

Seasonal and interannual variations in whole-ecosystem BVOC emissions from a subtropical plantation in China



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HIGHLIGHTS

- Terpenoid emissions exhibited strong diurnal, seasonal and interannual variations.
- Monoterpenes contributed 72% of terpenoid emissions in a *Pinus* plantation in China.
- Biomass burning and fluorescence influence BVOC emissions.
- No strong correlations between BVOC emissions and O₃ concentrations.
- Emission factors were 1.19 (mg m⁻² h⁻¹) for isoprene and 1.65 for monoterpenes.

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ABSTRACT

Measurements of BVOC emissions, ozone concentration and environmental parameters were carried out from May 2013 to January 2016 in a subtropical *Pinus* plantation in China. Isoprene and monoterpene emissions were measured using a relaxed eddy accumulation (REA) system and a gradient technique on an above-canopy tower. In 2013, isoprene comprised 21.2% of total terpenoid emissions, while α -pinene, camphene, β -pinene and limonene constituting 51.5%, 2.4%, 9.1%, and 13.0% of total emissions, respectively. Monoterpenes together were the dominant VOCs measured contributing 71.6%. α -pinene, camphene, β -pinene and limonene constituted 67.7%, 3.2%, 11.9%, 17.2% of total monoterpene emissions. Isoprene and monoterpene emissions displayed strong diurnal variations, with lower emissions in the morning and late evening, and the highest emissions around noon. BVOC peak emissions typically occurred a few hours after the noon PAR peak. Isoprene and monoterpene emissions varied with season and were the highest in summer, contributing more than half of the total annual emission, and the lowest emissions were in winter. Evident interannual variations of isoprene, monoterpenes and total BVOCs were observed. Compared to 2013, annual BVOC emissions decreased in 2015, associated with decreases of PAR, Temperature, water vapor, and an increase of all substances in gas, liquid and solid phases in the atmospheric column (e.g., S/Q, the ratio of solar scattered radiation to global radiation). Ozone concentration showed clear diurnal variation with PAR, higher around noon and lower in the early morning and late evening. Generally, there were no evident correlations between ozone concentrations and BVOC emissions, or the vertical gradients of ozone concentrations and BVOC concentrations. Under all sky conditions (including cloudy skies), no strong correlations at a high confidence level or very similar variation patterns were observed between any two following parameters, BVOC emissions, PAR, temperature, water vapor, and S/Q. The major factors controlling BVOC emissions were PAR and temperature but biomass burning smoke and phenology (pine fluorescence) may also play a role. The mean emission factors at standard conditions determined using the MEGAN model emission algorithms and empirical model of BVOC emissions were 0.71 and 1.19 mg m⁻² h⁻¹ for isoprene and 1.39 and 1.65 mg m⁻² h⁻¹ for total monoterpenes, respectively.

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1. Introduction

Terrestrial vegetation is the dominant source of atmospheric VOCs (Guenther et al., 1995). Isoprene and monoterpenes are the main components of the global biogenic volatile organic compound (BVOCs) emissions (Guenther et al., 2012). Many BVOCs have a high reactivity with atmospheric lifetimes ranging from minutes to hours or days (Atkinson and Arey, 2003) and play key roles in chemical and photochemical reactions in the atmosphere, i.e., the formation of O_3 and secondary organic aerosol (SOA) (e.g. Chameides et al., 1988; Yu et al., 1999; Claeys et al., 2004; Kanakidou et al., 2005). SOA can influence cloud condensation nuclei and the radiative budget of the atmosphere. Thus, BVOCs play important connections between gases, liquids and particles through chemical and photochemical reactions, and participate in solar energy transfer through the atmosphere (Bai, 2011, 2013).

Air pollution is a severe problem over large areas and cities in recent years in China. It is an urgent task to accurately know the amount of BVOC emitted from typical ecosystems and vegetation in cities and their contributions to O_3 and SOA formation. In China, some enclosure and a few above-canopy flux measurements (Baker et al., 2005; Bai et al., 2012, 2016; Situ et al., 2013) have been made at representative sites. BVOC emission data (i.e., flux, concentration) are important input parameters for regional and global models, but there are still limited measurements in typical forests in China that are available for application in emission model estimates (Guenther et al., 2006).

China's forests cover 195 million hectares over many climatic zones (Mark and Zhang, 2009). In southern China, tree plantations are an important ecosystem, accounting for 54.3% of forestation and 52.6% of carbon storage for mainland China (Liu et al., 2006). Long-term measurement of BVOC emissions and O_3 concentrations in this typical forest will improve our understanding of their basic characteristics, and our ability to correctly estimate BVOC emissions and their contributions to O_3 and $PM_{2.5}$ (secondary organic aerosol) formation. Seasonal and annual canopy-level BVOC emissions and O_3 concentrations from a subtropical plantation in Jiangxi province, China are reported in this study. The relationships between O_3 concentrations and BVOC emissions, as well as O_3 concentrations and BVOC concentrations at two vertical levels are discussed. The phenomena of BVOC emissions influenced by biomass burning smoke, rain and fluorescence are also reported.

2. Site description and methods

BVOC emissions, O_3 concentration, solar radiation and meteorological parameters were measured at Qianyanzhou subtropical *Pinus* plantation, Taihe county, Jiangxi province ($26^{\circ}44'48''$ N, $115^{\circ}04'13''$ E, 110.8 m) from 22 May 2013 to 4 January 2016. This plantation was planted in 1985. The site is a *Pinus* plantation in a subtropical region of China. Dominant tree species are *pinus massoniana*, *pinus elliottii*, *cunninghamia lanceolata*, and broadleaf trees, covering 42.0%, 49.6%, 5.8% and 2.6% of this landscape, respectively in 2005 (Liu et al., 2005), and 50.1%, 30.1%, 7.3% and 12.5%, respectively in 2011. Leaf area index is $3.6 \text{ m}^2 \text{ m}^{-2}$ (Yu et al., 2005). Under the canopy, the shrubs are mainly *Loropetalum chinense*, *Adinandra millettii*, and *Lyonia compta*, the herbs are *Woodwardia japonica*, *Dryopteris cycadina*, and *Dicranopteris pedata*. The main soil type of this area is krasnozem clay (or red soil). Around the flux tower, the forest covers about 90% in 1 km^2 and 70% in 100 km^2 , the mean canopy height is 18 m. The average slope of this study region is about 2.8° – 13.5° .

A 45-m tower was erected for CO_2 flux, solar radiation and

meteorological measurements surrounded by the coniferous plantation. Average annual precipitation is about 1485.1 mm, annual temperature is 17.9°C (Liu et al., 2005).

A Relaxed Eddy Accumulation (REA) system, consisting of a three-dimensional sonic anemometer (RM Young, Traverse City, Michigan, USA, Model 81000), a data logger (Campbell Scientific, Logan Utah, USA, Model CR1000) and a data acquisition and control unit, was used to collect air samples in stainless steel cartridges (Baker et al., 1999; Greenberg et al., 2003; Bai et al., 2015a, 2016). The REA system was located at the end of a 2-m boom positioned on a platform at a height of 23 m above ground level and approximately 5 m above the top of the canopy. More detailed information about this REA system, cartridge usage and storage is given by Bai et al. (2016). Starting from 23 July 2014, air samples were collected by a gradient method, i.e., samples were collected by pumps (HL-2 sampler, Beijing municipal institute of labor protection, China) at two levels, 20 and 28 m, as well as 24 m sometimes. The accuracy of the flow rate was 5% over 8 h. The collecting time of samples was 30 min. The same three-dimensional sonic anemometer and a data logger used for the gradient technique were also used for the REA system.

The basic equation to derive fluxes of a given BVOCs species (F_i) from the REA system is:

$$F_i = b\sigma_w(C_{up} - C_{down}) \quad (1)$$

where σ_w is the standard deviation of the vertical wind velocity, and C_{up} and C_{down} are the concentrations of the BVOCs species of interest in the updraft and downdraft cartridges, respectively. b , an empirical coefficient, was calculated from the sensible heat flux measured with the sonic anemometer by virtual conditional sampling of the sonic temperature and then inverting equation (1).

The equation to derive fluxes of a given BVOCs species (F_i) from the gradient technique is:

$$F_i = K_{diff} \times (\Delta C / \Delta z) \quad (2)$$

Where K_{diff} is the eddy diffusion coefficient, $K_{diff} = (k \times (u^*) \times (z - d))$ for neutral atmospheric stability, $k = 0.4$ (von Karman's constant) and z is the measurement height (geometric value), d is the displacement height and assumed to be $2/3$ canopy height. The mean canopy height is 18 m around the tower region.

At Qianyanzhou station, solar global radiation (Q) and direct radiation (D) were measured with a frequency of 1 Hz at the top of a building, 800 m away from the flux tower. Simultaneously, PAR (photosynthetically active radiation) was also measured with a LI-190SA Quantum sensor (LI-COR, Inc., Lincoln, NE, USA). Solar scattered radiation (S) is derived from $S = Q - D$. All solar radiation sensors were cleaned every morning before sunrise and more often if needed. More detailed introductions about the solar radiation system are described by Bai et al. (2012). In this subtropical coniferous plantation, other meteorological conditions (temperature, relative humidity) were also measured by a HOBO weather station (Model H21, Onset Company, USA) during this campaign. O_3 was measured by an ozone monitor (Model 205, 2B Technologies Inc., USA) installed at the same height as the REA and sonic anemometer. The precision (1σ , rms noise) of the O_3 monitor is the greater of 1.0 ppb or 2% of reading for 10-s average, and its resolution is 0.1 ppb (Bai et al., 2016).

Air samples were collected in stainless steel cartridges that were 10 cm in length and 1/4 inch in diameter and filled with Tenax GR and Carbograph 5TD (Markes International Inc., USA). The cartridges collected by the REA system were shipped to a lab at the National Center for Atmospheric Research (NCAR) in Boulder, CO, U.S.A. for analysis, while the cartridges collected using the gradient

method were analyzed in the lab at Beijing, the Institute of Atmospheric Physics, Chinese Academy of Sciences. All cartridges were analyzed within 25 days after the collection. The procedures for sample analyses and calibrations at NCAR have been described by Duhl et al. (2013), Greenberg et al. (1999a, 1999b) and Bai et al. (2002, 2016). The procedures for sample analyses and calibrations by gas chromatographs equipped with flame ionization detector (GC-FID) at the laboratory (IAP, CAS) in Beijing, China were similar to that described by Greenberg et al. (2003), i.e., a chromatographic column (Rtx-624, 30 m \times 0.25 mm internal diameter, (ID), 1.4 μ m film thickness (df), Restek Corp., Bellefonte, PA, USA), and temperature program (initial temperature 40 $^{\circ}$ C, 2 min hold, then 10 $^{\circ}$ C min $^{-1}$ to 240 $^{\circ}$ C, then hold 5 min) were used. The identification of isoprene and monoterpenes was made from the retention times compared to a mixture of isoprene and monoterpenes analyzed repeatedly. Quantification of concentrations was made with a mixture of butane in nitrogen (National standard materials research center, Beijing, China, 10.4 ppm). The precision of the GC-FID analysis was approximately 10% for α -pinene.

