Title
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Journal
Chemosphere, 93(1)

ISSN
0045-6535

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Publication Date
2013-09-01

DOI
10.1016/j.chemosphere.2013.04.058

Chemosphere 93 (2013) 35–46

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Seasonal trends of biogenic terpene emissions

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HIGHLIGHTS

- Full year study on biogenic volatile organic compounds emissions.
- Description of seasonal changes of basal emission rates.
- Investigation of seasonal behavior of temperature response.
- Sensitivity analysis for modeling of biogenic volatile organic compound emissions.

ARTICLE INFO

Article history:
Received 2 October 2012
Received in revised form 16 April 2013
Accepted 21 April 2013
Available online 1 July 2013

Keywords:
Biogenic volatile organic compound emissisons
Seasonal changes
Emission modeling
Emission rate
Beta factor

ABSTRACT

Biogenic volatile organic compound (BVOC) emissions from six coniferous tree species, i.e. *Pinus ponderosa* (Ponderosa Pine), *Picea pungens* (Blue Spruce), *Pseudotsuga menziesii* (Rocky Mountain Douglas Fir) and *Pinus longaeva* (Bristlecone Pine), as well as from two deciduous species, *Quercus gambelii* (Gamble Oak) and *Betula occidentalis* (Western River Birch) were studied over a full annual growing cycle. Monoterpene (MT) and sesquiterpene (SQT) emissions rates were quantified in a total of 1236 individual branch enclosure samples. MT dominated coniferous emissions, producing greater than 95% of BVOC emissions. MT and SQT demonstrated short-term emission dependence with temperature. Two oxygenated MT, 1,8-cineol and piperitone, were both light and temperature dependent. Basal emission rates (BER, normalized to 1000 μmol m^{-2} s^{-1} and 30 °C) were generally higher in spring and summer than in winter; MT seasonal BER from the coniferous trees maximized between 1.5 and 6.0 μg g^{-1} h^{-1}, while seasonal lows were near 0.1 μg g^{-1} h^{-1}. The fractional contribution of individual MT to total emissions was found to fluctuate with season. SQT BER measured from the coniferous trees ranged from <0.01 to 0.15 μg g^{-1} h^{-1}. BER of up to 1.2 μg g^{-1} h^{-1} of the SQT germacrene B were found from *Q. gambelii*, peaking in late summer. The β-factor, used to define temperature dependence in emissions modeling, was not found to exhibit discernible growth season trends. A seasonal correction factor proposed by others in previous work to account for a sinusoidal shaped emission pattern was applied to the data. Varying levels of agreement were found between the data and model results for the different plant species seasonal data sets using this correction. Consequently, the analyses on this extensive data set suggest that it is not feasible to apply a universal seasonal correction factor across different vegetation species. A modeling exercise comparing two case scenarios, (1) without and (2) with consideration of the seasonal changes in emission factors illustrated large deviations when emission factors are applied for other seasons than those in which they were experimentally determined.

1. Introduction

Most vegetation emits an array of biogenic volatile organic compounds (BVOC). BVOC are of interest to atmospheric scientists, among other fields, due to their chemical reactions once released into the atmosphere. Important products of BVOC oxidation include secondary organic aerosols (SOA) and ozone, both of which may adversely affect human health. Recent studies have highlighted uncertainty in the ability to model monoterpene (MT) and sesquiterpene (SQT) emission rates over a seasonal cycle (Guenther, 1997; Staudt et al., 2000; Holzinger et al., 2006; Barkley et al., 2009); which to a large extend is due to the fact that only few experimental studies describe MT and SQT BVOC emissions over the course of a complete growing season and that findings vary considerably between plant species that were studied (i.e. Hakola et al., 2001, 2012; Staudt et al., 2002; Holzke et al., 2006; Fares et al., 2012; Noe et al., 2012; Matsunaga et al., 2013). Despite the

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0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.04.058

call for more phenologically based descriptors to accompany BVOC emission rate data sets, most emission data currently available are expressed solely by empirical light and temperature dependence algorithms (Duhl et al., 2008). Light and temperature based emission rate data sets are commonly normalized to standard light and temperature conditions, termed the basal emission rate (BER), which are used as input variables for atmospheric chemistry and transport models (Guenther et al., 1993).

Despite normalization to light and temperature, BER have been found to vary with season; they were highest during the growing season between late spring and fall at higher latitudes. The relative ratio of seasonal BVOC BER maxima to minima reported in the literature varies greatly from <10 (Kuhn et al., 2004; Hakola et al., 2001; Holzinger et al., 2006; Holzke et al., 2006; Keenan et al., 2009; Geron and Arnts, 2010) to 45–100 (Staudt et al., 2000; Pio et al., 2005; Rivoal et al., 2010).

This study investigates BVOC emission patterns utilizing light and temperature adjusted emission data sets with the goal of accounting for seasonal variation. MT and SQT emissions of four coniferous and two deciduous tree species native to Colorado forests were monitored monthly over the course of one year. Changes in BER magnitude, emission speciation by compound, and the empirical temperature parameter β were investigated for seasonal trends. Additionally, the application of a seasonal emission correction factor proposed by Staudt et al. (2000) is evaluated.

2. Methods

Sampling was conducted over a one-year period between February 2009 and February 2010 at a tree nursery in Boulder, CO (40°2′N, 105°12′W). Four coniferous species were investigated, including two *Pinus ponderosa* (A & B) trees (Ponderosa Pine), one *Picea pungens* (Blue Spruce), one *Pseudotsuga menziesii* (Rocky Mountain Douglas-fir), and one *Pinus longaeva* (Bristlecone Pine) tree. The tree specimens were 4–6 years of age and 1–2 m in height. Additionally, two deciduous species were examined, including a 6-year-old *Quercus gambelii* (Gamble Oak) and a 7-year-old *Betula occidentalis* (Western River Birch), each ~2 m tall. Tree species were selected based on abundance in Colorado and expected health in a tree nursery setting. All tree species were housed in planting pots (0.5 m diameter, 0.5 m tall) and topped over with mulch. Supplemental irrigation was supplied regularly. Each tree specimen was allowed one month to acclimate before sampling commenced.

Sampling methods and equipment followed recommendations for branch enclosure sampling outlined by Ortega and Helmig (2008) and are briefly described here. A schematic of the setup, simplified from the one shown in Fig. 1 in Ortega et al. (2008), is presented in Supplementary materials Fig. S1. One limb was selected per tree specimen for repeated measurement throughout the study period to reduce results being affected by branch-to-branch emission variability (Bertin et al., 1997; Pio et al., 2005). For sample collection, a Tedlar bag (Jensen Inert Products, Coral Springs, FL) was placed over the branch and cinched at the base of the limb by a bungee cord, enclosing a volume of 30–60 L of air around the vegetation. A purge air stream leading to the enclosure was supplied by a high capacity oil-free pump (Medo Corporation, Hanover Park, IL). The purge air was first scrubbed of VOC and particulates using a combination of an organic vapor and particulate respirator filter cartridge (Mersorb Part No. 463532; Mine Safety Appliances Company, Pittsburgh, PA) and charcoal scrubber (Fisher, 05-685A, 6-14 mesh). The enclosure purge air was further scrubbed free of ozone using a customized scrubber composed of 40 MnO_2-coated copper screens (O.B.E. Corp. Fredericksburg, TX) and dried using a condensing water trap (1 m length coiled 0.95 cm o.d. copper tubing submerged in an ice bath). Ozone was periodically monitored from the enclosure to ensure the purge air was free of ozone to less than 2 ppb (Monitor Labs 8810, Teledyne Technologies Inc., Englewood, CO). The purge air was delivered to the bag enclosure through 0.95 cm o.d. Teflon tubing at a mass flow controlled (MFC) flow rate. Purge rates of 40 L min^{-1} were used during hot summer months to reduce greenhouse heating within the enclosure while lower flow rates of 20 L min^{-1} were used during the winter season to maximize sensitivity for BVOC sampling. Likewise, sampling volumes varied between 12 L and 24 L dependent on season and time of day; larger sample volumes were collected in winter and at night to enhance the sensitivity of the emission rate determination. Following these methods, the lowest detectable emission rates for individual compounds, dependent on purge flow rate and sampling volume, were on the order of 10–20 ng g^{-1} h^{-1}. A reference gas standard composed of five aromatic compounds spanning a similar volatility and GC retention time range to MT and SQT was added to the enclosure purge air for analyte recovery analysis and identification. The reference gas standard was mixed with the enclosure purge air at a constant rate of 5 mL min^{-1} for the duration of each enclosure study. A 0.31 cm o.d. Teflon sample line extended from the branch enclosure to an automated adsorbent cartridge sampler (Helmig et al., 2004). A flow rate of 800 mL min^{-1} was extracted from the enclosure, of which 200 mL min^{-1} was directed to the sampler.

