00 PST) summer BVOC data from the 9 July–8 September 1999 study period. The dashed lines are the stacked modeled result, while the colored section denotes the stacked range of each model. Net ecosystem exchange data (stars) are shown on the left y-axis with a  $\pm 1$  standard deviation ( $\sigma$ ) prediction limit. b: The average contribution of each BVOC to the total modeled flux at 30 °C. Colors are the same as in Fig. 2a (light blue: MBO, dark blue: methanol, maroon: ethanol, green: acetone, orange: acetaldehyde, black: total monoterpenes, red: methyl chavicol, gray: total sesquiterpenes). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** A: Cumulative carbon lost as monoterpene (MT) and MBO emissions. B: Cumulative net ecosystem exchange (NEE) over the 22 May 1999–21 May 2000 period sorted by day of year (January–December).

were considered. This clearly shows the effect of seasonality on the emissions, the increased emission rates due to spring growth, rain and snow events. MBO was lost at a rate of 2.32 (1.86–2.78)  $\text{g C m}^{-2} \text{y}^{-1}$  using the summer model parameters. The cumulative NEE over this time period was  $-233$  ( $-158$  to  $-308$ )  $\text{g C m}^{-2}$  (Fig. 3b) and the cumulative GPP was  $-1500$  ( $-1020$  to  $-1980$ )  $\text{g C m}^{-2}$  (data not shown). Uncertainty for the annual estimation of NEE is 12–32% as noted by Loescher et al. (2006); we used a range of  $\pm 32\%$  for annual NEE, GPP, and ecosystem respiration values. Therefore, 0.8 (0.3–1.8) % and 1.0 (0.6–1.8) % of the NEE carbon is lost annually as monoterpenes and MBO, respectively. The annual loss of total BVOC is likely much higher than this value but will depend on the seasonality of emissions, which may be strong (cf. Bouvier-Brown et al. (2009c)) but is not well characterized for most of the BVOCs measured. If we assumed that the percent contribution of total monoterpenes plus MBO was the same as that calculated for the summer (44.7%, Fig. 2b), the annual loss of carbon from BVOC emissions at Blodgett Forest would be 9.4 (6.2–12.5)  $\text{g C m}^{-2}$ . This would then be 4.0 (2.0–7.9) % of the annual NEE and 0.6 (0.3–1.2) % of the annual GPP. This calculated annual loss of BVOCs is similar to the estimated global average of 7  $\text{g C m}^{-2}$  reported by Guenther (2002) and within, but at the low end, of the range of the global estimate of 3.5–39% NEE reported by Kesselmeier et al. (2002). The BVOC percent relative to annual GPP is also similar to the values estimated by Kesselmeier et al. (2002). To put our 4% NEE-based annual BVOC loss value into context, the systematic error caused by omitting these emissions is larger than the error from eddy covariance instrument noise (0–2%), it is on the lower end of frequency loss (0–16%), but it is less than the potential error from sonic anemometer coordinate rotation or averaging interval choices (0–25%) (uncertainties compiled in Loescher et al. (2006) and references therein).

The data in this analysis was collected from a young forest, and the contribution to NEE of carbon lost as BVOCs is likely to increase with the age of the forest. There will be an enhancement of BVOC emissions as the leaf area index and plant density increases. A mature forest will not sequester carbon as rapidly (Magnani et al., 2007), and because the level of gross productivity plays the largest role in determining NEE over time (Law et al., 2001; Arain and Restrepo-Coupe, 2005), NEE will be more stable over time (Magnani et al., 2007). While the forest is in this steady-state, any fluctuation in BVOC emissions should cause a more significant contribution to the NECB calculation. The study site, a ponderosa pine plantation, is also a forest controlled by management practices. Plantations show a decrease in net ecosystem production with time due to age-related growth reduction (Arain and Restrepo-Coupe, 2005). Even with a decrease in productivity, there will still be a very similar amount of leaf biomass from year to year, so BVOC emissions should not decrease. Active management practices also impact the relative importance of BVOC emissions. For example, pre-commercial thinning and mastication at Blodgett Forest described in Section 3.2 resulted in a large burst of monoterpene emissions (Schade and Goldstein, 2003). Thinning increased light levels, and thus temperature, so temperature-dependent BVOC emissions responded. In addition, many BVOCs are easily vaporized following any mechanical stress that ruptures the leaf cuticle. There will also be an increase in BVOC emissions from debris left on site (e.g. oxygenated VOCs, Schade and Goldstein, 2001). While these management practices caused a burst of BVOC emissions, the absolute value of NEE decreased due to the dramatic loss of gross primary productivity and relatively unchanged ecosystem respiration (Misson et al., 2005). As the forest ages and is actively managed, there will likely be an increase in the relative contribution of BVOCs to NEE, thus these emissions should be considered when calculating NECB.