The REA cartridges were thermally desorbed using an Ultra autosampler (Series 2, model ULTRATD, Markes International, Llantrisant, RCT, UK) and analytes were then cryo-focused onto a Unity thermal desorber (Markes International, Llantrisant, RCT, UK) operated in splitless mode. Samples were subsequently injected into a gas chromatograph (GC) containing an HP-5MS column (30 m \times 0.25 mm, 0.25 μ m, Agilent Technologies, Inc., Santa Clara, CA, USA) and equipped with both flame ionization (FID) and mass selective (MS) detectors (GC7890 and MSD5975C, Agilent Technologies, Inc., Santa Clara, CA, USA). The MSD was run simultaneously in both SIM and SCAN modes. Flow path temperatures were maintained at \sim 175 $^{\circ}$ C. The procedures for sample analyses and calibrations have been described by Duhl et al. (2013) and Greenberg et al. (1999a, 1999b).

Briefly, compounds detected in samples were quantified using the FID along with an external gas-phase standard containing isoprene and camphene, and an internal standard consisting of trans-decahydronaphthalene.

Both opened and unopened blanks were analyzed to determine potential contributions to detected analytes from background concentrations or cartridge usage, which were determined to be negligible for both types of blanks. Single concentration measurements have an uncertainty between 8 and 15% (Greenberg et al., 1999a) and the uncertainty of the REA BVOC flux measurement technique is about 25% (Guenther et al., 1996; Lamb et al., 1996).

The BVOC measurements were carried out periodically from 22 May 2013 to 4 January 2016 (Table 1). Air samples were collected: 1) every 3 h from sunrise to sundown for five samples, and 2) a single sample was collected mostly around noon, although samples were collected at other times on a few days. A total of 451 BVOC fluxes, averaged over 30 min, are summarized in Table 1.

The emission factors of BVOCs at a standard set of conditions, i.e., a Leaf Area Index of 5 m 2 m $^{-2}$ at an above canopy temperature of 30 $^{\circ}$ C and PAR of 1500 μ mol m $^{-2}$ s $^{-1}$ were calculated by the Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGANv2.1) (Guenther et al., 2012). The averaged emission factors during 9:00 to 15:30 were selected as representatives for sampling periods in this subtropical *Pinus* plantation.

3. Results and discussion

3.1. BVOC emissions and controlling factors, ozone concentration

To get reliable estimates of terpenoid emissions (mg m $^{-2}$ h $^{-1}$), 2 σ standard criteria was used to reject outliers. Taking 2013 as an

Table 1
BVOC emission flux sampling periods from 22 May 2013 to 4 January 2016, numbers in parentheses are the number of samples used for analyses of BVOC emissions.

Year	Experimental periods
2013	A: 22 May–28 May (26)
2014	E: 18 Jan.–19 Jan. (16)
2015	G: 14 Jan. – 19 Jan. (39)
	H: 22 Apr. – 30 Apr. (30)
	I: 6 June – 16 June (43)
	F: 23 July – 27 July (9, 9, 9)
	B: 29 June–6 July (29)
	C: 6 Aug.–13 Aug. (36)
	J: 23 Aug. – 4 Sep. (30)
	K: 2 Nov. – 7 Nov. (36)
	D: 7 Sep. – 11 Sep. (30)
	L: 31 Dec. 2015–4 Jan., 2016 (37)

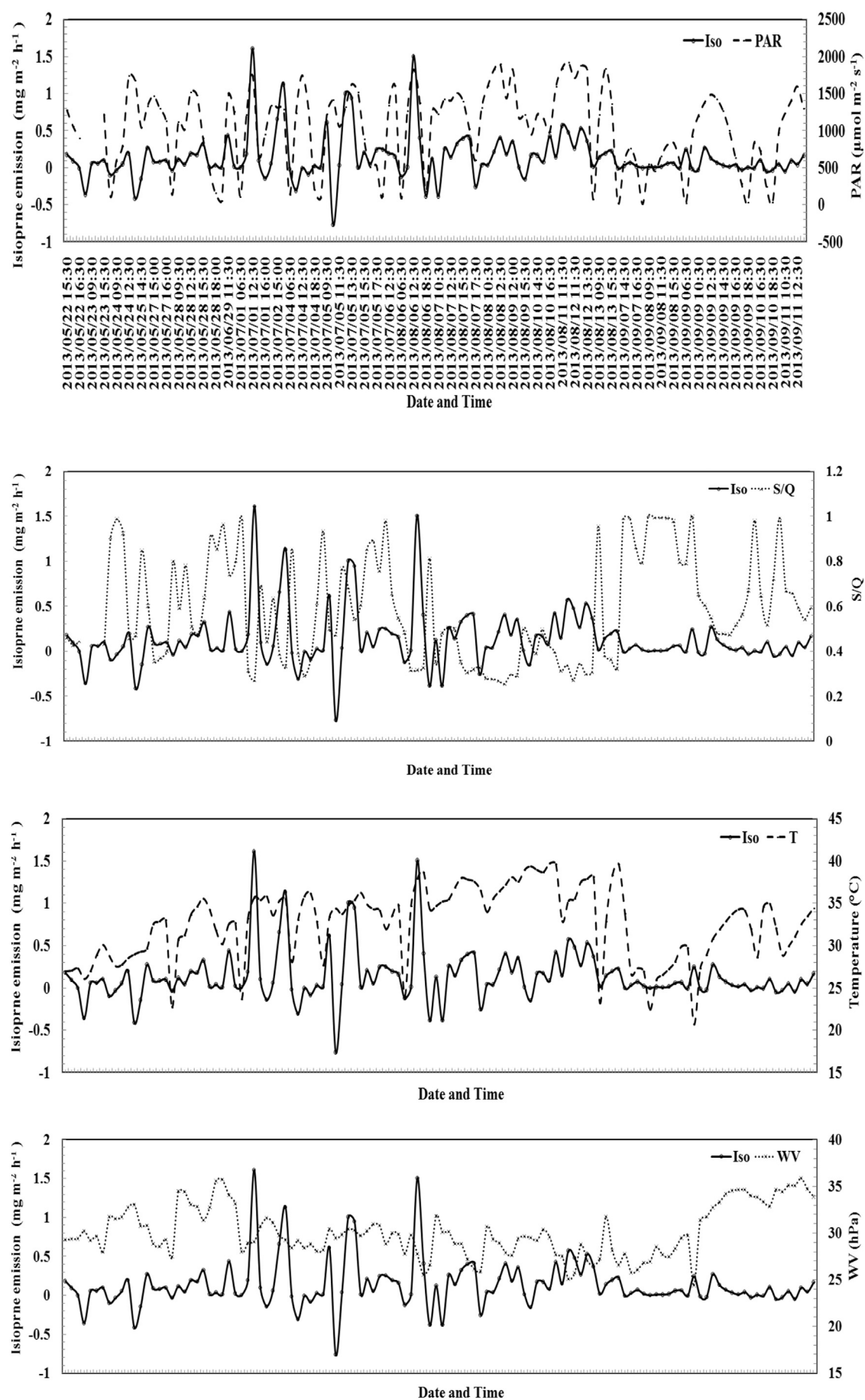


Fig. 1. Isoprene emission flux (Iso), PAR, S/Q, temperature (T) and water vapor pressure at the ground (WV) observed during 2013 at the subtropical *Pinus* plantation.

example, the main terpenoid “annual” emissions (including periods A, B, C, and D) from *Pinus* plantation were isoprene (0.136, 0.060, −0.764 to 1.610), α -pinene (0.332, 0.272, −0.981 to 2.619), camphene (0.016, 0.013, −0.067 to 0.124), β -pinene (0.058, 0.056, −0.154 to 0.297), limonene (0.084, 0.049, −0.554 to 0.646), 2 unidentified sesquiterpenes (SQT) (0.011, 0.009, −0.093 to 0.096) and (0.006, 0.003, −0.091 to 0.095), respectively, longifolene emission was very low (9×10^{-4} , 5×10^{-4} , −0.010 to 0.010). The numbers in parentheses are average, median and variation range. Isoprene in 2013 comprised 21.2% of total observed terpenoid emissions, α -pinene, camphene, β -pinene and limonene constitute 51.5%, 2.4%, 9.1%, 13.0% of total emissions, respectively. Monoterpenes are the dominant emission category contributing 71.6% in this subtropical *Pinus* plantation. For monoterpene components, α -pinene, camphene, β -pinene and limonene constitute 67.7%, 3.2%, 11.9%, 17.2% of total monoterpene emissions. Taking the average of daily values in 2013 as a comparison, isoprene comprised 21.7% of total observed terpenoid emissions, α -pinene, camphene, β -pinene and limonene constitute 58.8%, 2.6%, 9.6%, 6.9% of total emissions, respectively. Generally, the normal statistical values and daily statistical values agree well for BVOC compositions. During this campaign, BVOC measurements were carried out in daytime. Considering that SOA can be formed by oxidation of monoterpenes and the role of nitrate radicals at night (e.g. Fry et al., 2014; Lee et al., 2006), and monoterpenes can have temperature-based fluxes at night, future investigations should focus on night-time BVOC emissions and fate. Variations of isoprene and monoterpene emissions, PAR, temperature, water vapor pressure at the ground, S/Q factor (the ratio of solar scattered radiation to global radiation, an indicator of total amount of atmospheric constituents in the whole column of the atmosphere (Bai et al., 2015a, 2015b)) observed in 2013 at the subtropical *Pinus* plantation are shown in Fig. 1 and Fig. 2.

Isoprene emission exhibited obvious diurnal variations, i.e., a morning increase, an afternoon maximum, and a decrease in the evening. For example, under clear skies, the highest emission appeared at 12:30 on 1 July and 6, August 2013, and coincided with PAR (Fig. 1). Similarly, the highest monoterpene emissions appeared at 12:30 on 1 July 2013, and coinciding with PAR, and 15:30 on 6, August 2013, later than PAR maximum (Fig. 2). Average diurnal variation of BVOCs under all sky conditions is shown in Fig. 3 to illustrate isoprene and monoterpene variations (total number of samples, $n = 102$). According to diurnal and seasonal variation patterns, isoprene and monoterpenes displayed closer relations with PAR than temperature, water vapor, and S/Q (Figs. 1 and 2). Isoprene and monoterpene emissions varied with season and were the highest in summer (i.e., periods B and C, 2013), then decreased rapidly in autumn D, 2013, i.e., when average PAR was $793.5 \mu\text{mol m}^{-2} \text{s}^{-1}$, average T was 29.4°C , and average WV was 33.3 hPa , and the lowest in winter (i.e., in January and December 2015). The total emissions of isoprene, α -pinene, camphene, β -pinene and limonene in summer (i.e., periods B and C) take up 83.6%, 66.4%, 70.8%, 70.4%, and 60.8% in all 4 periods in 2013, respectively.

As for statistical results, most averages and medians of BVOC emissions in different periods for normal statistical averages were closer (Table 3a and 3b), and similar to the daily median (Table 4a and 4b). Considering the uncertainty of the BVOC flux measurement technique, more statistical results are necessary to investigate their emission characteristics thoroughly.

Frequent negative fluxes of isoprene were measured in this subtropical plantation. This may be related to the local mixture of tree species, as the two dominant pine species in the plantation are not isoprene emitters. The low isoprene and monoterpene emissions in August 2015 were mainly caused by large decreases of PAR

and temperature and water vapor, i.e., average PAR dropped to lower than $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$, average temperature lower than 30°C , and average WV lower than 35 hPa .

