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Seasonal and interannual variations in whole-ecosystem isoprene and monoterpene emissions from a temperate mixed forest in Northern China

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ABSTRACT

Measurements of BVOC emissions, meteorological parameters, and solar radiation were carried out in a temperate forest, China during the summer seasons in 2010 and 2011. Terpenoid emissions were measured using the Relaxed Eddy Accumulation (REA) technique on an above-canopy tower. Isoprene contributed 79.1% and 82.0% of terpenoid emissions in 2010 and 2011 summer. The monoterpene emissions were dominated by α -pinene, contributing 6.3% and 12.2% of the total terpenoid emissions in 2010 and 2011 summer. Terpenoid emissions exhibited strong diurnal variations. Isoprene and monoterpene emissions maxima typically occurred a few hours after the noon PAR peak and coincided with the daily temperature maximum. During 2011 summer, the mean isoprene emission flux ($\text{mg m}^{-2} \text{h}^{-1}$) was 0.889, mean total monoterpene emission flux was 0.143. Emission factors, representing the emission expected at a temperature of 30 °C, for this site were $0.32 \text{ mg m}^{-2} \text{h}^{-1}$ for total monoterpenes and $4.3 \text{ mg m}^{-2} \text{h}^{-1}$ for isoprene. The observations were used to evaluate the isoprene and monoterpene emission magnitude and variability predicted by the MEGANv2.1 model. Canopy scale isoprene and monoterpene emission factors based on these observations fall within the range of emission factors assigned to locations within 50 km of the site by the MEGANv2.1 emission model. When using the site specific landcover data for the site, the measured emission factors are 12% for isoprene and 20% for monoterpenes lower than the MEGANv2.1 emission factors. MEGANv2.1 predicts that variations in light intensity should result in significant changes in isoprene emissions during the study but this was not evident in the observations. Observed diurnal, seasonal and interannual variations in isoprene and monoterpene emissions were strongly correlated with air temperature which was the dominant driving variable for MEGANv2.1 during the study period. The observed temperature response for isoprene and monoterpenes is similar to the temperature sensitivity of the MEGANv2.1 response functions.

Keywords: Biogenic volatile organic compounds, emission flux, isoprene, monoterpene, emission model

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1. Introduction

Emissions from the biosphere dominate the global total volatile organic compounds (VOCs) entering the atmosphere (Singh and Zimmerman, 1992; Lathiere et al., 2006). The annual global non-methane biogenic VOCs (BVOCs) flux is estimated to be about 1 000 Tg, dominated by isoprene (53%) and monoterpenes (15%; Guenther et al., 2012). BVOCs are important precursors for O₃ formation in the troposphere (e.g. Chameides et al., 1988; Monson and Holland, 2001; Atkinson and Arey, 2003). Organic peroxy (RO₂) and HO₂ radicals formed during the photooxidation of biogenic and anthropogenic VOCs react with NO to form NO₂. The photodissociation of NO₂ then leads to net O₃ formation. By influencing OH radical and O₃ in chemical and photochemical processes, BVOCs play important roles in the oxidative capacity of the atmosphere. They also provide condensable oxidation products in gases, liquids and particles, e.g., secondary organic aerosol (SOA) and peroxyacyl nitrates (Yu et al., 1999; Claeys et al., 2004; Kanakidou et al., 2005) that can act as cloud condensation nuclei and affect radiative transfer through the atmosphere (Monson and Holland, 2001; Atkinson and Arey, 2003; Fowler et al., 2009; Spracklen et al., 2011). BVOC emissions are a chief uncertainty in calculating the production of important atmospheric constituents like tropospheric ozone and SOA, reflecting either imperfect chemical

oxidation mechanisms, uncertain emission estimates, or both (Spracklen et al., 2011).