Branch enclosures were allowed 24 h after installation to equilibrate before sampling commenced. Analyses of data collected on sequential diurnal cycles showed reproducible short term temperature (or light/temperature) dependency of monitored emissions. This finding provides confidence that the multi-day bag enclosures were not impairing the sampled trees. Each tree specimen was sampled once per month. 10–20 Adsorbent cartridge samples were collected over a 2 or 3 d period to capture multiple diurnal emission cycles. Biomass dry weight was estimated by measuring the length of each needle cohort (to ~0.5 cm accuracy) and respective needle dimension, noting the age of the cohort per sample period. A similar method was applied to leaf foliage species, noting leaf area growth. Leaves and needles were not collected from the sample branch to reduce risk of injuring the plant, which might adversely affect emissions. An equivalent amount of needles and leaves were collected from other, same species trees in the nursery for determination of a biomass dry weight estimate of each enclosure experiment. Each sampled limb was cut at the end of the sampling season for final dry-weight measurements.

Temperature was monitored both within and outside of the enclosure using fine gauge type K thermocouples (TC) (Omega Engineering). Within the enclosure, two TC were physically attached to the foliage while a third TC measured the ambient air temperature. Photosynthetically active radiation (PAR) was measured at a central location common to all sample trees. Relative humidity and ozone were monitored within the enclosure for control purposes. Leaf temperature was not recorded for a limited number of samples collected in July due to a sensor failure. For these samples, normalized emission rate data were estimated using temperature data collected from a nearby meteorological station. These data were adjusted to compensate for the expected differences between ambient and leaf temperature based on previous measurements.

BVOC emissions were collected onto adsorbent cartridges made in house (9 cm long, 0.64 cm o.d. glass tubes, packed with 0.126 g Tenax GR and 0.145 g Carboxen 1016 solid adsorbent (Sigma-Aldrich)). Samples were stored in a freezer within sealed glass jars for a maximum period of 2 weeks before analysis. Sample cartridges were analyzed by a thermal desorption (Perkin-Elmer ATD400) gas chromatography – flame ionization/mass spectrometry (GC-FID/MS) instrument (Hewlet-Packard 5890/5970) following methods described in Helmig et al. (2004). Chromato-

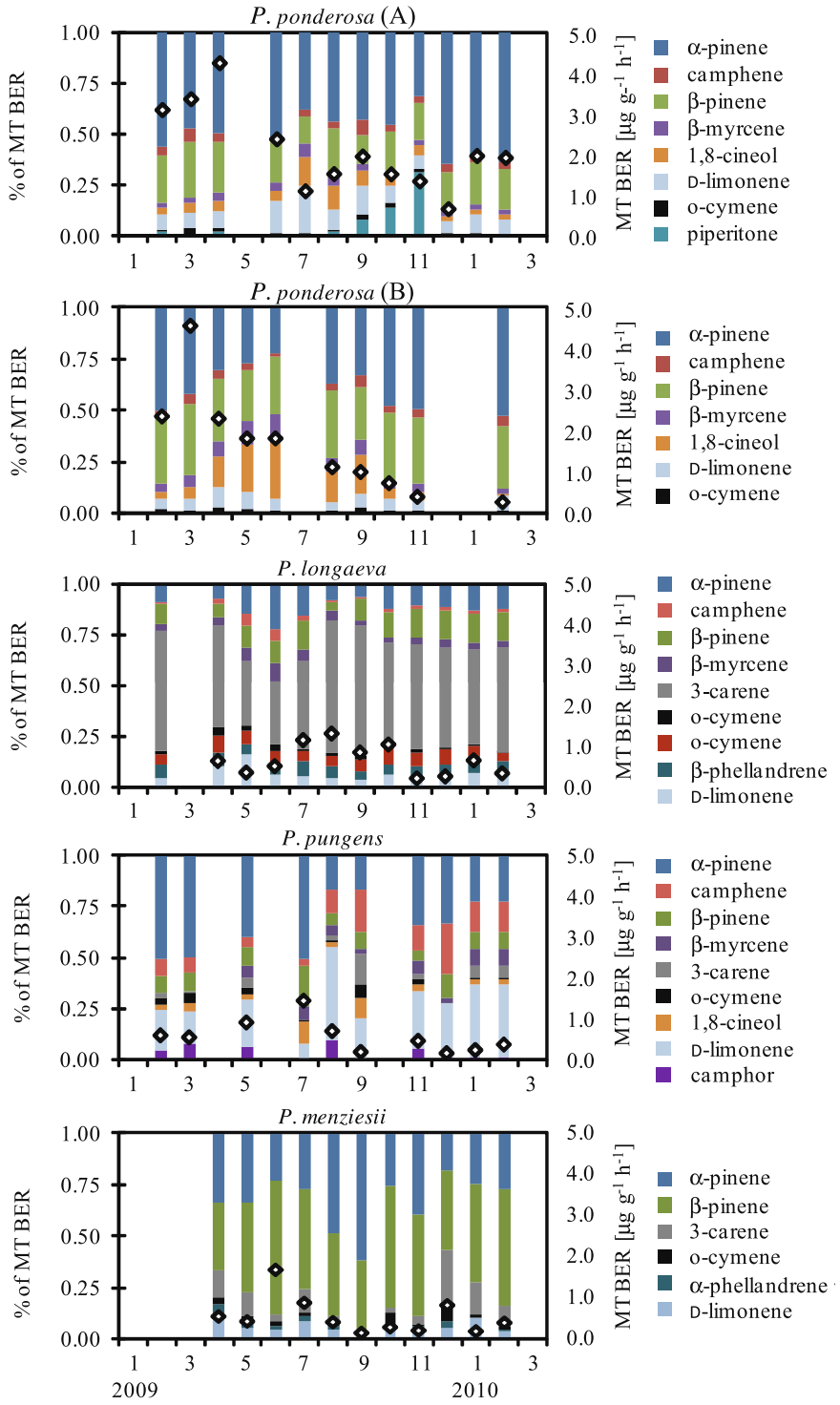

Fig. 1. Monthly averaged BER (open diamond symbols, right axis scale) and the fractional contribution to the total BVOC BER (vertical bars, left axis scale). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

grams were manually integrated for MT, oxy-MT, and SQT. BVOC compounds were identified using authentic standards where possible, and tentatively by comparison of retention index (RI) (Adams, 1989) and mass spectra library match using the NIST MS Search v.2.0 library.

Raw emission rates (ER) were normalized to temperature (30 °C) or light-and-temperature (1000 µmol m^{-2} s^{-1} PAR and 30 °C) to obtain BER (Guenther et al., 1995). Temperature dependence of emissions, per compound as well as total MT and SQT, were examined by evaluating the empirically derived value β (K^{-1}), following Eq. (1) (Guenther et al., 1993)

$$ER = BER_{ST} \cdot e^{(\beta(T-T_{ST}))} \quad (1)$$

where ER is the measured emission rate at temperature T (K) and BER_{ST} is the basal emission rate at a standard temperature T_{ST} (303 K).

Few studies to date have examined the application of an additional correction factor to compensate for seasonal emission

Table 1
BVOC BER data summary, listed by vegetation specimen in order of sample date.