Table 2 shows average and median measured BVOC emissions, PAR, water vapor pressure at the ground, temperature. Monoterpenes include α -pinene, camphene, β -pinene and limonene. Additional measured parameters (O_3 concentration, S/Q) are also shown in Table 2. The normalized isoprene and monoterpene emission factors at standard conditions (30°C , $1500 \mu\text{mol m}^{-2} \text{s}^{-1}$) calculated by MEGAN and empirical model of BVOC emissions (EMBE) are shown as EF MEGAN and EF EMBE.

The EMBE empirical model of isoprene and monoterpene emissions is based on PAR energy balance above canopy level (Bai et al., 2015b, 2015c), which considers 1) BVOC (i.e., isoprene or monoterpenes) emissions, 2) PAR energy absorption and consumption by GLPs (gases, liquids and particles), and 3) The scattering roles of GLPs. According to the same data criteria, i.e., BVOC emission fluxes bigger than twice their standard deviations were not considered, the same BVOC emission models for isoprene and monoterpenes (equations (3) and (4)) for subtropical *Pinus* plantations as a temperate forest and a subtropical bamboo forest (Bai et al., 2015b, 2015c) were developed:

$$e^{-k_1 I_{tm}} \times \cos(Z) = A_1 \text{PAR} + A_2 e^{-kW_m} \times \cos(Z) + A_3 e^{-S/Q} + A_0 \quad (3)$$

$$e^{-k_2 M_{tm}} \times \cos(Z) = B_1 \text{PAR} + B_2 e^{-kW_m} \times \cos(Z) + B_3 e^{-S/Q} + B_0 \quad (4)$$

where k_1 and k_2 are the absorption coefficients of isoprene and monoterpenes, presumed to be unity, I and M are isoprene and monoterpene emission estimates ($\text{mg m}^{-2} \text{h}^{-1}$), $I = 0.05 \times \text{EFI}$, $M = 0.5 \times \text{EFM}$, EFI and EFM are emission fluxes of isoprene and monoterpenes. $e^{-kW_m} = 1 - \Delta S/I_0$, $\Delta S = 0.172 (\text{mW})^{0.303}$, $W = 0.021 \text{WV} \times 30$, WV is the average of water vapor pressure (hPa) at the ground during the sampling period, I_0 (solar constant) = $1.94 \text{ cal min}^{-1} \text{cm}^{-2}$ ($=1367 \text{ W m}^{-2}$), and k is the averaged absorption coefficient of water vapor in the wavelength range of $0.70\text{--}2.845 \mu\text{m}$. The simulation results for Changbai Mountain temperate forest (CBS), LinAn subtropical bamboo forest (LA), Qianyanzhou subtropical plantation (QYZ) are summarized in Table 2, including coefficients and constants (Coe_1 , Coe_2 , Coe_3 , C_0), coefficient of determination (R^2), average of the absolute relative bias $\bar{\delta}$, ($\bar{\delta} = |y_{\text{cal}} - y_{\text{obs}}| \times 100 / |y_{\text{obs}}|$, y_{cal} and y_{obs} are calculated and observed emission fluxes), normalized mean square error (NMSE).

It should be mentioned that based on the above-mentioned criteria, observational data were selected for establishing the isoprene emissions model, $n = 13$ and $n = 21$ groups for individual 2010 or 2011, respectively, the similar results were obtained as $n = 34$ groups for 2010 and 2011 (Bai et al., 2015b). Similar results were also obtained for monoterpenes as isoprene at Changbai Mountains temperate forest (Bai et al., 2015b). Later, these BVOC empirical models were applied to a subtropical bamboo forest and this subtropical plantation, similar results were obtained and reported in Table 2. The first 2 coefficients of the isoprene emission model were very close for the 3 representative forests, indicating their basic emission mechanism was the same, which was also corresponding to MEGAN using the same coefficients for isoprene emission. For the monoterpene emissions model, the first coefficient was not close for 3 forests, which means monoterpene emissions have different relations with PAR, the second coefficient was closer, which means monoterpenes play similar roles in chemical and photochemical reactions. Furthermore, isoprene plays the same chemical and photochemical role as monoterpenes

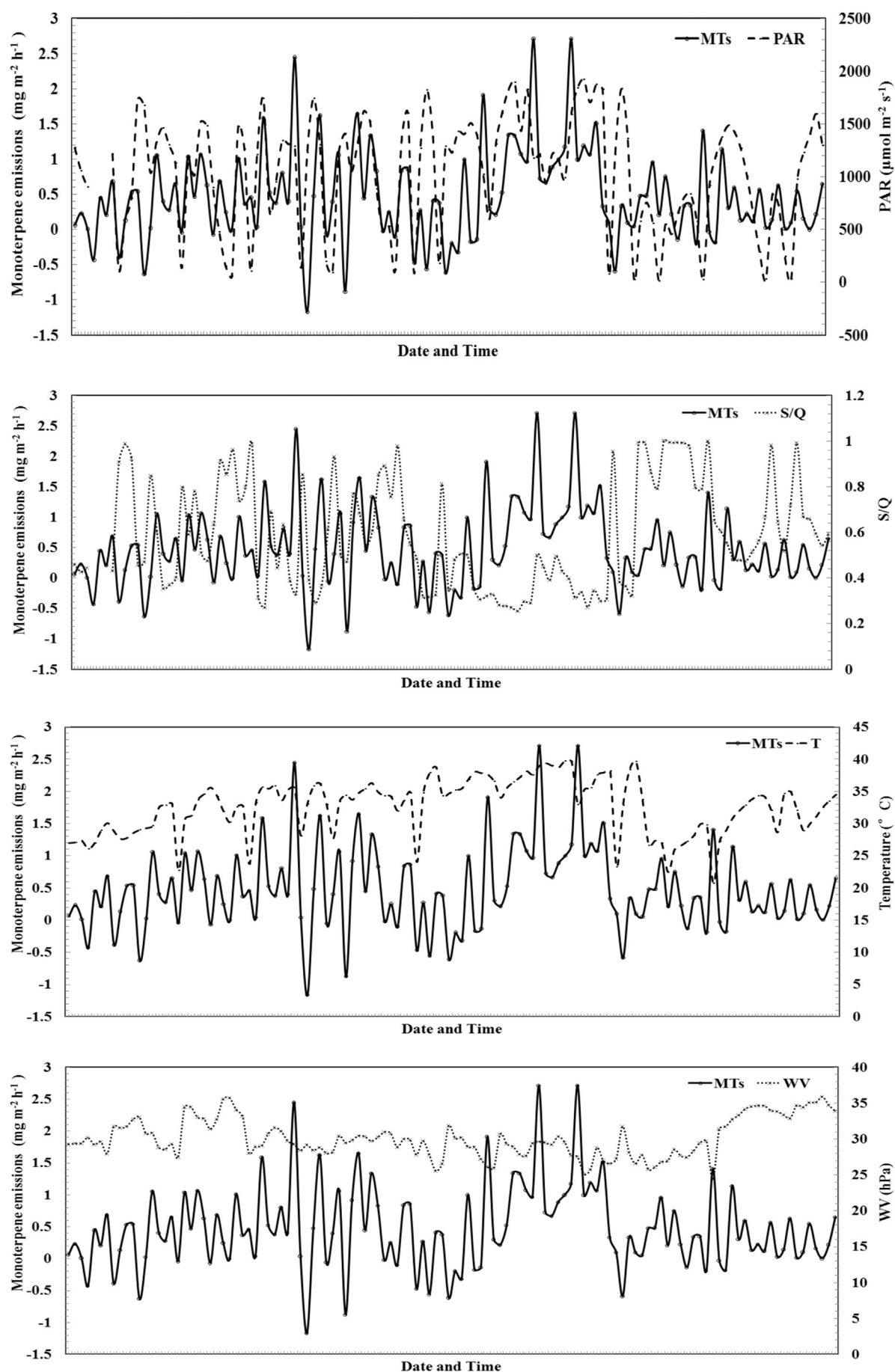


Fig. 2. Same as Fig. 1, but for monoterpene emissions (MTs). Note that the x-axes of Figs. 1 and 2 are the same.

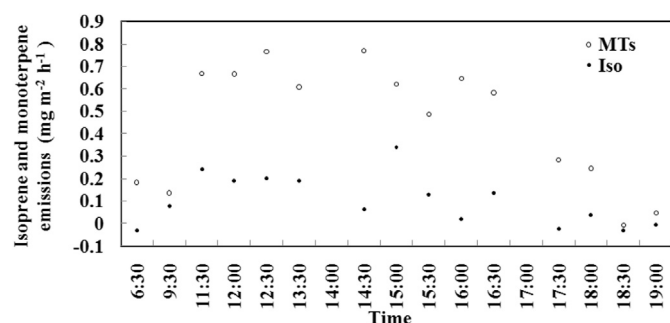


Fig. 3. Average diurnal variation of isoprene and monoterpene emission fluxes (Iso, MTs) observed during 2013 at the subtropical *Pinus* plantation.

Table 2

Simulation results of isoprene and monoterpene emission models for Changbai Mountain temperate forest (CBS), LinAn subtropical bamboo forest (LA) and Qianyanzhou subtropical plantation (QYZ).

Site	Model	Coe ₁	Coe ₂	Coe ₃	C ₀	R ²	$\bar{\delta}(\%)$	NMSE	n
CBS	Iso	−0.049	1.292	0.112	−0.065	0.964	39.3	0.133	34
CBS	MTs	−0.054	1.371	0.184	−0.204	0.973	27.1	0.973	37
LA	Iso	−0.050	1.3307	0.2981	−0.2263	0.932	20.3	0.031	12
LA	MTs	−0.024	1.2945	0.2033	−0.1059	0.998	21.8	2.020	14
QYZ	Iso	−0.052	1.408	0.106	−0.036	0.999	32.8	0.092	18
QYZ	MTs	−0.175	1.5839	0.0905	−0.2363	0.997	2.55	0.001	8

in 3 forests. The differences in the third coefficient for isoprene and monoterpenes at the 3 sites imply that isoprene and monoterpenes play different roles in the formation and destruction of secondary organic aerosols.

When calculating emission factors (EF) of isoprene and monoterpenes, a temperature of 30 °C and PAR of 1500 $\mu\text{mol m}^{-2} \text{s}^{-1}$ were applied by MEGAN and EMBE. To obtain reliable BVOC emission factors for different periods, mean emission factors in 9:00–15:30 were selected. Water vapor pressure (WV) at standard condition of 30 °C and was derived from the formulation between WV and temperature and relative humidity (RH). The parameters relative humidity (RH) and S/Q were taken as the averages of RH and S/Q in each period. Emission factors of isoprene and monoterpenes varied with season, higher in winter and lower in summer, which associated with the variation of relative humidity, water vapor, and atmospheric substances. Their averages for the entire campaign (A–L) were 1.151 (ranged from −0.126 to 2.128) for isoprene, and 1.648 (ranged from 1.136 to 2.348) $\text{mg m}^{-2} \text{h}^{-1}$. More stable emission factors were obtained, when the parameters RH and S/Q were used as the averages of RH and S/Q in entire campaign. New emission factors were 1.188 (ranged from 0.789 to 1.802) for isoprene, and 1.650 (ranged from 1.290 to 2.300) $\text{mg m}^{-2} \text{h}^{-1}$.