## 6. Conclusions

Emissions of biogenic volatile organic compounds are a measurable loss of carbon from ecosystems. At Blodgett Forest, BVOC emissions contributed a flux of 9.4 (6.2–12.5)  $\text{g C m}^{-2}$  during the 1999–2000 year in addition to the 1260 (860–1670)  $\text{g C m}^{-2}$  respiration that year. Total BVOC emission thus accounted for 0.7 (0.4–1.5) % of the annual respiration and 4.0 (2.0–7.9) % of the annual net ecosystem exchange. The systematic error of omitting these BVOC emissions in NEE-based net ecosystem carbon balance calculations is similar to that of several other potential eddy covariance systematic measurement errors. In ecosystems that are not storing carbon as rapidly, where photosynthesis and respiration are more closely balanced, similar BVOC emissions would cause an even larger discrepancy between NEE and NECB.

Continued flux measurement improvements will provide a greater constraint on the uncertainties of BVOC models, thus improving the above estimate. As ongoing analytical improvements enable researchers to detect and quantify more and more BVOCs, this contribution may continue to increase. For example, in this analysis alone,  $\sim 8\%$  of the total BVOC carbon comes from sesquiterpenes and methyl chavicol – all semi-volatile compounds only recently quantified at this site (Bouvier-Brown et al., 2009a, 2009c). On the other hand, BVOC and particle deposition may provide yet unexplored carbon inputs, which cannot yet be weighed against better quantified carbon losses.

We argue that current evidence from BVOC flux measurements suggests a systematic and significant loss of carbon from ecosystems that can be implemented into NECB calculations. Ignoring this additional loss term very likely results in an overestimation of carbon stored in the ecosystem.

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## Appendix A

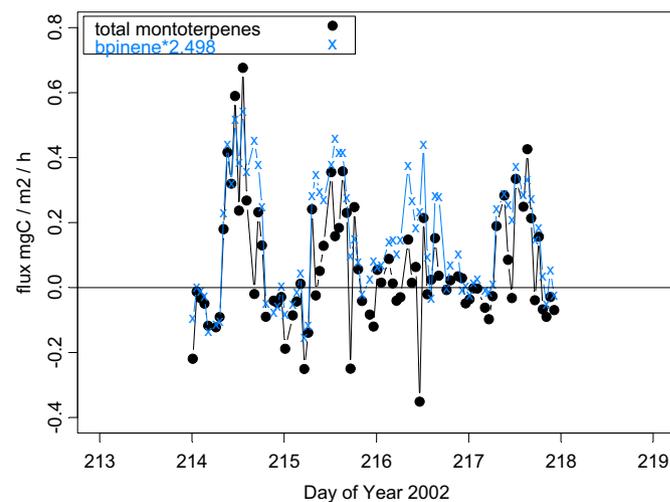


Fig. A1. Total monoterpene ( $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, limonene, camphene,  $\alpha$ -terpinene,  $\gamma$ -terpinene, and terpinolene) flux measured in 2002 was comparable to  $\beta$ -pinene flux scaled by a factor of 2.498 ( $R^2 = 0.6$ ). Data reported by Lee et al. (2005).

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