Sample Dates	Total # of samples analyzed	# of samples in which BVOC where identified		# of compounds per BVOC class		Temperature range		Total MT BER	MT β	*MT* R^2	Total SQT BER	SQT β	SQT R^2	Observed SQT: MT Ratio	(T / PAR) for SQT: MT Ratio
		MT	SQT	MT	SQT	T_{min} (°C)	T_{max} (°C)	($\mu g\ g^{-1}h^{-1}$)	(K)		($\mu g\ g^{-1}h^{-1}$)	(K)			(°C/μmol $m^{-2}\ s^{-1}$)
P. ponderosa (A)															
February 27–28, '09	6	6	4	7	3	−8	19	3.15	0.10	0.83	–			0.04	(20/1000)
March 16−18, '09	12	12	2	7	6	5	32	3.41	0.11	0.91	–			0.04	(27/350)
April 6–8, '09	20	20	4	8	2	−1	30	6.03	0.11	0.10	0.07	0.03	0.13	0.01	(30/1600)
April 25–26, '09	10	10	–	7	–	8	11	2.58	0.11	0.19	–			–	
June 9–10, '09	10	10	3	7	1	9	27	3.11	0.10	0.94	–			0.01	(27/700)
June 20–21, '09	10	10	3	7	1	13	24	1.71	0.14	0.64	–			0.03	–
July 11–12, '09	10	10	4	7	3	18	36	1.14	0.10	0.62	–			0.02	–
August 8–9, '09	10	10	–	7	–	17	35	1.10	0.13	0.78	–			–	
August 19–21, '09	18	18	4	8	1	11	31	1.96	0.13	0.79	–			0.01	(31/1650)
September 16–17, '09	16	16	1	8	1	10	24	2.00	0.11	0.79	–			0.01	(24/350)
October 16–17, '09	8	8	3	8	2	0	32	1.19	0.08	0.84	–			0.02	(31/1050)
October 30–31, '09	9	9	4	8	1	−7	24	1.92	0.14	0.71	–			<0.01	(20/1000)
November 6–10, '09	20	20	10	8	1	0	31	1.38	0.13	0.94	0.01	0.08	0.69	0.01	(31/1050)
December 21–24, '09	20	20	3	8	1	−4	21	0.70	0.10	0.71	–			0.01	(21/600)
January 11–13,'10	16	16	3	7	1	−6	27	2.01	0.13	0.92	–			0.01	(23/850)
February 6–10,'10	20	20	2	7	1	−13	12	1.96	0.12	0.95	–			0.01	(12/1150)
P. ponderosa (B)															
February 20–22, '09	19	19	4	7	1	−9	19	2.38	0.14	0.94	0.10	0.15	0.77	0.04	(19/900)
March 6–8, '09	9	9	–	7	–	2	15	4.59	0.18	0.93	–			–	
April 15–16, '09	5	5	1	7	1	6	26	2.32	0.15	0.94	–			0.02	(26/650)
May 27–28, '09	6	6	5	7	1	9	26	1.84	0.09	0.81	0.03	0.09	0.54	0.03	(25/1000)
June 29–30, '09	8	8	3	7	1	18	35	1.84	0.15	0.83	–			0.01	
August 21–24, '09	17	17	3	7	1	11	35	1.14	0.08	0.76	–			0.01	(35/1500)
September 15–17, '09	26	26	–	7	–	12	35	1.02	0.11	0.83	–	–			
October 16–20, '09	20	20	7	7	1	0	30	0.75	0.11	0.81	0.03	0.11	0.74	0.03	(29/1200)
November 12–14, '09	20	20	3	7	1	2	33	0.41	0.08	0.91	–			0.03	(33/1000)
February 6–10,'10	20	18	–	7	–	−13	12	0.28	0.11	0.68	–			–	
P. longaeva															
February 23–25, '09	17	17	3	12	1	2	31	7.41[a]	0.23	0.88	–			<0.01	(28/800)
April 22–24, '09	10	10	–	12	–	6	37	0.62	0.09	0.90	–			–	
May 9–10, '09	10	10	–	12	–	11	26	0.34	0.09	0.78	–			–	
June 6–7, '09	10	10	–	12	–	10	26	0.74	0.12	0.53	–			–	
June 18–19, '09	10	10	–	12	–	10	26	0.59	0.13	0.89	–			–	
June 27–28, '09	10	10	–	12	–	15	36	0.16	0.07	0.54	–			–	
July 7–8, '09	6	6	5	13	1	14	28	1.51	0.13	0.83	0.01	0.07	0.61	0.01	(28/1450)
July 16–17, '09	10	10	2	13	1	20	39	0.77	0.11	0.71	–			<0.01	(37/–)
August 19–21, '09	17	17	–	10	–	11	31	1.15	0.08	0.56	–			–	
August 26–27, '09	11	11	5	13	1	11	40	1.46	0.07	0.72	0.07	0.10	0.81	<0.01	(40/1600)
September 29–30, '09	10	10	2	13	1	10	39	0.84	0.15	0.98	–			<0.01	(39/1200)
October 30–31, '09	10	10	–	12	–	−7	21	1.03	0.16	0.97	–			–	
November 6–10, '09	10	10	3	12	1	9	33	0.28	0.12	0.94	–			0.01	(32/1000)
November 17–19, '09	8	8	2	12	1	−1	24	0.11	0.06	0.35	–			0.02	(24/900)
December 15–15, '09	10	8	–	10	–	−5	17	0.25	0.10	0.88	–	–			
January 28–30,'10	20	16	–	11	–	−6	18	0.64	0.12	0.92	–			–	
February 2–4,'10	17	16	–	10	–	−5	21	0.42	0.12	0.93	–	–			
February 16–17,'10	10	10	–	9	–	−10	18	0.22	0.08	0.82	–	–			

P. pungens															
February 16–18, '09	20	18	–	7	–	0	29	0.76	0.15	0.77	–			–	
February 25–27, '09	19	17	–	7	–	−3	36	0.44	0.09	0.75	–			–	
March 4–6, '09	19	16	–	8	–	0	34	0.55	0.13	0.88	–			–	
March 25–26, '09	8	8	–	7	–	2	9	3.48[b]	0.10	0.44	–			–	
April 17–19, '09	19	4	–	4	–	3	12	<0.10	–		–			–	
May 7–8, '09	9	9	–	9	–	11	36	0.96	0.11	0.88	–			–	
May 29–30, '09	10	10	–	9	–	9	36	0.87	0.11	0.76	–			–	
July 2–3, '09	10	10	5	8	1	14	31	1.45	0.12	0.89	0.01	0.12	0.81	0.01	(31/–)
August 11–12, '09	16	16	–	7	–	11	45	0.75	0.05	0.64	–			–	
August 21–24, '09	15	15	–	7	–	12	34	0.66	0.15	0.86	–			–	
September 2–13, '09	5	5	–	7	–	14	26	0.19	0.02	0.45	–			–	
November 11–14, '09	20	19	–	9	–	2	31	0.46	0.13	0.93	–			–	
December 3–5, '09	10	10	–	6	–	−17	7	0.16	0.06	0.83	–			–	
January 17–20,'10	17	17	–	8	–	−4	17	0.24	0.08	0.85	–			–	
February 11–13,'10	20	20	–	–	–	−8	25	0.38	0.07	0.64	–			–	
P. menziesii															
April 20–22, '09	18	18	–	9	–	6	39	0.52	0.08	0.93	–			–	
May 12–13, '09	10	10	–	9	–	10	43	0.33	0.10	0.91	–			–	
May 19–20, '09	9	9	–	9	–	15	44	0.47	0.09	0.94	–			–	
June 13–14, '09	4	4	–	7	–	11	29	2.51	0.08	0.79	–			–	
June 25–26, '09	10	10	–	9	–	18	33	0.80	0.08	0.54	–			–	
July 8–9, '09	5	5	–	8	–	13	26	1.03	0.13	0.77	–			–	
July 14–15, '09	9	9	–	9	–	14	37	0.68	0.12	0.70	–			–	
August 11–14, '09	18	18	–	9	–	11	45	0.67	0.00	0.69	–			–	
August 24–25, '09	18	18	–	4	–	12	35	0.09	0.04	0.10	–			–	
September 15–18, '09	30	28	–	4	–	12	35	0.12	0.05	0.44	–			–	
October 22–24, '09	10	10	–	5	–	3	24	0.26	0.08	0.94	–			–	
November 17–20, '09	20	20	–	6	–	−3	28	0.18	0.06	0.85	–			–	
December 10–13, '09	20	11	–	6	–	−16	24	0.79	0.12	0.87	–			–	
January 22–26,'10	29	26	–	5	–	−7	30	0.16	0.07	0.60	–			–	
February 11–14,'10	19	19	–	6	–	−8	27	0.37	0.08	0.96	–			–	
Q. gambelii															
July 2–3, '09	10	–	5	–	1	14	28	–			0.35	0.19	0.81	–	
August 15–16, '09	10	–	6	–	1	15	25	–			0.33	0.14	0.31	–	
August 26–27, '09	14	–	9	–	1	11	37	–			0.45	0.14	0.69	–	
September 23–24, '09	12	–	–	–	–	9	15	–			–			–	
September 25–26, '09	10	–	3	–	1	7	25	–			1.17	0.26	1.00	–	
September 27–29, '09	20	–	9	–	1	4	25	–			0.78	0.18	0.75	–	
October 7–9, '09	17	–	9	–	1	4	31	–			0.07	0.09	0.84	–	
October 13–16, '09	19	–	9	–	1	4	33	–			0.01	0.05	0.70	–	
B. occidentalis															
August 14–October 15, '09	107	–	–	–	–			–			–			–	

[a,b] Considered outlier values based on irregular sampling conditions, as discussed in Section 3.1.

Table 2
Seasonally averaged MT basal emission rates (BER) reported with respect to BVOC speciation (%) and BER for the most prevalent compounds. Seasons are defined by month listed in brackets (i.e. 'Summer [JJA]' represents averaged data between June, July and August).