Comparing and analyzing the relations between BVOC emissions, PAR, temperature, water vapor, S/Q factors for Changbai temperate forest, LinAn subtropical bamboo forest and Qianyanzhou subtropical plantation, little correlation was found between any two parameters, including BVOC (i.e., isoprene or monoterpenes) emissions and PAR, temperature, water vapor and S/Q. BVOC emission peaks appeared at the same time with the maximum of PAR on clear days and were delayed several hours for other sky conditions, suggesting non-linear relationships in BVOC emission and photochemistry, and PAR is an important process controlling BVOC emissions and their photochemistry.

Clear annual variations of isoprene, monoterpenes and total BVOCs can be seen from Table 3. Annual mean values were calculated by averaging parameters in all periods in one year. The value

ratios of 2015 to 2013 for isoprene, monoterpenes and total BVOCs were −0.24, 0.74, 0.53, respectively, which corresponding to the emission decreases of isoprene, monoterpenes and total BVOCs 0.163, 0.129, 0.292 ($\text{mg m}^{-2} \text{h}^{-1}$), respectively, and were associated with the ratios 0.66, 0.68, 0.75, 1.28 for PAR, T, water vapor, S/Q, respectively, corresponding to the decreases of 346.0 $\mu\text{mol m}^{-2} \text{s}^{-1}$, 10.2 °C, 7.5 hPa for PAR, T, water vapor, respectively, and an increase in S/Q of 0.17. Therefore, the evident decreases of annual emissions of isoprene, monoterpenes and total BVOCs in 2015 were caused by the decreases of controlling factors, PAR, T, and possibly water vapor and the increase of all substances in gas, liquid and solid phases in atmospheric column (i.e., S/Q, the ratio of solar scattered radiation to global radiation). The negative isoprene emissions for most periods and annual average (−0.032) in 2015 were also caused by large decreases of PAR, T and possibly water vapor. For annual averages of 2013 and 2014, isoprene and monoterpenes contribute to total BVOC emissions by 21.0%, 23.5% and 76.3% and 76.5%, respectively, which also demonstrate that monoterpenes are dominant terpenoid emissions in subtropical *Pinus* plantation.

Emission factors of isoprene and monoterpenes estimated by MEGAN and EMBE models exhibited similar seasonal variations, higher in dry seasons (e.g., in Nov., Dec., Jan.), lower and relatively stable in the wet seasons (Table 3 and Fig. 4). The mean emission factors for the entire campaign estimated by the EMBE models were 1.19 for isoprene, and 1.65 $\text{mg m}^{-2} \text{h}^{-1}$ for monoterpenes, respectively. Monoterpene emissions were about 40% higher than isoprene and the mean emission factors calculated by MEGAN were about 38% lower than the EMBE values.

A recent LAI 6.83 $\text{m}^2 \text{m}^{-2}$ (Ma et al., 2008) was used in MEGAN model, the mean emission factors calculated by MEGAN were 41% for isoprene and 16% for monoterpenes lower than the EMBE values, which means real time LAI is an important parameter.

3.2. Comparison of BVOC emissions and O₃ concentrations at different periods

Compared to the average of periods B and C to A, isoprene and monoterpene emissions increased about a factor of 5 and 2, respectively, O₃ concentrations also increased by 20% (~8 ppb), which were associated with increases of PAR from lower than 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ to higher than 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$, and temperature from less than 30 °C to higher than 30 °C, respectively, whereas water vapor remained relatively constant. These atmospheric conditions promote higher BVOC emissions and ozone production. The inverse effect can be seen from the comparison of the average of periods D to B, isoprene and monoterpene (including α -pinene, camphene, β -pinene, limonene) emissions decreased by 80% and 55%, respectively, O₃ also decreased by ~1 ppb, associated with a decrease of PAR from higher than 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ to lower than 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$, temperature from higher than 30 °C to less than 30 °C, respectively, whereas water vapor remained relatively constant.

Comparing the average of periods D to A, isoprene and monoterpene emissions remained relatively constant, but, O₃ increased about 8 ppb, PAR decreased from 979.0 $\mu\text{mol m}^{-2} \text{s}^{-1}$ to 793.5 $\mu\text{mol m}^{-2} \text{s}^{-1}$, while temperature and water vapor remained relatively constant. This implies that ozone precursors, other than BVOCs, influenced O₃ formation during period D at this plantation. The concentrations of NO_x (NO + NO₂) were measured by a NO_x analyzer (Model EC9841, Ecotech company, Australia) at an open site, 230 m away from the flux tower from 12 June to 16 October 2014. The inlet was about 8 m high. The NO₂ and NO_x concentrations were 3.46, 8.67 ppb at period D (7–11, September) in 2014, and 3.12 and 5.15 ppb in September in 2014, respectively. These NO_x concentrations can be as a relative reference in this forest region.

Table 3a

Average and median of BVOC emission fluxes (average value, median value, $\text{mg m}^{-2} \text{h}^{-1}$), normalized isoprene and monoterpene emission factors (Iso EF and MT EF) calculated by MEGAN and EMBE (MEGAN and EMBE, $\text{mg m}^{-2} \text{h}^{-1}$), PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$), temperature ($^{\circ}\text{C}$), S/Q (scattering factor), WV (water vapor pressure at the ground, hPa) and O_3 concentrations (average, maximum, ppb) during different periods described in Table 1. Median BVOC emission fluxes were also given in Table 3 (average, median).

	A (22 May–28 May 2013)	B (29 June–6 July 2013)	C (6 Aug.–13 Aug., 2013)	D (7 Sep.–11 Sep., 2013)	E (18 Jan.–19 Jan., 2014)	F (23 July –27 July 2014)
Isoprene	0.042,0.056	0.237,0.079	0.203,0.177	0.044,0.025	0.087,0.000	0.259,0.302
α -pinene	0.248,0.275	0.434,0.482	0.432,0.382	0.190,0.193	0.188,0.044	0.389,0.354
Camphene	0.007,0.013	0.017,0.016	0.025,0.017	0.010,0.009	0.182,0.029	0.065,0.060
β -pinene	0.037,0.050	0.084,0.086	0.077,0.086	0.031,0.027	0.130,0.010	0.172,0.139
Limonene	0.028,0.046	0.069,0.044	0.128,0.179	0.099,0.054		
Longifolene	0.001,0.000	0.001,0.000	0.002,0.002	0.000,0.000		
Unidentified SQT	0.005,0.003	0.009,0.011	0.021,0.016	0.008,0.004		
Unidentified SQT	0.008,0.004	0.004,0.010	0.006,0.002	0.008,0.003		
Iso EF (MEGAN, EMBE)	0.163,1.012	0.466,0.369	0.184,-0.126	0.142,1.175	–1.190	0.404,1.058
MT EF (MEGAN, EMBE)	1.002,1.428	1.154,1.201	0.726,1.136	0.853,1.528	1.381,1.965	1.165,1.394
PAR	979.0	1043.9	1292.6	793.5	705.9	896.2
T	29.9	33.5	36.1	29.9	11.6	31.9
WV	31.2	29.9	28.3	31.5	6.8	36.2
S/Q	0.64	0.62	0.41	0.74	0.61	0.76
O_3 (avg,max)	34.4,64.4	43.6,75.6	41.1,63.4	42.8,59.3	51.4,71.6	49.0,110.9

	G (14 Jan. – 19 Jan., 2015)	H (22 Apr. – 30 Apr., 2015)	I (6 June –16 June 2015)	J (23 Aug. – 4 Sep., 2015)	K (2 Nov. – 7 Nov., 2015)	L (31 Dec. 2015–4 Jan., 2016)
isoprene	–0.059,0.000	–0.087,-0.085	–0.090,0.000	–0.124,-0.327	0.107,0.007	0.065,0.000
α -pinene	0.059,0.055	0.058,0.029	0.713,0.734	–0.255,-0.420	0.407,0.173	0.268,0.139
camphene	0.061,0.009	–0.047,-0.048	0.018,0.049	–0.090,-0.065	0.050,0.005	0.334,0.141
β -pinene	0.048,0.014	0.055,0.029	0.332,0.187	–0.108,0.010	0.136,0.094	0.162,0.000
limonene	–0.012,-0.061	–0.154,-0.089	–0.046,0.029	0.059,0.010	0.024,0.000	0.065,0.000
Iso EF (MEGAN, EMBE)	1.310,1.885	0.590,1.003	0.920,0.876	1.053,1.240	1.247,2.168	1.272,1.970
MMT EF (MEGAN, EMBE)	1.913,2.348	1.583,1.376	1.487,1.355	1.709,1.454	1.781,2.263	1.893,2.333
PAR	480.9	930.4	860.4	943.9	376.1	494.5
T	10.9	24.2	30.9	29.4	21.1	16.3
WV	9.6	22.9	33.6	33.3	22.1	14.8
S/Q	0.76	0.73	0.71	0.74	0.89	0.77
O_3 (avg,max)	39.0,67.7	45.3,63.4	37.3,47.4	36.5,87.8	32.2,50.5	33.0,49.5

3.3. The relationships between BVOC emission fluxes and ozone concentrations

Isoprene and monoterpene emissions sometimes had a similar diurnal pattern as O_3 concentration and PAR (Fig. 5), for example, on 6 July (cloudy day), 6 and 13 (clear day), August 2013, 16 June (hazy day), 2015 (data not shown). But, in most cases, O_3 and BVOC emissions did not display similar variations. The correlations between isoprene and monoterpene emissions and O_3 concentrations were very low, 0.09 and 0.02 (REA measured fluxes, $n = 120$), and -0.15 and -0.08 (gradient technique measured fluxes, $n = 193$), respectively. This result was similar as that in a subtropical bamboo forest (Bai et al., 2015a). Therefore, these phenomenon and statistically analysis indicated that complicated relationships exist between BVOCs and O_3 chemistry and photochemistry in forest regions and that there is not a simple linear

relationship.

The relationships between isoprene, monoterpenes, all BVOC emissions and O_3 concentrations during 2013, 2014 and 2015 campaigns were calculated, respectively (Table 5 and Table 6). Other related parameters including solar ultraviolet radiation (UV, Wm^{-2}) and relative humidity RH (%) are shown in these tables. It can be seen that: 1) no evident linear correlations exist between BVOC emissions and O_3 concentrations under some atmospheric conditions, 2) during warm, sunny atmospheric conditions (i.e., situations c, b, a), $\text{UV} > 20.0 \text{ Wm}^{-2}$, $\text{PAR} > 1030 \mu\text{mol m}^{-2} \text{s}^{-1}$, $T > 30^{\circ}\text{C}$, higher O_3 concentrations were generally associated with higher BVOC emissions; 3) during other atmospheric conditions (i.e., situations f, e, d), $\text{UV} < 21.0 \text{ Wm}^{-2}$, $\text{PAR} < 1030 \mu\text{mol m}^{-2} \text{s}^{-1}$, $T < 30^{\circ}\text{C}$, higher O_3 concentrations were generally associated with lower BVOC emissions.

Table 3b

Average and median concentrations (average value, median value, ppb) of BVOC species in up (u) and down (d) levels measured by gradient technique during different periods.

	F (23 July –27 July 2014)	G (14 Jan. – 19 Jan., 2015)	H (22 Apr. – 30 Apr., 2015)	I (6 June –16 June 2015)	J (23 Aug. – 4 Sep., 2015)	K (2 Nov. – 7 Nov., 2015)	L (31 Dec. 2015–4 Jan., 2016)
Isoprene u	1.319,1.087	0.395,0.348	0.476,0.323	1.533,1.334	1.354,0.816	0.376,0.332	0.164,0
α -pinene u	1.125,1.177	0.239,0.176	0.439,0.359	0.895,0.789	0.571,0.580	0.897,0.692	0.430,0.358
camphene u	0.254,0.236	0.173,0.155	0.071,0.065	0.218,0.139	0.102,0.104	0.483,0.160	0.701,0.256
β -pinene u	0.420,0.380	0.119,0.063	0.179,0.122	0.395,0.306	0.317,0.282	0.393,0.348	0.234,0.055
limonene u		1.296,1.305	1.294,1.032	2.028,2.231	1.149,0.840	0.136,0	0.068,0
Isoprene d	1.082,0.581	0.534,0.400	0.558,0.510	1.579,1.511	1.475,0.781	0.273,0.277	0.060,0
α -pinene d	0.996,0.992	0.206,0.127	0.412,0.345	0.704,0.602	0.714,0.703	0.707,0.520	0.326,0.242
camphene d	0.237,0.214	0.146,0.136	0.094,0.083	0.198,0.138	0.145,0.150	0.516,0.180	0.591,0.398
β -pinene d	0.370,0.353	0.093,0.042	0.166,0.132	0.306,0.258	0.357,0.287	0.317,0.201	0.141,0
limonene d		1.582,1.202	2.442,1.529	6.872,3.100	2.667,1.030	1.292,0	0.012,0

Table 4a

For daily averages, all parameters are the same as in Table 3a.

	A (22 May–28 May 2013)	B (29 June–6 July 2013)	C (6 Aug.–13 Aug., 2013)	D (7 Sep.– 11 Sep., 2013)	E (18 Jan.–19 Jan., 2014)	F (23 July –27 July 2014)
isoprene	0.040,0.076	0.267,0.229	0.226,0.201	0.051,0.051	0.093,0.093	0.257,0.196
α -pinene	0.294,0.229	0.564,0.511	0.550,0.436	0.180,0.183	0.188,0.188	0.581,0.508
camphene	0.008,0.006	0.024,0.019	0.026,0.022	0.012,0.011	0.067,0.067	0.074,0.069
β -pinene	0.042,0.036	0.101,0.085	0.086,0.088	0.030,0.028	0.183,0.183	0.226,0.207
limonene	0.028,0.033	0.017,0.068	0.165,0.260	0.094,0.058		
longifolene	0.001,0.000	0.001,0.001	0.003,0.003	0.000,0.000		
Unidentified SQT	0.002,0.002	0.020,0.009	0.026,0.032	0.003,0.007		
Unidentified SQT	0.005,0.004	–0.008,0.003	0.010,0.008	0.003,0.007		
PAR	1033.4	1183.6	1338.7	788.6	705.9	903.1
T	29.6	33.6	36.3	30.5	11.6	31.8
WV	30.7	30.3	28.2	30.7	6.8	35.5
S/Q	0.61	0.59	0.40	0.73	0.61	0.77
O ₃ (avg,max)	37.6,59.2	40.6,74.3	42.1,49.8	41.2,56.7	51.4,52.0	54.5,94.3
	G (14 Jan. – 19 Jan., 2015)	H (22 Apr. – 30 Apr., 2015)	I (6 June – 16 June 2015)	J (23 Aug. – 4 Sep., 2015)	K (2 Nov. – 7 Nov., 2015)	L (31 Dec. 2015–4 Jan., 2016)
isoprene	–0.125,–0.143	–0.094,–0.094	–0.029,0.213	–0.306,–0.316	0.110,0.098	0.081,0.107
α -pinene	0.058,0.038	0.041,–0.018	0.663,0.712	–0.220,–0.661	0.352,0.157	0.328,0.242
camphene	0.077,0.047	–0.039,–0.054	0.036,0.017	–0.130,–0.178	0.095,–0.17	0.412,0.396
β -pinene	0.065,0.025	0.035,–0.013	0.380,0.366	–0.103,0.095	0.143,0.148	0.051,0.140
limonene	0.003,–0.154	0.026,–0.146	–0.093,–0.094	–0.036,–0.036	0.026,0.000	0.039,0.000
PAR	459.4	1017.0	937.6	938.0	346.5	597.3
T	11.3	25.0	31.6	29.3	20.9	19.2
WV	9.6	23.6	33.6	33.1	22.0	16.8
S/Q	0.81	0.69	0.69	0.76	0.89	0.67
O ₃ (avg,max)	40.9,57.1	46.6,52.1	38.7,46.0	39.8,70.1	32.0,47.9	37.9,46.6

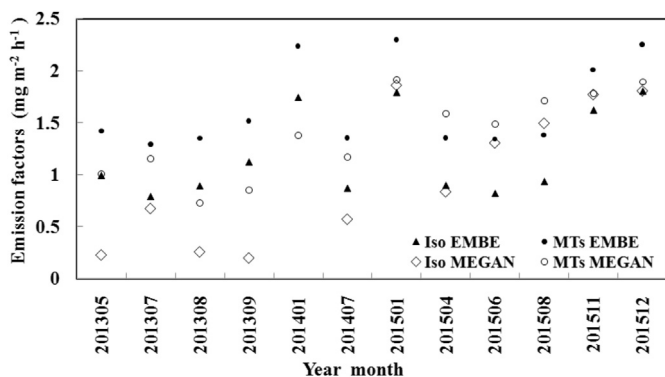
Table 4b

Average and median concentrations (average value, median value, ppb) of BVOC species in up (u) and down (d) levels measured by gradient technique (for daily averages).

	F (23 July –27 July 2014)	G (14 Jan. – 19 Jan., 2015)	H (22 Apr. – 30 Apr., 2015)	I (6 June – 16 June 2015)	J (23 Aug. – 4 Sep., 2015)	K (2 Nov. – 7 Nov., 2015)	L (31 Dec. 2015–4 Jan., 2016)
Isoprene u	1.280,1.390	0.384,0.357	0.409,0.415	1.593,1.353	1.132,0.250	0.379,0.328	0.134,0.112
α -pinene u	1.129,1.198	0.228,0.181	0.405,0.375	0.860,0.798	0.571,0.460	0.885,0.748	0.425,0.370
camphene u	0.227,0.211	0.174,0.176	0.070,0.071	0.223,0.157	0.088,0.086	0.478,0.550	0.923,1.312
β -pinene u	0.423,0.424	0.123,0.067	0.157,0.125	0.391,0.405	0.383,0.328	0.421,0.382	0.165,0.054
limonene u		2.160,1.868	3.225,2.938	7.786,8.374	1.393,1.393	1.458,0	0.042,0
Isoprene d	1.120,1.181	0.546,0.589	0.505,0.488	1.619,1.328	1.386,0.577	0.261,0.242	0.035,0
α -pinene d	0.978,1.058	0.195,0.129	0.387,0.363	0.695,0.670	0.730,0.731	0.708,0.669	0.317,0.276
camphene d	0.211,0.196	0.140,0.128	0.088,0.088	0.204,0.135	0.150,0.119	0.494,0.513	0.861,0.956
β -pinene d	0.370,0.373	0.086,0.045	0.149,0.135	0.299,0.264	0.433,0.391	0.338,0.292	0.123,0.054
limonene d		2.196,1.659	3.238,2.849	7.750,8.478	1.419,1.419	1.435,0	0.007,0

3.4. The relationships between BVOC concentrations and ozone concentrations

The concentrations of isoprene and monoterpenes at the upper and lower sampling levels were similar and varied in similar patterns. At some sky conditions, they varied with PAR, i.e., on 23 and 24, July 2014. Generally, BVOC concentrations were higher around noon and lower in the early morning and late evening. O₃ showed clear diurnal variation similar to PAR, higher around the noon or afternoon, lower in the early morning and late evening, which was also typically driven by photochemistry and similar as that in a tropical forest and a subtropical bamboo forest, China (Bai et al., 1999; Bai and Wang, 2001; Bai et al., 2016). Generally, no strong correlations were found between the concentrations of O₃ and isoprene, monoterpenes at two heights, respectively (Figs. 4 and 5), the correlation coefficients between concentrations of O₃ and isoprene, monoterpenes were –0.145 ($n = 160$), –0.193 ($n = 191$) for the upper level, respectively, and –0.076 ($n = 160$) and –0.259

**Fig. 4.** Emission factors of isoprene and monoterpenes calculated by MEGAN and EMBE models.

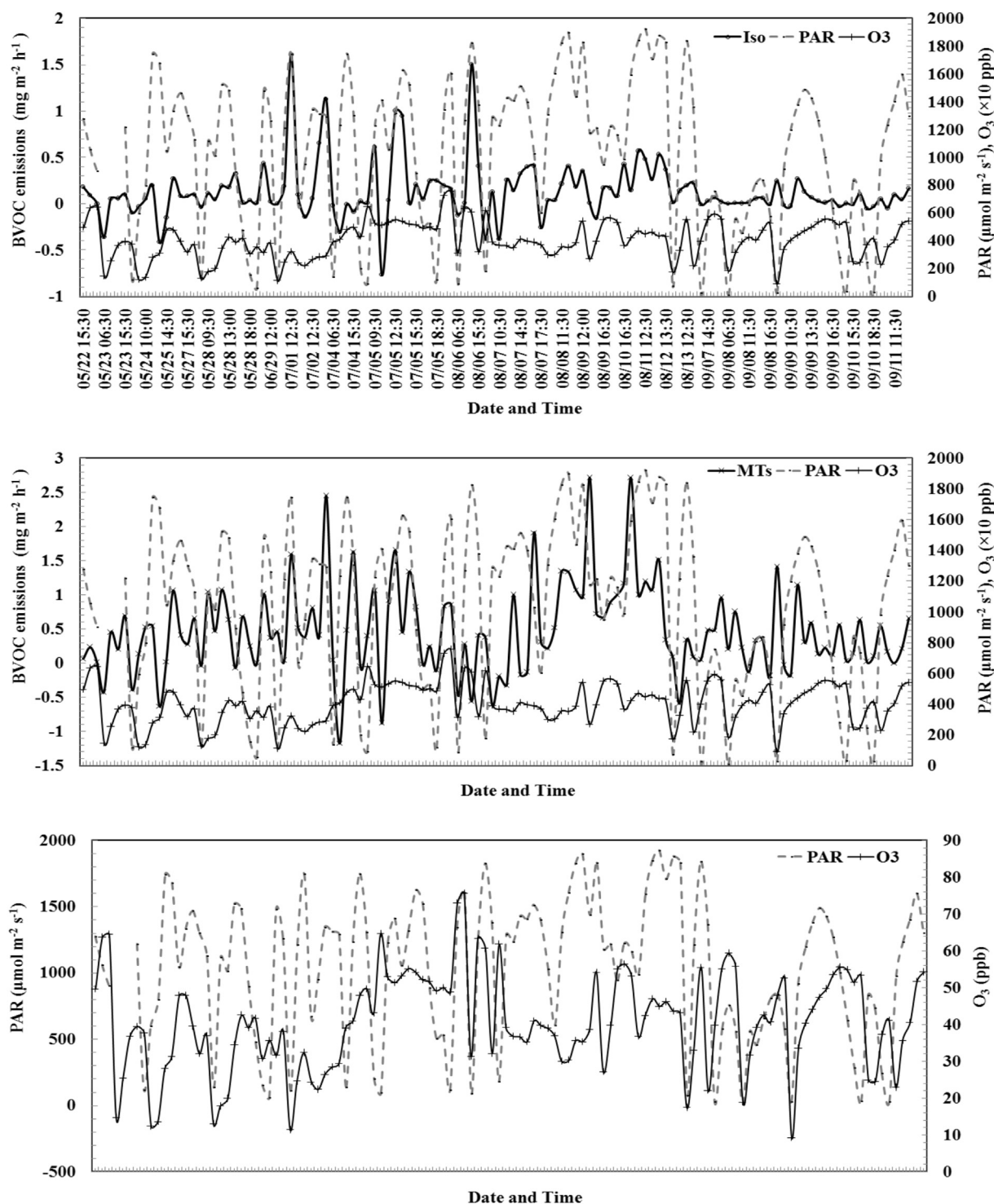


Fig. 5. BVOC emission fluxes and ozone concentration, PAR during 2013 at the subtropical plantation site. The x-axes of Fig. 5 are the same.