Compound name	Winter '09 [F]		Spring '09 [MAM]		Summer '09 [JJA]		Fall '09 [SON]		Winter '10 [DJF]	
	%	BER ($\mu g\ g^{-1}\ h^{-1}$)	%	BER ($\mu g\ g^{-1}\ h^{-1}$)	%	BER ($\mu g\ g^{-1}\ h^{-1}$)	%	BER ($\mu g\ g^{-1}\ h^{-1}$)	%	BER ($\mu g\ g^{-1}\ h^{-1}$)
P. ponderosa (A)										
α-Pinene	56	1.60	49	2.05	46	0.96	42	0.48	63	1.01
Camphene	4	0.10	5	0.10	3	0.05	4	0.04	4	0.03
β-Pinene	23	0.54	26	0.99	20	0.33	18	0.26	20	0.36
β-Mycrene	3	0.10	4	0.07	5	0.09	3	0.05	3	0.03
1,8-Cineol	3	0.06	5	0.55	9	0.21	5	0.12	3	0.04
D-limonene	7	0.15	8	0.20	15	0.19	10	0.19	7	0.07
piperitone	2	<0.01	1	0.51	1	0.37	17	0.68	–	–
Total MT		2.54		4.47		2.21		1.82		1.53
P. ponderosa (B)										
α-Pinene	50	1.04	33	0.75	29	0.36	43	0.29	53	0.19
Camphene	4	0.04	4	0.04	3	0.03	4	0.02	5	<0.01
β-Pinene	32	0.86	30	1.13	30	0.42	31	0.21	30	0.07
β-Mycrene	3	0.03	8	0.19	10	0.13	5	0.04	2	0.01
1,8-Cineol	3	0.04	15	0.27	21	0.33	10	0.09	1	<0.01
D-limonene	6	0.05	8	0.06	5	0.08	6	0.04	7	0.01
Piperitone	–	–	–	–	–	–	–	–	–	–
Total MT		2.06		2.44		1.36		0.69		0.27
P. longaeva										
α-Pinene	9	–	11	0.07	15	0.21	10	0.05	12	0.03
Camphene	1	–	4	0.02	3	0.03	2	0.01	2	<0.01
β-Pinene	10	–	9	0.05	10	0.12	12	0.06	14	0.04
β-Mycrene	3	–	5	0.03	7	0.07	3	0.01	3	0.01
3-Carene	59	–	41	0.24	46	0.58	55	0.33	49	0.19
o-Cymene	2	–	3	0.01	2	0.02	2	0.01	–	–
p-Cymene	4	–	7	0.04	5	0.06	7	0.04	6	0.04
β-phellandrene	7	–	6	0.03	6	0.08	5	0.03	6	0.03
D-limonene	4	–	13	0.02	5	0.06	5	0.02	7	0.01
Total MT		–[a]		0.51		1.24		0.56		0.35
P. pungens										
α-Pinene	51	0.28	43	0.31	28	0.28	25	0.13	27	0.05
Camphene	8	0.03	6	0.04	9	0.06	17	0.02	20	0.05
β-Pinene	8	0.04	9	0.07	10	0.11	7	0.02	8	0.01
β-Mycrene	–	–	4	0.04	6	0.08	5	0.01	5	0.03
3-Carene	2	0.02	4	0.03	1	0.01	9	0.01	2	0.01
o-Cymene	3	0.02	4	0.03	1	0.02	4	0.01	1	<0.01
1,8-Cineol	3	0.01	3	0.03	5	0.10	7	0.00	1	<0.01
D-limonene	20	0.09	20	0.17	33	0.26	25	0.07	35	0.11
Camphor	4	0.02	7	0.06	6	0.05	2	0.01	2	0.01
Total MT		0.50		0.79[b]		0.96		0.29		0.27
P. menziesii										
α-Pinene			33	0.13	33	0.23	42	0.05	23	0.07
β-Pinene			40	0.20	51	0.53	49	0.13	48	0.17
3-Carene			12	0.06	6	0.10	2	<0.01	18	0.06
o-Cymene			3	0.14	2	0.02	3	<0.01	4	0.01
α-Phellandrene			4	0.03	2	0.02	–	–	1	0.01
D-limonene			7	0.04	6	0.06	4	0.01	6	0.01
Total MT				0.60		0.96		0.19		0.34

[a] *P. longaeva* MT BER data sampled February 23–25, '09 is considered to be an outlier. Compound speciation is presented for comparison.
[b] *P. pungens* MT BER data sampled March 25–26, '09 is considered to be an outlier.

changes. Staudt et al. (2000) proposed a method of correcting light and temperature normalized BER data to compensate for an observed sinusoidal cycling pattern associated with growing season. Using an additional coefficient, C_S, the method builds on the standard light and temperature BER formulation by characterizing the length of the active emission season, emission amplitude, and timing of peak emissions, illustrated in the following equation:

$$BER_{Season} = BER \cdot C_S \quad (2)$$

$$C_S = 1 - \rho \cdot \left[1 - e^{\left(\frac{(D-D_O)^2}{\tau}\right)}\right] \quad (3)$$

ρ describes the emission amplitude ($BER_{max} - BER_{min}$)/BER_{max} over the growing season, where BER_{max} and BER_{min} are the extremes observed over a season. D is the month of year, D_O is the month in which highest emissions are observed and τ is the length of the active-emitting season in months. Steinbrecher et al. (2009) applied Eqs. (2) and (3) to model seasonal BVOC emissions within Europe and neighboring countries. Keenan et al. (2009) applied an asymmetric exponential function similar to Eq. (3) to estimate seasonal variation in basal emission rates, finding strong correlation between measured and predicted emissions from *Quercus ilex* and *Pinus pinea* with correlation coefficients of $r = 0.83$ and $r = 0.86$, respectively. Pio et al., 2005 used curve fitting software to develop a study specific seasonal BER algorithm.

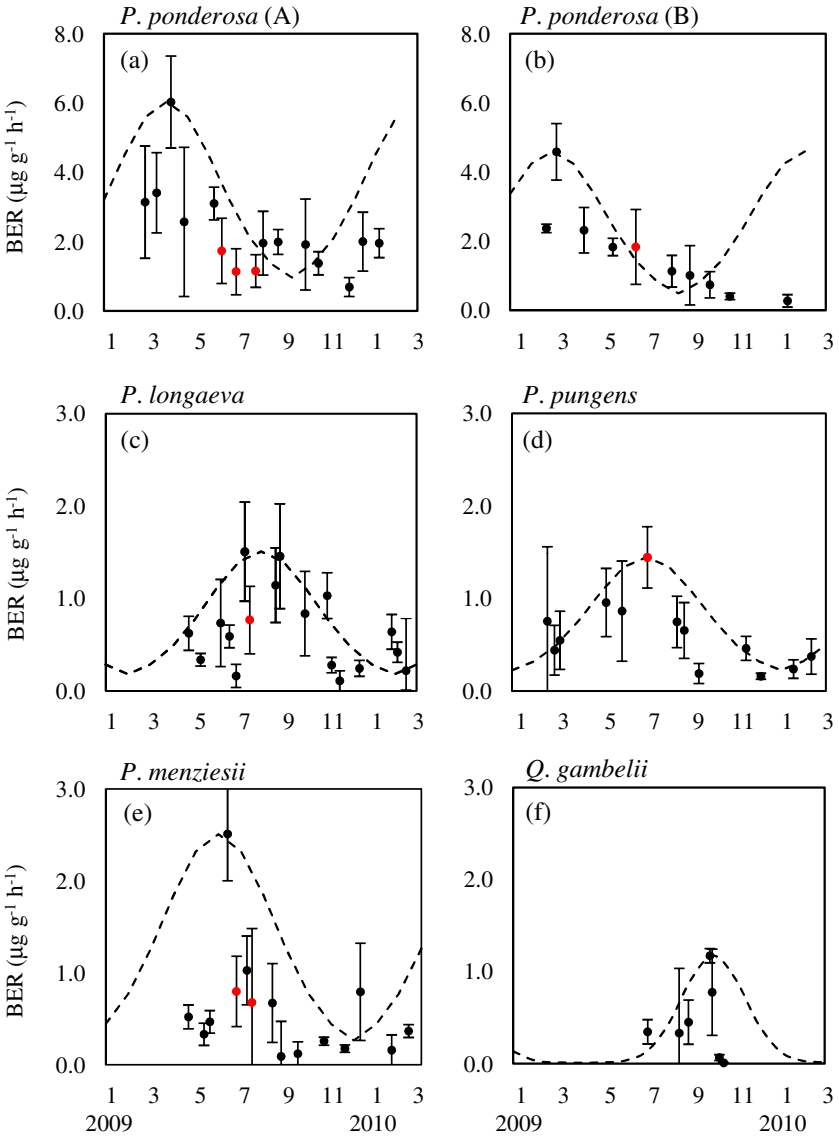

Fig. 2. Measured total MT+SQT BVOC BER (dots) and Modeled BER_{Season} (curve). Red dots indicate BER data calculated using estimated leaf temperature, discussed in Section 2. Error bars express one standard deviation.