($n = 191$) for the lower level, respectively, which indicated that there are nonlinear relationships between O₃ and BVOC concentrations associated with other factors, such as solar UV and visible radiation, NO_x, OH radicals, ozone transport from other areas (Bai and Wang, 2001; Bai et al., 2006; Calfapietra et al., 2013).

Average and median BVOC concentrations (average, median, ppb) for normal and daily statistical results, PAR (μmol m⁻² s⁻¹), temperature (°C), S/Q, WV (hPa) and O₃ concentrations (ppb)

during different periods were given in Tables 3b and 4b.

Similarly, the relations between the concentrations of BVOCs at different levels and O₃, and BVOC fluxes and O₃ were calculated (Table 7). Stronger correlations were found between concentrations than for the fluxes for isoprene, but not for monoterpenes. For all O₃ levels, O₃ and isoprene showed higher negative correlations than with monoterpenes, which were associated with higher UV, PAR, T, and WV, reflecting the chemical and photochemical reactions

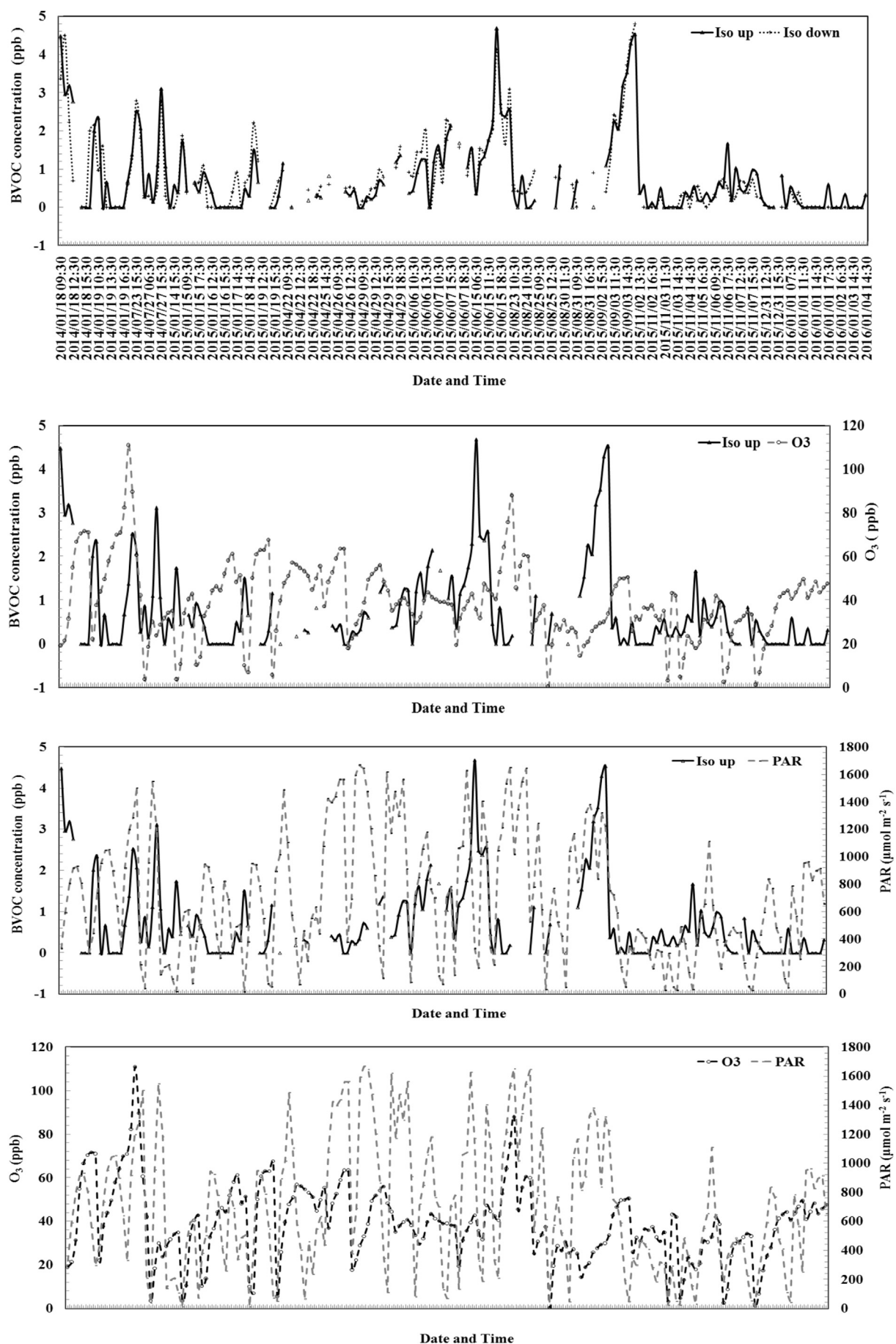


Fig. 6. Concentrations of isoprene at up and down levels, O₃ and PAR during 2014 and 2015 campaign. The x-axes of Fig. 6 are the same.

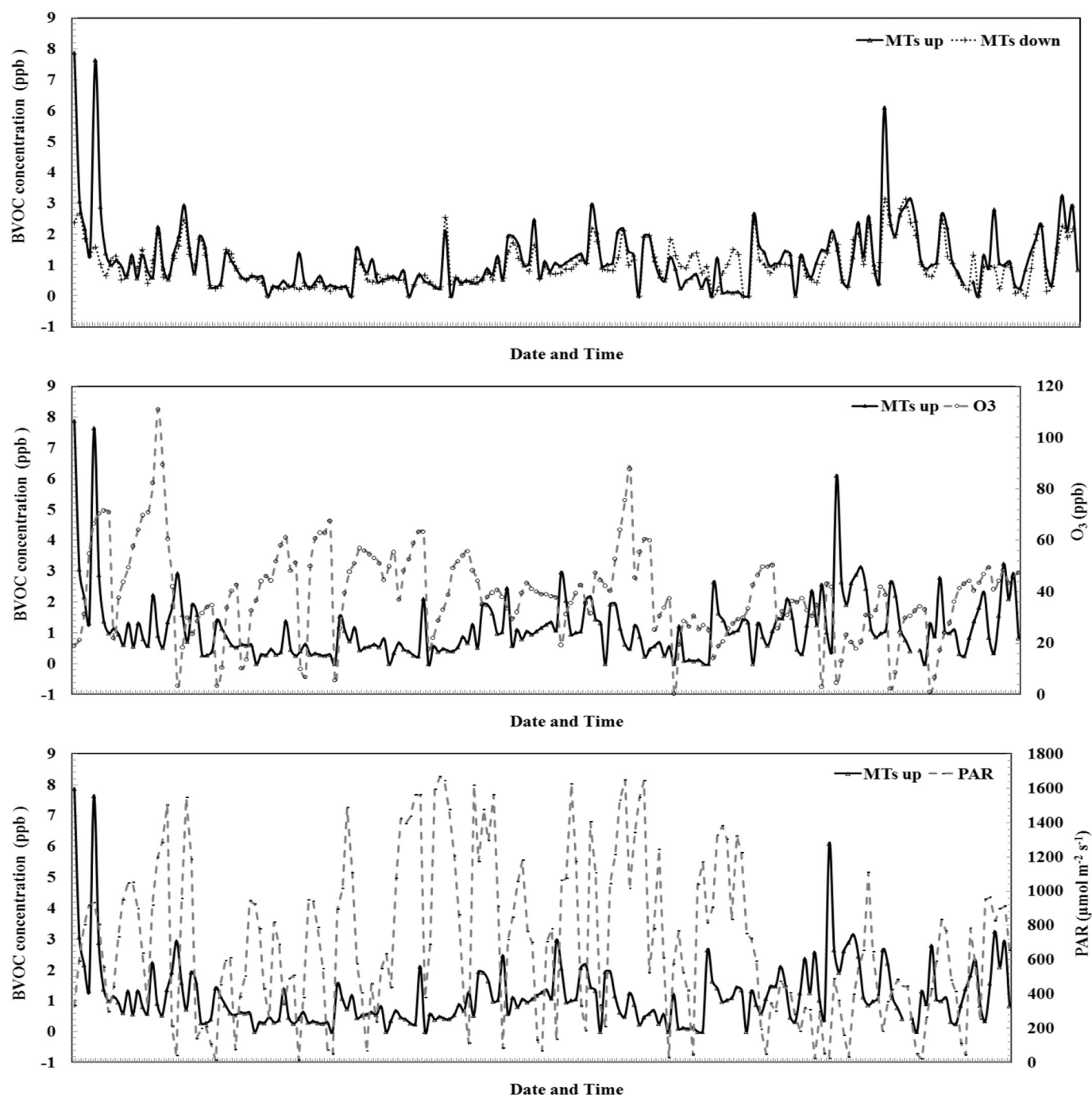


Fig. 7. Concentrations of monoterpenes at up and down levels, O_3 , and PAR during 2014 and 2015 campaign. The x-axes of Figs. 6 and 7 are the same.

between O_3 and BVOCs, but not for O_3 and BVOC emissions. This demonstrates the need to consider not only BVOC emissions, but also their concentrations. The concentrations of monoterpenes were higher than isoprene at both levels by 30%–70% and 0–35% for sample periods D, E, and F, respectively. Isoprene concentrations in this subtropical pine plantation were several ppb, which was similar to that measured in Dinghushan biosphere reserve, Guangdong province (Bai et al., 2001).

The mean concentrations of NO_2 and NO_x from 6:00 to 19:00 at period F were 1.31 and 1.90 ppb, respectively. The ratio of BVOCs to NO_x ($BVOCs/NO_x$) was 1.64 and 1.41 for up and down levels during period F, respectively.

3.5. Comparison of the statistical values of BVOC emissions and concentrations

To evaluate different statistical values, i.e., period averages and their ratios for daily mean and normal average of BVOC concentrations (Tables 4b–Table 3b) were calculated, and all relative bias for each species was less than 5%.

The ratios of period averages for daily mean and normal average of BVOC emissions (Tables 4a–Table 3a) were calculated, and their average was 1.06, ranged from 0.62 to 1.28, which was greater than the corresponding concentration ratio, reflecting the difference in observational error between flux and concentration.

Table 5

Correlation coefficients of emission fluxes ($\text{mg m}^{-2} \text{h}^{-1}$) of isoprene, monoterpenes (R_1 , R_2 , R_3), and all BVOCs with O_3 concentrations, the average of all parameters for different O_3 situations (a: $\text{O}_3 > 55$ ppb, b: $\text{O}_3 > 50$ ppb, c: $\text{O}_3 > 40$ ppb) during 2013 campaigns. The new parameters in Table 5 are: Solar ultraviolet radiation, UV (Wm^{-2}), relative humidity RH (%).

O_3	R_1	R_2	R_3	Iso	MTs	UV	PAR	S/Q	T	RH	WV	O_3	n
a	−0.117	−0.063	−0.131	0.204	0.507	20.0	1030.7	0.598	32.7	60.2	28.9	60.9	16
b	0.035	0.017	0.032	0.164	0.487	20.4	1044.8	0.606	33.4	60.1	30.2	56.8	32
c	0.058	0.039	0.056	0.153	0.491	22.1	1113.0	0.592	33.1	60.8	30.1	51.3	59

Table 6

Correlation coefficients of emission fluxes of isoprene, monoterpenes (R_4 , R_5 , R_6), and all BVOCs with O_3 concentrations, the average of all parameters for different O_3 situations (d: $\text{O}_3 > 55$ ppb, e: $\text{O}_3 > 50$ ppb, f: $\text{O}_3 > 40$ ppb) during 2014 and 2015 campaigns.

O_3	R_4	R_5	R_6	Iso	MTs	UV	PAR	S/Q	T	RH	WV	O_3	n
d	−0.545	−0.636	−0.662	−0.215	−0.057	20.6	1021.0	0.664	25.8	64.5	23.9	66.6	23
e	−0.230	−0.444	−0.424	−0.193	0.058	18.6	919.0	0.688	24.4	66.4	22.2	61.6	35
f	0.112	0.021	0.061	−0.052	0.334	17.0	795.2	0.689	23.7	70.5	22.2	52.2	79

Table 7

Correlation coefficients of concentrations of isoprene, monoterpenes at up and down levels (R_7 , R_8 , up, down) with O_3 concentrations, the concentrations of isoprene and monoterpenes at up and down levels (up, down) the average of all parameters for different O_3 situations (d: $\text{O}_3 > 55$ ppb, e: $\text{O}_3 > 50$ ppb, f: $\text{O}_3 > 40$ ppb) during 2014 and 2015 campaigns.

O_3	R_7	R_8	Iso	MTs	UV	PAR	T	RH	WV	O_3
d	−0.673, −0.520	−0.300, 0.019	0.542, 0.760	0.719, 0.737	20.6	1021.0	25.8	64.5	23.9	66.6
e	−0.592, −0.566	−0.078, 0.094	0.472, 0.659	0.720, 0.687	18.6	919.0	24.4	66.4	22.2	61.6
f	−0.320, −0.410	0.240, 0.242	0.521, 0.585	0.875, 0.784	17.0	795.2	23.7	70.5	22.2	52.2

3.6. BVOC emissions in different ecosystems in China

To fully recognize BVOC emission characteristics in different representative ecosystems in China, a summary of measured emissions is given in Table 8. In comparison with other ecosystems in China, isoprene emission was the lowest and monoterpene emissions were the highest in this subtropical *Pinus* plantation. In comparison to a subtropical bamboo forest, isoprene emissions were lower and monoterpene emissions were higher in this subtropical *Pinus* plantation in each sampling season (Bai et al., 2015a and this study).

3.7. Other factors affecting BVOC emissions

Apart from the main controlling factors, PAR, temperature, other factors may influence BVOC emissions. In 2014, a biomass burning smoke was blown to the flux tower from the west during 12:00–12:30 on 23 July, and there was a rain event during the sampling period at 12:00–12:30 on 26 July, BVOC emissions and atmospheric conditions can be seen from Table 9. Compared to 12:00–12:30, 25 July, the influence from the biomass burning was found during 12:00–12:30 on 23 July, isoprene emission decreased

and monoterpene emissions increased, total BVOC emissions increased by $0.340 \text{ mg m}^{-2} \text{h}^{-1}$ (about 20%), which was associated with a PAR decrease of $303.7 \mu\text{mol m}^{-2} \text{s}^{-1}$, T and WV increase by 3.4°C and 4.8 hPa , respectively, O_3 concentration increased by 50.3 ppb (~83%), corresponding to an increase of BVOC emissions. During the rain event, ozone concentration decreased by 18.5 ppb (~31%), which was associated with a PAR decrease of $1288.9 \mu\text{mol m}^{-2} \text{s}^{-1}$, T and WV increase by 4.8°C and 3.1 hPa , respectively. In another example, BVOC emissions and O_3 were also influenced by biomass burning smoke during 17:00–17:30, on 2 Nov., 2015 (Table 9). Isoprene emission decreased and monoterpene emissions increased, total BVOC emissions increased by $0.231 \text{ mg m}^{-2} \text{h}^{-1}$ (~96%), which was associated with a PAR decrease by $146.6 \mu\text{mol m}^{-2} \text{s}^{-1}$, T and WV increase by 2.1°C and 0.3 hPa , respectively. An O_3 concentration decrease was expected, but instead it increased by 0.7 ppb , along with the increase of BVOC emissions. There was also rain during 9:00–9:30, 12:00–12:30, on 6 November 2015, O_3 decreased by 11.5 ppb (~39%), which was associated with a slight PAR increase by $53.8 \mu\text{mol m}^{-2} \text{s}^{-1}$, T and WV increased by 8.9°C and 12.7 hPa , respectively, compared to the average of the same parameters during 10:00–10:30, 11:00–11:30, and 12:00–12:30, without rain on 3 November 2015.

Table 8

Average (avg) and maximum (max) measurements of above canopy fluxes ($\text{mg m}^{-2} \text{h}^{-1}$) of isoprene and monoterpenes at different ecosystems in China.

Sites	isoprene		Monoterpenes		measuring period	References
	avg	max	avg	Max		
China Grassland	0.77				June–Sep., 2002; Sep., 2003	Bai et al. (2003)
China tropical forest	1.0				July 2002	Bai et al. (2005)
China subtropical forest		0.215		0.313	Fall 2010	Baker et al. (2005)
China temperate forest	1.275	4.775	0.195	1.061	19 June to 30 June 2010	Situ et al. (2013)
China subtropical Lei bamboo forest	0.95	10.32	0.010	0.176	7 July 2012 to 19 Jan., 2013	Bai et al. (2015a)
China subtropical Lei bamboo forest	2.81	10.32	0.011	0.121	7 July to 13 July 2012	Bai et al. (2016)
China subtropical pine plantation	0.137	1.610	0.474	2.711	22 May to 11, Sep., 2013	Bai et al. (2016)
China subtropical pine plantation	−0.001	1.938	0.357	3.995	1 Jan., 2014 to 4 Jan., 2016	This study

Table 9

BVOC emission fluxes ($\text{mg m}^{-2} \text{h}^{-1}$), PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$), temperature ($^{\circ}\text{C}$), S/Q (scattering factor), WV (water vapor pressure at the ground, hPa) and O_3 concentrations (ppb) during different sampling periods.

	12:00–12:30, 23 July 2014	12:00–12:30, 25 July 2014	12:00–12:30, 26 July 2014	16:00–16:30, 2 Nov., 2015	17:00–17:30, 2 Nov., 2015	10:00–15:30, 22 Apr., 2015
event	Smoke		rain		smoke	fluorescence
isoprene	0.308	0.779		0.096	0	0
monoterpenes	1.704	0.893		0.145	0.472	0.693
PAR	1195.5	1499.2	210.3	194.4	47.9	1013.1
T	36.5	33.2	28.4	15.7	13.5	20.8
WV	40.1	35.3	32.2	15.4	15.1	18.6
S/Q	0.76	0.61	0.97	0.79	0.98	0.79
O_3	110.9	60.6	42.1	49.8	50.5	44.3
	10:00–16:30, 26 Apr., 2015		Avg in 10:00–12:30, 3 Nov., 2015		Avg in 9:00–12:30, 6 Nov., 2015	
event					Rain	
isoprene	–0.154		0.089			
monoterpenes	–0.169		0.610			
PAR	1376.3		371.6		425.4	
T	26.1		15.4		24.3	
WV	23.7		15.9		28.6	
S/Q	0.62		0.98		0.94	
O_3	52.0		29.8		18.2	

During the *Pinus* flowering period in April 2015, 5 samples were collected during 10:00–16:30 on 22 April, and a fragrant odor was noted during all sampling periods on that day. Five samples collected during 9:00–13:30 on 26 April, without a noticeable fragrant odor was selected for comparison. Isoprene and monoterpene emissions increased by 0.154 and 0.862 $\text{mg m}^{-2} \text{h}^{-1}$, respectively, total BVOC emissions increased by 1.016 $\text{mg m}^{-2} \text{h}^{-1}$, which was associated with PAR decrease by 363.3 $\mu\text{mol m}^{-2} \text{s}^{-1}$, T and WV decrease by 5.3 $^{\circ}\text{C}$ and 5.1 hPa, respectively, O_3 decreased by 7.8 ppb ($\sim 18\%$), corresponding to the increase of BVOC emissions. It should be recognized that the O_3 decrease was likely caused by the atmospheric conditions, i.e., lower PAR, temperature, water vapor, for example, compared to that during 12:00–12:30, 23 July 2014 (Table 9).

According to the above examples during the campaign, additional factors likely influence BVOC emissions and O_3 chemical and photochemical formation and destruction including PAR energy, water vapor related with OH radical production, and S/Q (atmospheric substances), which may be important controlling factors and play integrated and complicated roles in BVOC + O_3 chemistry and photochemistry.

There were clear inverse correlations between isoprene and monoterpene emissions and S/Q for most atmospheric situations in 2013 campaign (Figs. 1 and 2), revealing higher GLPs in the atmosphere attenuate PAR and lead to lower BVOC emissions. But, there were a few cases in which isoprene and monoterpene emissions peaked concurrently with S/Q peaks at low S/Q values, e.g., emission and S/Q values were 0.57 and 0.34 for isoprene at 11:30 on 11 Aug., 1.00 and 0.50, and 2.71 and 0.50 for monoterpenes at 12:30 on 7 Aug., and at 14:30 on 9 Aug., respectively, which could imply SOA formation from BVOC oxidation. More careful investigations are necessary to understand the interactions between isoprene and monoterpene emissions and S/Q, i.e., the relations between BVOC emissions and SOA formation under different S/Q levels in the future.