3. Results and discussion

3.1. Emission identification and rates

Basal emission rate data per sample tree are listed in Table 1. Included in the table are the number of BVOC compounds observed, leaf temperature range, total MT and SQT BER, as well as the β-factor describing the temperature dependency of total MT and SQT emissions, and corresponding exponential regression statistics for each enclosure experiment. Total compound categories (total MT and SQT) refer to the sum of individual compound emissions per compound class. Identified oxygenated MT were included in the total MT emissions. The coniferous species were strong MT emitters; SQT emissions were much lower, found near or below the detection limit of the experiment. Due to limited SQT observations, the SQT BER could often not be calculated. Instead, the ratios of the raw emission rate of SQT to MT are listed along with the temperature and light levels at which emissions were observed.

The sample trees exhibited a pronounced response to short-term diel temperature cycling. MT and SQT were found to be solely temperature dependent. Emissions of the oxygenated MT 1,8-cineol (*P. ponderosa* and *P. pungens*) and piperitone (*P. pungens*) were light and temperature dependent.

Table 2 summarizes emission data with regard to seasonally averaged BER and speciation of the dominant BVOC compounds. The study period was divided into quarters using the following definition: Winter '09 (February '09), Spring '09 (March, April and May '09), Summer '09, (June, July and August '09), Fall '09 (September, October and November '09) and Winter '10 (December '09, January and February '10).

P. ponderosa was the highest MT emitter, total MT BER peaked in early spring at rates as high as 6.0 and 4.6 μg g^{-1} h^{-1} for plants A and B, respectively (Table 1). The MT signal was dominated by α- and β-pinene. Combined, they contributed 59–83% of the BVOC total emission. The oxygenated MT 1,8-cineol fluctuated in emission intensity with season varying between 1% and 21% of the total

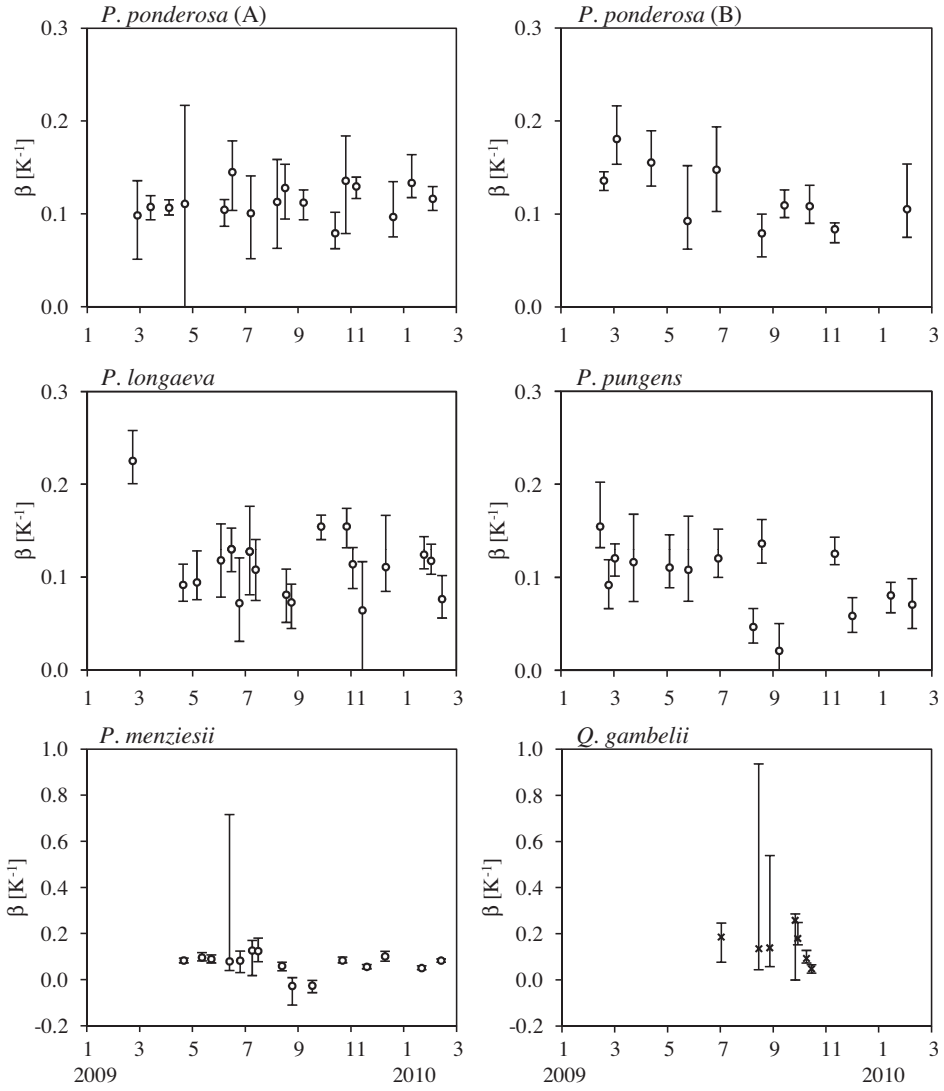

Fig. 3. BER temperature correction factor β, of total MT (circle) and the SQT germacrene B (*x*-mark) are shown with respect to sample date. Error bars indicate a 90% confidence interval. Please note the change in *y*-axis scale between plots.

BVOC BER in winter and summer, respectively (Table 2). *P. ponderosa* was observed to emit six SQT. Three SQT were positively identified as β-bourbonene, β-caryophyllene and γ-muurolene. β-caryophyllene accounted for 80% of the SQT emission. Total SQT BER ranged between <0.01–0.10 μg g^{-1} h^{-1}, 1.1% of the total BVOC emission, peaking in spring (Table 1).

Table 1 reports two extraneous BER measurements from *P. longaeva* and *P. pungens*. In the first instance *P. longaeva* samples collected between February 23–25, 2009, produced a high BER of 7.4 μg g^{-1} h^{-1}, likely a stress response resulting from overheating within the bag enclosure due to an extended power failure. In another instance an abnormally high total MT BER of 3.5 μg g^{-1} h^{-1} was measured in March from *P. pungens,* which may be attributed to a narrow enclosure temperature range, 2–9 °C, resulting in poor temperature-based BER extrapolation (R^2 = 0.44). Outlier data are presented in Table 1 to illustrate these findings. However, both data points are excluded from all datasets and discussion herein. *P. longaeva* and *P. pungens* emission rates peaked during the summer months with total MT BER of 1.24 and 0.96 μg g^{-1} h^{-1}, respectively (Table 2). Low seasonal total MT BER were observed in winter at 0.35 and 0.27 μg g^{-1} h^{-1} for *P. longaeva* and *P. pungens*, respectively (Table 2). Several instances of low total MT BER were observed from both *P. longaeva* and *P. pungen* enclosure samples through the study period. For *P. longaeva*, low total MT BER were observed in June (0.16 μg g^{-1} h^{-1}) in addition to winter months. For *P. pungens*, low total MT BER of less than 0.20 μg g^{-1} h^{-1} were measured in April, September and December (Table 1). 3-carene was the dominant MT emission from *P. longaeva*, contributing 41–59% of the total BVOC emission (Table 2). α-Pinene (25–51%) and D-limonene (17–35%) were the most significant emissions from *P. pungens*. SQT were found in a limited number of enclosure experiments. Total SQT BER ranged between <0.01–0.07 μg g^{-1} h^{-1} (4.8% of total BVOC) for *P. longaeva*, and <0.01 μg g^{-1} h^{-1} (<1.0% of total BVOC) for *P. pungens* (Table 1). Low levels of β-caryophyllene and the tentatively identified saturated C_{15} hydrocarbon farnesane were observed from *P. pungens*. α-Copaene was the only quantifiable SQT observed from *P. longaeva*.

P. menziesii BVOC emissions were greatest in mid June with total MT BER of 2.5 μg g^{-1} h^{-1}. Low total MT BER of 0.09 and 0.16 μg g^{-1} h^{-1} were observed in August 2009 and January 2010, respectively (Table 1). A high BER of 0.79 μg g^{-1} h^{-1} in December 2009, four times higher than rates observed in November 2009 and January 2010, may be an unusual response caused by sustained cold temperatures (mean daily temperatures ranging between −15 °C to −2 °C, December 2 through December 11, 2009) followed by rapid warming (up to 24 °C within the enclosure on

Table 3
Study averaged β-factor and statistics from the multiple experiment results of the top three emitted compounds per sample tree. 'Total MT' represents the weighted average of all monoterpenes observed.