4. Summary and conclusions

Whole ecosystem terpenoid emissions were measured using an REA system and a gradient technique in a subtropical *Pinus* plantation in Taihe county, Jiangxi province, China, from 22 May 2013 to 4 January 2016. BVOCs emitted from this coniferous plantation in

2013 consisted of isoprene (21.2%), α -pinene (51.5%), camphene (2.4%), β -pinene (9.1%) and limonene (13.0%). Monoterpenes are the dominant emission category (71.6%). Isoprene and monoterpene emissions showed diurnal variations with the highest emissions in midday and the lowest emissions in the early morning and late evening. BVOC emissions exhibited seasonal variations, higher in summer and lower in winter. Interannual variation of BVOC emissions was also observed. Mean annual isoprene, monoterpenes and total BVOCs emissions in 2015 decreased by 0.163, 0.129, 0.292 $\text{mg m}^{-2} \text{h}^{-1}$, respectively, which were associated with the decreases of 346.0 $\mu\text{mol m}^{-2} \text{s}^{-1}$ for PAR, 10.2 $^{\circ}\text{C}$ for temperature, 7.5 hPa for water vapor, respectively, and the increase of S/Q, 0.17. Isoprene and α -pinene emission peaks occurred at about the same time as the temperature maximum, and usually a half hour to 3 h later than PAR maximum.

The average emission factors for the entire campaign calculated by MEGAN and EMBE models were 0.71 and 1.19 for isoprene, and 1.39 and 1.65 $\text{mg m}^{-2} \text{h}^{-1}$ for monoterpenes, respectively. Isoprene emission was the lowest and monoterpene emissions were the highest in this subtropical *Pinus* plantation in comparison to other ecosystems measured in China.

O_3 concentrations above the canopy level showed diurnal variations. There were not strong correlations between O_3 concentrations and either BVOC emissions or BVOC concentrations. The evident influences of biomass burning and fluorescence on BVOC emissions, as well as O_3 were observed. BVOC emissions and O_3 increased during the biomass burning was associated with increases of total BVOC emissions and O_3 . With fluorescence, both isoprene and monoterpene emissions increased. The relations between O_3 concentrations and BVOC emissions are likely complicated and dependent on atmospheric conditions, i.e. UV, PAR, temperature, and oxides of nitrogen. More detailed studies including modeling are needed to understand the relationship between O_3 and BVOCs chemistry and photochemistry.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2017.05.002>.

References

- Atkinson, R., Arey, J., 2003. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. *Atmos. Environ.* 37, 197–219.
- Bai, J.H., 2011. Analysis of ultraviolet radiation in clear skies in Beijing and its affecting factors. *Atmos. Environ.* 45 (38), 6930–6937.
- Bai, J.H., 2013. Photosynthetically active radiation loss in the atmosphere in North China. *Atmos. Pollut. Res.* 4 (4), 411–419. <http://dx.doi.org/10.5094/APR.2013.047>.
- Bai, J.H., Wang, M.X., 2001. The primary study on the regularity of atmospheric photochemical process for surface ozone. *Clim. Environ. Res.* 6 (1), 91–102.
- Bai, J.H., Wang, M.X., Graham, J., Prinn, R.G., Kong, G.H., Huang, Z.L., 1999. The analysis for the variation characteristics of surface ozone and NO_x in Dinghushan Station. *Acta Sci. Circumstantiae* 19 (3), 262–265.
- Bai, J.H., Wang, M.X., Graham, J., Prinn, R.G., 2001. A study of the nonmethane hydrocarbons at subtropical forest, Part II: diurnal variation. *Clim. Environ. Res.* 6 (4), 456–466.
- Bai, J.H., Wang, M.X., Hu, F., Greenberg, J.P., Guenther, A.B., 2002. Analyzing method on biological volatile organic compounds. *Adv. Atmos. Sci.* 19 (1), 64–72.
- Bai, J.H., Wang, G.C., Meng, Z.Y., Xu, X.B., 2006. Primary study on the characteristics of trace gas in clean area of North China. *Res. Environ. Sci.* 19 (6), 15–19.
- Bai, J.H., Lin, F.Y., Wan, X.W., Guenther, A., Turnipseed, A., Duhl, T., 2012. Volatile organic compound emission fluxes from a temperate forest in Changbai Mountain. *Acta Sci. Circumstantiae* 32 (3), 545–554.
- Bai, J.H., Guenther, A., Turnipseed, A., Duhl, T., 2015a. Seasonal and interannual variations in whole-ecosystem isoprene and monoterpene emissions from a temperate mixed forest in Northern China. *Atmos. Pollut. Res.* 6.
- Bai, J.H., Duhl, T., Hao, N., 2015b. Biogenic volatile compound emissions from a temperate forest, China: model simulation. *J. Atmos. Chem.* <http://dx.doi.org/10.1007/s10874-015-9315-3>.
- Bai, J.H., Duhl, T., Yu, S.Q., Wang, B., Hao, N., 2015c. Simulation of BVOC emissions in a subtropical bamboo forest in China. *Ecol. Environ. Sci.* 24 (12), 1923–1937.
- Bai, J.H., Guenther, A., Turnipseed, A., Duhl, T., Yu, S.Q., Wang, B., 2016. Seasonal variations in whole-ecosystem BVOC emissions from a subtropical bamboo plantation in China. *Atmos. Environ.* 124, 12–21.
- Baker, B., Guenther, A., Greenberg, J., Goldstein, A., Fall, R., 1999. Canopy fluxes of 2-methyl-3-buten-2-ol over a ponderosa pine forest by relaxed eddy accumulation: field data and model comparison. *J. Geophys. Res.* 104, 26,107–26,114.
- Baker, B., Bai, J., Johnson, C., Cai, Z., Li, Q., Wang, Y., Guenther, A., Greenberg, J., Klinger, L., Geron, C., Rasmussen, R., 2005. Wet and dry season ecosystem level fluxes of isoprene and monoterpenes from a southeast Asian secondary forest and rubber tree plantation. *Atmos. Environ.* 39 (2), 381–390.
- Calfapietra, S., Fares, F., Manes, A., Morani, G., Sgrigna, F., Loreto, F., 2013. Role of Biogenic Volatile Organic Compounds (BVOC) emitted by urban trees on ozone concentration in cities: a review. *Environ. Pollut.* <http://dx.doi.org/10.1016/j.envpol.2013.03.012>.
- Chameides, W.L., Lindsay, R.W., Richardson, J., Kiang, C.S., 1988. The role of biogenic hydrocarbons in urban photochemical smog: atlanta as a case study. *Science* 241, 1473–1475.
- Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M.O., Artaxo, P., Maenhaut, W., 2004. Formation of secondary organic aerosols through photooxidation of isoprene. *Science* 303, 1173–1176.
- Duhl, T.R., Gochis, D., Guenther, A., Ferrenberg, S.M., Pendall, E., 2013. Emissions of BVOC from lodgepole pine in response to mountain pine beetle attack in high and low mortality forest stands. *Biogeosciences* 10, 483–499. <http://dx.doi.org/10.5194/bg-10-483-2013>.
- Fry, J.L., Draper, D.C., Barsanti, K.C., Smith, J.N., Ortega, J., Winkler, P.M., Lawler, M.J., Brown, S.S., Edwards, P.M., Cohen, R.C., Lee, L., 2014. Secondary organic aerosol formation and organic nitrate yield from NO₃ oxidation of biogenic hydrocarbons. *Environ. Sci. Technol.* 48 (20), 11944–11953.
- Greenberg, J.P., Guenther, A., Zimmerman, P.R., Baugh, W., Geron, C., Davis, K., Helmig, D., Klinger, L.F., 1999a. Tethered balloon measurements of biogenic VOCs in the atmospheric boundary layer. *Atmos. Environ.* 33, 855–867.
- Greenberg, J.P., Guenther, A.B., Madronich, S., Baugh, W., Ginoux, P., Druilhet, A., Delmas, R., Delon, C., 1999b. Biogenic volatile organic compound emissions in central Africa during the Experiment for the Regional Sources and Sinks of Oxidants (EXPRESSO) biomass burning season. *J. Geophys. Res.* 104, 30,659–30,671.
- Greenberg, J.P., Guenther, A., Harley, P., Otter, L., Veenendaal, E.M., Hewitt, C.N., James, A.E., Owen, S.M., 2003. Eddy flux and leaf-level measurements of biogenic VOC emissions from mopane woodland of Botswana. *J. Geophys. Res.* 108 (D13), 8466. <http://dx.doi.org/10.1029/2002JD002317>.
- 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, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. *J. Geophys. Res.* 100, 8873–8892.
- Guenther, A., Baugh, W., Davis, K., Hampton, G., Harley, P., Klinger, L., Vierling, L., Zimmerman, P., 1996. Isoprene fluxes measured by enclosure, relaxed eddy accumulation, surface layer gradient, mixed layer gradient, and mixed layer mass balance techniques. *J. Geophys. Res.* 101, 18555–18567.
- Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.L., Geron, C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (model of emissions of gases and aerosols from nature). *Atmos. Chem. Phys.* 6, 3181–3210.
- 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.* 5 (6), 1471–1492.
- Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., Wilson, J., 2005. Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* 5, 1053–1123. <http://www.atmos-chem-phys.net/5/1053/2005/>.
- Lamb, B., Pierce, T., Baldocchi, D., Allwine, E., Dilts, S., Westberg, H., Geron, C., Guenther, A., Klinger, L., Harley, P., Zimmerman, P., 1996. Evaluation of forest canopy models for estimating isoprene emissions. *J. Geophys. Res.* 101 (D17), 22787–22797.
- Lee, A., Goldstein, A.H., Keywood, M.D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N.L., Flagan, R.C., Seinfeld, J.H., 2006. Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes. *J. Geophys. Res.* 111 <http://dx.doi.org/10.1029/2005JD006437>.
- Liu, Y.F., Song, X., Yu, G.R., Sun, S.M., Wen, X.F., Chn, Y.R., 2005. Seasonal dynamics of CO₂ fluxes from subtropical plantation coniferous ecosystem. *Sci. China Ser. D. Earth Sci.* 48 (Suppl. I), 123–132.
- Liu, Y.F., Yu, G.R., Wen, X.F., Wang, Y.H., Song, X., Li, J., Sun, X.M., Yang, F.T., Chen, Y.R., Liu, Q.J., 2006. Seasonal dynamics of CO₂ fluxes from subtropical plantation coniferous ecosystem. *Sci. China D Earth Sci.* 49 (Suppl. II), 99–109.
- Ma, Z.Q., Liu, Q.J., Xu, W.J., Li, X.R., Liu, Y.C., 2008. A preliminary study on biomass of woodwardia japonica community under a coniferous plantation in subtropical China. *J. Plant Ecol.* 31 (1), 88–94 (in Chinese).
- Mark, P., Zhang, L., 2009. China's Forestry Resource Inventory, Gain Report Number. CH9132.
- Situ, S., Guenther, A., Wang, X., Jiang, X., Turnipseed, A., Wu, Z., Bai, J., Wang, X., 2013. Impacts of seasonal and regional variability in biogenic VOC emissions on surface ozone in the Pearl River Delta region, China. *Atmospheric Chemistry and Physics* 13 (23), 11803–11817.
- Yu, J.Z., Cocker III, D.R., Griffin, R.J., Flagan, R.C., Seinfeld, J.H., 1999. Gas-phase ozone oxidation of monoterpenes: gaseous and particulate products. *J. Atmos. Chem.* 34, 207–258.
- Yu, G.R., Wen, X.F., Li, Q.K., Zhang, L.M., Ren, C.Y., Liu, Y.F., Guan, D.S., 2005. Seasonal patterns and environmental control of ecosystem respiration in subtropical and temperate forests in China qianyanzhou changbai. *Sci. China Ser. D. Earth Sci.* 48 (Suppl. I), 93–105.