	Total MT	α-Pinene	Camphene	β-Pinene	3-Carene	1,8-Cineol	D-Limonene	Germacrene B
P. ponderosa (A)								
Mean	0.11	0.10		0.10		0.12		
Std Dev	0.03	0.03		0.03		0.05		
Median	0.11	0.10		0.11		0.12		
min	0.02	0.02		0.01		0.01		
max	0.14	0.14		0.14		0.21		
P. ponderosa (B)								
Mean	0.10	0.11		0.14		0.12		
Std Dev	0.03	0.04		0.07		0.03		
Median	0.11	0.10		0.14		0.11		
min	0.04	0.08		0.05		0.08		
max	0.16	0.20		0.26		0.18		
P. longaeva								
Mean	0.11	0.05		0.10	0.11			
Std Dev	0.06	0.19		0.05	0.04			
Median	0.10	0.10		0.12	0.11			
min	0.02	0.00		0.00	0.06			
max	0.28	0.00		0.21	0.23			
P. pungens								
Mean	0.10	0.11	0.06				0.08	
Std Dev	0.04	0.04	0.03				0.03	
Median	0.10	0.12	0.07				0.09	
min	0.02	0.04	0.03				0.02	
max	0.15	0.17	0.09				0.15	
P. menziesii								
Mean	0.08	0.08	0.08		0.09			
Std Dev	0.03	0.04	0.02		0.05			
Median	0.08	0.08	0.08		0.08			
min	0.04	0.01	0.04		0.03			
max	0.13	0.16	0.13		0.19			
Q. gambelii								
Mean								0.13
Std Dev								0.08
Median								0.14
min								0.05
max								0.26

December 12, 2009), which potentially resulted in accumulation of a pool of BVOC and subsequent enhanced BVOC volatilization. The most prominent MT emissions were α- and β-pinene, producing 23–42% and 40–51% of the total MT emission, respectively (Table 2). No SQT were observed.

Q. gambelii was acquired late into the growing season and had fully developed foliage by the time sampling commenced in July. The SQT germacrene B was the only detectable BVOC emission, with BER ranging between <0.01–1.17 μg g^{-1} h^{-1} (Table 1). Normalized emissions peaked late in the growing season, immediately preceding foliage senescence. *B. occidentalis* was only monitored between August and October; no MT or SQT emissions were detected.

3.2. Comparison of SQT results

In a previous study SQT BER from several pine trees were 16% of the total MT emission (Helmig et al., 2007). Some pines, such as *P. taeda*, *P. ponderosa*, and *P. virginiana* have been measured to emit SQT at levels equal to or greater than MT (Helmig et al., 2006; Bouvier-Brown et al., 2009; Geron and Arnts, 2010). In this study SQT were scarcely observed from all four pine species despite low instrument detection limits of 50 pptv for SQT. Total SQT BER of the *P. ponderosa* studied here ranged between <0.01–0.07 μg g^{-1} - h^{-1}, up to 4% of the total MT emission, significantly less than the 16% reported in our earlier work (Helmig et al., 2007). Kim et al. (2010) also found lower BER, between 0.006 and 0.034 μg g^{-1} h^{-1}, 1% of the total MT signal, using a PTR-MS at a Ponderosa woodland in southern Colorado. Baker and Sinnott (2009) and Bouvier-Brown et al. (2009) studied *P. ponderosa* in the Sierra Nevada Mountains, CA, finding BER of up to 0.21 μg g^{-1} h^{-1}, 20–200% of the total MT signal. Additionally, they reported a different set of dominant SQT compounds, comprised of α- and β-farnesene, and α-bergamotene. These results indicate that the ratio of SQT to MT can vary significantly, even for a single species.

β-Caryophyllene BER of *P. pungens* varied between <0.01–0.15 μg g^{-1} h^{-1}, 1% of the measured total MT emission signal. Ortega et al. (2008) found maximum SQT BER of 0.04 μg g^{-1} h^{-1}, a value lower than reported here, however, the SQT emission from this species is more significant in comparison to the MT emission signal with a fraction of 20% of the measured total MT BER. α-Copaene was the only identified SQT emitted from *P. longaeva*, with peak BER of 0.07 μg g^{-1} h^{-1}, 2% of the total MT emission. No SQT were identified in the emissions from *P. menziesii*. *Q. gambelii* was the largest SQT emitter, BER of germacrene B varied between <0.01–1.17 μg g^{-1} h^{-1}. Due to the limited seasonal SQT emissions data obtained in this study, no inferences could be made about the SQT BER seasonal behavior.

3.3. Seasonal patterns

Monthly averaged total BVOC BER and the compound speciation that make up the total emission signal are shown in Fig. 1. Despite normalization to light and temperature, BVOC basal emission rates were found to fluctuate throughout the one-year study period. BER results were varied among species studies, but in general were higher from the early spring to late summer months, falling to lower rates in the winter.

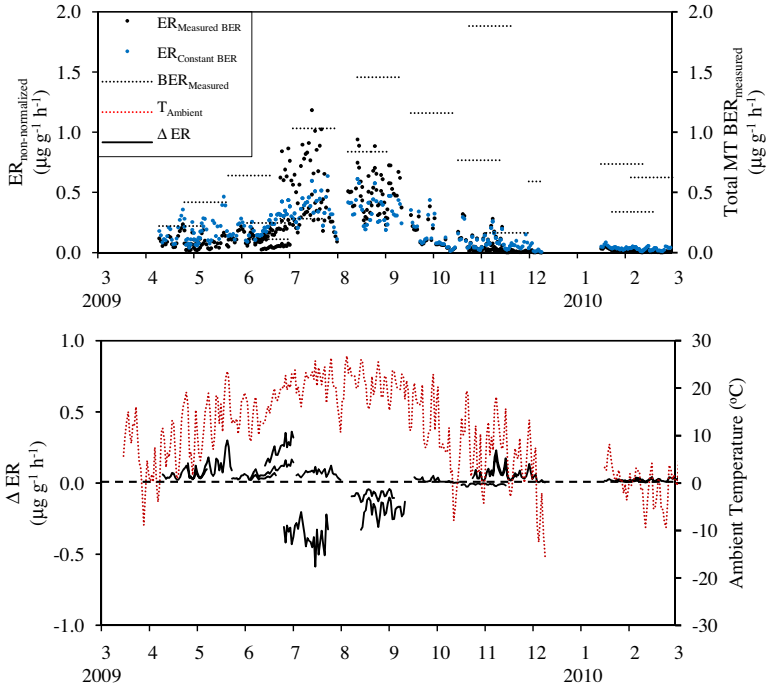

Fig. 4. Emission rates were modeled for two-weeks windows bracketing experimental data. For case 1, emission rates ($ER_{constant\_BER}$) (left axis) were calculated applying a summer-averaged constant BER of 0.94 μg g^{-1} h^{-1} (blue dots) year-round. These results are compared with model results applying the determined seasonal BER ($ER_{Measured\ BER}$) during each 2-week period (black dots). Measured BER are indicated as horizontal dotted black lines (right axis scale) for each ± 2-week time interval surrounding the respective enclosure period. The ambient temperature record (red) and the difference between the two case scenarios, $ER_{measuredBER} - ER_{constantBER}$ (black data), are shown in the bottom graph. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

P. ponderosa BER peaked in the spring coinciding with bud break and needle expansion. High rates of 6.0 and 4.6 μg g^{-1} h^{-1} were observed in early spring for test trees A and B, respectively. Geron and Arnts (2010) and Kim (2001) report similar emission enhancement at bud break and needle growth of *Pinus taeda* and *Pinus elliottii*. Seasonal lows were observed in winter at total MT BER of 0.70 and 0.28 μg g^{-1} h^{-1}, respectively. *P. longaeva* produced heightened emission rates during summer months. While less pronounced, *P. pungens* and *P. menziesii* also appear to emit at slightly elevated rates during summer months than in winter. *P. longaeva*, *P. pungens* and *P. menziesii* did not reflect the elevated emission rates at bud break as observed with *P. ponderosa*. SQT emission rates from *Q.* gambelii were found at higher levels immediately preceding leaf senescence than during the rest of the measurement season. Elevated MT emissions prior to litterfall were also observed by Geron and Arnts (2010) for *Pinus taeda* and *Pinus virginiana*.

Compound speciated emissions were found to vary with time of year. Some compounds, such as α and β-pinene observed from *P. ponderosa* A & B, *P. longaeva* and *P. pungens*, were emitted consistently and at a constant rate relative to each other throughout the study period. In contrast, the emission strength of 1,8-cineol, piperitone, 3-carene, and D-limonene varied more dramatically, with irregular or sporadic presence relative to other compounds, with respect to the time of season. 1,8-Cineol was a prominent emission of *P. ponderosa* B during summer months falling to lows through the winter, in agreement with observations by Holzke et al. (2006). 3-carene, the strongest emission of *P. longaeva,* decreased in strength in early summer relative to the total emission. Fluctuations in emission speciation with growth season have been reported by several others. These available data suggest that the variation may be tree or tree species dependent rather than displaying a common trend (Llusia and Peñuelas, 2000; Hakola et al., 2001; Rivoal et al., 2010).

3.4. Application of a seasonal emission correction factor

Staudt et al. (2000) proposed a method of correcting the light and temperature normalized BER for the seasonal changes in BER. The BER determined in our seasonal experiments, as reported in Table 1, are plotted in Fig. 2 with respect to sampling date and are overlaid with a curve projecting the seasonally corrected basal emission rate, BER_{Season}, following the method outlined in Section 2. Fitting results for the seasonal curve parameters (D_o = timing of BER_{max} and τ = length of growing season) defining the seasonal correction term, C_S, (Eq. (2)) and regression statistics between BER and BER_{Season} (r = Pearson's correlation coefficient) are (a) *P. ponderosa* (A) $D_o = 4$, $\tau = 12$, $r = 0.68$; (b) *P. ponderosa* (B) $D_o = 3$, $\tau = 12$, $r = 0.50$; (c) *P. longaeva* $D_o = 8$, $\tau = 12$, $r = 0.53$; (d) *P. pungens* $D_o = 6$, $\tau = 12$, $r = 0.72$; (e) *P. menziesii* $D_o = 6$, $\tau = 12$, $r = 0.45$; (f) *Q. gambelii* $D_o = 9$, $\tau = 4$, $r = 0.21$.

Unlike the strong correlation ($r = 0.83$ and 0.86) between measured and modeled emissions from *Quercus ilex* and *Pinus pinea* reported by Keenan et al. (2009), a more moderate correlation was found between measured BER and modeled BER_{Season} in our data. *P. ponderosa* (A) and *P. pungens* displayed the strongest correlation with Pearson's regression coefficient, $r = 0.68$, and $r = 0.72$, respectively. Observed BER rates of *P. menziesii* demonstrated a similar profile to the predicted BER_{Season}; however, inclusion of the abnormally high BER_{max} of 2.5 μg g^{-1} h^{-1} that was determined in one experiment in June causes an apparent overestimation of the seasonal emission. The BER_{Season} curve poorly characterizes the observed BER of *P. ponderosa* and *Q. gambelii*. Due to the late season BER burst of *Q. gambelii*, the BER_{Season} curve over-predicts the integrated, all-year SQT emission by a factor of two, misinterpreting the timing of the growth season. Observed BER of *P. ponderosa* had not begun to rise by the end of the sample season in 2010 as the BER_{Season} projected, resulting in poor correlation and

overestimation of the all-year MT emission. The cases of *P. ponderosa* (B), *P. menziesii* and *Q. gambelii* demonstrate that inclusion of the seasonal correction term may run the risk of overestimating all-year total MT emissions by a substantial margin.

3.5. Seasonal variation of the temperature correction factor β

The β-factor, an empirical parameter used to describe the slope of the exponential regression of observed ER with leaf temperature, was investigated for possible seasonal characteristics. The results for the empirically determined β-factor are shown in Fig. 3 for the total MT, and for the SQT germacrene emitted from Gamble Oak. Results for individual MT are depicted in Supplemental materials Fig. S2. Error bars indicate a 90% confidence interval generated using the bootstrapping technique, a method of measuring the precision of an estimator. A histogram display of the bootstrapping results for the β-factor confidence interval determination of MT emissions from *P. ponderosa* A is shown in Supplementary materials Fig. S3. Table 3 lists a summary of study-wide averaged β-factor results. No discernible seasonal trends were identified in β over the one-year study period. Determined β-factor results are scattered around a nominal value unique to the BVOC compound and vegetation species. Averaged β-factors were found to range between 0.06 and 0.14 K^{-1} for individual MT. The average MT β-factor of all data was between 0.10–0.11 K^{-1} for all vegetation except *P. menziesii*, which had a value of 0.08 K^{-1}. These findings agree with the value (0.1 K^{-1}) used by Guenther et al. (2012), which is slightly higher than the value of 0.09 K^{-1} suggested by Guenther et al. (1993) earlier for estimating temperature-dependent MT emissions. *Q. gambelii* SQT emissions generated a β of 0.14 K^{-1}. Ortega et al. (2008) reported β-factors in the range of 0.12–0.17 K^{-1} for MT and 0.15–0.21 K^{-1} for SQT.

3.6. Seasonal emission rate sensitivity

A sensitivity analysis was performed to investigate the difference in modeled emission rates using a generic, constant year-round BER versus a seasonally determined emission rate. Data collected from *P. longaeva* were used here to model emission rates throughout a one-year period. ER were calculated according to Eq. (1) for two cases. For case 1, a BER rate determined from the summer season measurements, i.e. an averaged BER of 0.94 μg g^{-1} h^{-1}, was used to proxy results from a short-term emission rate study, as commonly found in the literature. As the alternative, the seasonally changing BER data listed in Table 1 were used to model the seasonal change in emissions, termed case 2. For each case, a one-year ambient air temperature record from a nearby meteorological station was used to back-calculate ER. A β-factor of 0.11 K^{-1} was applied to both cases. Hourly ER estimates were calculated for two weeks before and after each enclosure study for case 2. The results for both scenarios are shown in Fig. 4.

Case 1, using the constant BER, estimates suppressed emission rates between June and October and elevated rates through fall, winter and spring relative to case 2. Case 2 predicts a strong, focused emission burst during the summer months, reaching daytime maximum ER in July of 1.20 μg g^{-1} h^{-1}, falling to below 0.3 μg g^{-1} - h^{-1} between October and May. Case 1 predicts maximum ER of 0.6 μg g^{-1} h^{-1} in August with more modest emission rates through the spring and fall months. The relative difference between both scenarios is on the order of 50% during several periods throughout the year. It should also be noted that day-to-day summer season fluctuations are greater in case 2 than in case 1 while the reverse is true through the winter period. Annually integrated MT ER were found to be approximately equal between the cases, however, the timing and magnitude of expected emissions is obviously misrepresented if the seasonal changes in BER are neglected (case 1).

4. Summary and conclusion

MT were the dominant BVOC emitted from the four coniferous tree species studied. The SQT germacrene B was found to be the dominant emission from *Q. gambelii*. It should be noted that the analytical system was tuned for MT and SQT, consequently not all potential BVOC were detected by these measurements. Normalized BER were found to vary throughout the one-year study, with highest BER observed in spring and summer months, measured at a level of two to eight times greater than emission levels observed in the fall or winter seasons. The fractional contribution of individual BVOC compounds of the total emissions varied by season. α- and β-pinene were consistently emitted year-round and at a near constant ratio to each other. In contrast, 1,8-cineol, 3-carene, D-limonene, and piperitone varied in seasonal timing and emission strength relative to other emitted compounds. Total SQT emission rates observed from the coniferous species were 1–4% of the total MT signal. These results are in the lower range of several previous studies that report SQT emissions with respect to MT. Factors such as geographical setting, physiological condition and genetic differences may be root causes for these differences. The application of a seasonal correction factor, C_S, according to the algorithm proposed by Staudt et al. (2000) applied to light and temperature-normalized BER gave variable results, with good representation for some species but rather poor description for others. For the data examined here, the calculated seasonal corrections factors appear to be sensitive to isolated high BER results, which led to an overestimation and shifts in the seasonal timing of emissions compared to directly measured emission rates. It is recommended to apply seasonal correction factors only to well-characterized growth season and experimentally determined emission rate data sets from the particular species.

The temperature correction factor β, used for defining temperature dependent behavior in emissions, did not demonstrate any discernible seasonal trends. Rather, variation in the β-factor seems to be scattered around a nominal value, specific to the type of emitted compound and vegetation species. The averaged MT β-value measured in this study was found to be 0.11 K^{-1}. A sensitivity analysis examined two scenarios representative of the use of short-term versus comprehensive long-term emission datasets. Results illustrate deviations of up to~50% in modeled ER, which stresses the importance of incorporating accurate seasonally corrected BER data into model inputs to better account for the timing and magnitude of BVOC emissions during a year's period.

Acknowledgements

Funding was provided by the U.S. National Science Foundation Grant ATM-0608582. We thank the Creekside Tree Nursery (Boulder, CO) for their support and for providing the experimental field site, and T. Mefford of CIRES and NOAA for providing meteorological data. J. Hueber, D. Tanner, C. Borke, and C. Baroch, all at the University of Colorado, assisted with experimental work, and C. Geron, US EPA Research Triangle Park, NC, provided comments on the manuscript. This study does not necessarily reflect the views of the funding agencies, and no official endorsements should be inferred.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.04.058.

References

Adams, R.P., 1989. Identification of Essential Oils by Ion Trap Mass Spectrometry. Academic Press, San Diego.

Baker, B., Sinnott, M., 2009. Analysis of sesquiterpene emissions by plants using solid phase microextraction. J. Chrom. A 1216, 8442–8451. http://dx.doi.org/10.1016/j.chroma.2009.10.002.

Barkley, M.P., Palmer, P.I., De Smedt, I., Karl, T., Guenther, A., Van Roozendael, M., 2009. Regulated large-scale annual shutdown of Amazonian isoprene emissions? Geophys. Res. Lett. 36, L04803. http://dx.doi.org/10.1029/2008GL036843.

Bertin, N., Staudt, M., Hansen, U., Seufert, G., Ciccioli, P., Foster, P., Fugit, J.L., Torres, L., 1997. Diurnal and seasonal course of monoterpene emissions from Quercu Ilex (L.) under natural conditions – application of light and temperature algorithms. Atmos. Environ. 31, 135–144. http://dx.doi.org/10.1016/S1352-2310(97)00080-0.

Bouvier-Brown, N.C., Holzinger, R., Palitzsch, K., Goldstein, A.H., 2009. Large emissions of sesquiterpenes and methyl chavicol quantified from branch enclosure measurements. Atmos. Environ. 43, 389–401. http://dx.doi.org/10.1016/j.atmosenv.2008.08.039.

Duhl, T.R., Helmig, D., Guenther, A., 2008. Sesquiterpene emissions from vegetation: a review. Biogeosciences 5, 761–777. http://dx.doi.org/10.5194/bg-5-761-2008.

Fares, S., Park, J.-H., Gentner, D.R., Weber, R., Ormeño, E., Karlik, J., Goldstein, A.H., 2012. Seasonal cycles of biogenic volatile organic compound fluxes and concentrations in a California citrus orchard. Atmos. Chem. Phys. 12, 9865–9880. http://dx.doi.org/10.5194/acp-12-9865-2012.

Geron, C., Arnts, R., 2010. Seasonal monoterpenes and sesquiterpene emission from Pinus teada and Pinus virginiana. Atmos. Environ. 44, 4240–4251. http://dx.doi.org/10.1016/j.atmosenv.2010.06.054.

Guenther, A.B., Zimmerman, P.R., Harley, P.C., Monson, R.K., Fall, R., 1993. Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses. J. Geophys. Res. 98, 12609–12617. http://dx.doi.org/10.1029/93JD00527.

Guenther, A.B., 1997. Seasonal and spatial variations in natural volatile organic compound emissions. Ecol. Appl. 7, 34–45. http://dx.doi.org/10.1890/1051-0761(1997) 007[0034:SASVIN]2.0.CO;2.

Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W.A., Pierce, T., Scholes, D., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. J. Geophys. Res. 100, 8873–8892. http://dx.doi.org/10.1029/94JD02950.

Guenther, A.B., Jiang, X., Heald, C.L., Sakulyanontvittaya, T., Duhl, T., Emmons, L.K., Wang, X., 2012. The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions. Geosci. Model Dev. Discuss. 5, 1503–1560. http://dx.doi.org/10.5194/gmdd-5-1503-2012.

Hakola, H., Laurila, T., Lindfors, V., Hellén, H., Gaman, A., Rinne, J., 2001. Variation of the VOC emission rates of birch species during the growing season. Boreal Environ. Res. 6, 237–249.

Hakola, H., Hellén, H., Hemmilä, M., Rinne, J., Kulmala, M., 2012. In situ measurments of volatile organic compounds in a boreal forest. Atmos. Chem. Phys. 12, 11665–11678. http://dx.doi.org/10.5194/acp-12-11665-2012.

Helmig, D., Bocquet, F., Pollmann, J., Revermann, T., 2004. Analytical techniques for Sesquiterpene emission rate studies in vegetation enclosure experiments. Atmos. Environ. 38, 557–572. http://dx.doi.org/10.1016/j.atmosenv.2003.10.012.

Helmig, D., Ortega, J., Guenther, A., Herrick, J.D., Geron, C., 2006. Sesquiterpene emissions from loblolly pine and their potential contribution to biogenic aerosol formation in the Southeastern US. Atmos. Environ. 40, 4150–4157. http://dx.doi.org/10.1016/j.atmosenv.2006.02.035.

Helmig, D., Ortega, J., Duhl, T., Tanner, D., Guenther, A., Harley, P., Wiedinmyer, C., Milford, J., Sakulyanontvittaya, T., 2007. Sesquiterpene emissions from pine trees – identifications, emission rates and flux estimates for the contiguous United States. Environ. Sci. Technol. 41, 1545–1553. http://dx.doi.org/10.1021/es0618907.

Holzinger, R., Lee, A., McKay, M., Goldstein, A.H., 2006. Seasonal variability of monoterpene emission factors for a ponderosa pine plantation in California. Atmos. Chem. Phys. 6 (5), 1267–1274. http://dx.doi.org/10.5194/acp-6-1267-2006.

Holzke, C., Hoffmann, T., Jaeger, L., Koppmann, R., Zimmer, W., 2006. Diurnal and seasonal variation of monoterpene and sesquiterpene emissions from Scots Pine (Pinus silvestris L.). Atmos. Environ. 40, 3174–3185. http://dx.doi.org/10.1016/j.atmosenv.2006.01.039.

Llusia, J., Peñuelas, J., 2000. Seasonal patterns of terpene content and emission from seven Mediterranean woody species in field conditions. American Journal of Botany 87 (1), 133–140.

Keenan, T., Niinemets, Ü., Sabate, S., Gracia, C., Peñuelas, J., 2009. Seasonality of monoterpenes emission potentials in Quercus ilex and Pinus pinea: implications for regional VOC emissions modeling. J. Geophys. Res. 114, D22202. http://dx.doi.org/10.1029/2009JD011904.

Kim, J.-C., 2001. Factors controlling natural VOC emissions in a southeastern US pine forest. Atmos. Environ. 35, 3279–3292. http://dx.doi.org/10.1016/S1352-2310(00)00522-7.

Kim, S., Karl, T., Guenther, G., Tyndall, G., Orlando, J., Harley, P., Rasmussen, R., Apel, E., 2010. Emissions and ambient distributions of biogenic volatile organic compound (BVOC) in a ponderosa pine ecosystem: interpretation of PTR-MS mass spectra. Atmos. Chem. Phys. 10, 1759–1771. http://dx.doi.org/10.5194/acp-10-1759-2010.

Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Ciccioli, P., Brancaleoni, E., Frattoni, M., Tavaares, T.M., Kesselmeier, J., 2004. Seasonal differences in isoprene and light-dependent monoterpenes emission by Amazonian tree species. Global Change Biol. 10, 663–682.

Matsunaga, S.N., Shigeru, N., Mochizuki, T., Tani, A., Kusumoto, D., Utsumi, Y., Enoki, T., Hiura, T., 2013. Seasonal variation in basal emission rates and composition of mono- and sesquiterpenes emitted from dominant conifers in Japan. Atmos. Environ. 69, 124–130. http://dx.doi.org/10.1016/j.atmosenv.2012.12.004.

Noe, S.M., Hüve, K., Niinemets, Ü., Copolovici, L., 2012. Seasonal variation in vertical volatile compounds air concentrations within a remote hemiboreal mixed forest. Atmos. Chem. Phys. 12, 3909–3926. http://dx.doi.org/10.5194/acp-12-3909-2012.

Ortega, J., Helmig, D., 2008. Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques – Part A. Chemosphere 72, 343–364. http://dx.doi.org/10.1016/j.chemosphere.2007.11.020.

Ortega, J., Helmig, D., Daly, R.W., Tanner, D.M., Guenther, A.B., Herrick, J.D., 2008. Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques – Part B: Applications. Chemosphere 72, 365–380. http://dx.doi.org/10.1016/j.chemosphere.2008.02.054.

Pio, C.A., Silva, P.A., Cerqueira, M.A., Nunes, T.V., 2005. Diurnal and seasonal emissions of volatile organic compounds from cork oak (Quercus suber) trees. Atmos. Environ. 39, 1817–1827. http://dx.doi.org/10.1016/j.atmosenv.2004.11.018.

Rivoal, A., Fernandez, C., Lavoir, A.V., Olivier, R., Lecareux, C., Greff, S., Roche, P., Vila, B., 2010. Environmental control of terpene emissions from Cistus monspeliensis L. in natural Mediterranean shrublands. Chemosphere 78, 942–949. http://dx.doi.org/10.1016/j.chemosphere.2009.12.047.

Staudt, M., Bertin, N., Frenzel, B., Seufert, G., 2000. Seasonal Variation in amount and composition of monoterpenes emitted by young Pinus pinea trees – Implications for emission modeling. J. Atmos. Chem. 35, 77–99. http://dx.doi.org/10.1023/A:1006233010748.

Staudt, M., Rambal, S., Joffre, R., Kesselmeier, J., 2002. Impact of drought on seasonal monoterpene emissions from Quercus ilex in southern France. J. Geophys. Res. 107, 4602. http://dx.doi.org/10.1029/2001JD002043.

Steinbrecher, R., Smiatek, G., Köble, R., Seufert, G., Theloke, J., Hauff, K., Ciccioli, P., Vautard, R., Curci, G., 2009. Intra- and inter-annual variability of VOC emissions from natural and semi-natural vegetation in Europe and neighboring countries. Atmos. Environ. 43, 1380–1391. http://dx.doi.org/10.1016/j.atmosenv.2008.09.072.