Leaf- and branch-level enclosure measurements have been carried out at field sites in China, including an Inner Mongolia grassland, Xishuangbanna tropical forest, Dinghushan subtropical forest, and urban landscapes in Shenzhen, Beijing, Hong Kong, Pearl River Delta (Li et al., 1994; Shao et al., 1994; Zhang et al., 1994; Bai et al., 1998; Mou et al., 1999; Yang et al., 2001; Klinger et al., 2002; Wang et al., 2002; Bai et al., 2003; Wang et al., 2003; He et al., 2004; Bai et al., 2006; Geron et al., 2006; Situ et al., 2009; Tsui et al., 2009; Huang et al., 2011; Wang et al., 2011; Situ et al., 2013) and these are the primary basis for emission factors used in biogenic emission models (Tie et al., 2006; Guenther et al., 2012). There have also been a few above-canopy flux measurements to evaluate biogenic emission model estimates but only for a short period of time (Baker et al., 2005; Situ et al., 2013). BVOC emission rates and fluxes measured in China and other sites have been used to parameterize BVOC emissions in regional and global models but there are few measurements available for evaluating these model emission estimates and their uncertainties. Additionally, most of these investigations have used branch or leaf-level enclosure techniques which have some disadvantages such as disturbing the plants (possibly causing artificial emissions bursts), and altering the

surrounding environment including solar radiation, temperature, and water vapor (Guenther et al., 2006). Emission rates measured using enclosures need to be corrected to the atmospheric conditions outside of the chamber because of differences in PAR, temperature, and water vapor concentrations inside and outside of the chamber (Bai and Baker, 2004). China's forests cover 195 million hectares over many climatic zones with a forest stocking volume of 13.7×10^9 cubic meters (Mark and Zhang, 2009). Investigations of BVOC emissions are needed for major representative ecosystems in China, to obtain accurate BVOC emission rates, to better understand BVOCs emission characteristics, including diurnal, day to day, seasonal and interannual variations.

The purpose of this study was to evaluate the isoprene and monoterpene emission magnitude and variability estimated by the widely used MEGANv2.1 emission model (Guenther et al., 2012). These field measurements were also intended to be used to refine emission models within China to help further our understanding of BVOCs' effects on atmospheric physics and chemistry and the implications for air quality and climate. In this study, we report seasonal and interannual canopy-level BVOC fluxes from a temperate mixed forest in the Changbai Mountains in Northeastern China ($42^\circ\text{--}46^\circ\text{N}$, $126^\circ\text{--}131^\circ\text{E}$) and compare them with MEGANv2.1 model simulations of BVOC emission. The forest area ($42^\circ\text{--}46^\circ\text{N}$, $126^\circ\text{--}131^\circ\text{E}$) is about 5.7×10^5 km², and covers over 30% of the region.

2. Site Description and Methods

Terpenoid (isoprene plus monoterpene) emission measurements were carried out at the Changbai Mountain Forest Ecology Research Station, Chinese Academy of Sciences ($42^\circ24'\text{N}$, $128^\circ6'\text{E}$, 738 m) during growing seasons in 2010 and 2011. The site is in an unmanaged mixture of deciduous broad-leaved and coniferous forest. The forest is a matured natural forest with multi-layer structure and understory coverage of 40%. At higher altitudes the ecosystems in this region include spruce, fir, and pine (1 100 to 1 700 m), birch, and larch forest (1 700 to 2 000 m) while lower altitudes (<600 m) are dominated by broadleaf forest with poplar and birch (Liu et al., 2002). The dominant trees at the site are *Pinus koraiensis*, *Tilia amurensis*, *Tilia mandshurica*, *Quercus mongolica*, *Fraxinus mandshurica*, *Acer mono* and *Acer mandshurica* contributing 19%, 19%, 8.9%, 17%, 14%, 13% and 9.0%, respectively, to the canopy cover in this landscape. *Pinus koraiensis* is the dominant monoterpene emitter at this site. The main shrubs are *Deutzia amurensis*, *Acer pseudosieboldiarum*, *Acer tegmentosum*, *Corylus mandshurica* with the herbs including *Carex* spp, *Brachybotrys paridiformis*, and *Equisetum hiemale* (Zou et al., 2001; Wu et al., 2005). LAI (Leaf Area Index) of Korean pine broad-leaved forest in the region of flux tower is 7.7 measured by Zhou et al. (2003) or 5.5 during the growing season measured by Guan et al. (2007). The mean forest canopy height is 26 m, the soil type of this area is composed of upland dark brown forest soil, and the average slope of this study site is about 2–4%. Annual mean temperature is 3.6 °C. Average annual precipitation is about 600–900 mm, mainly concentrated in June to August. A 62-meter micrometeorological tower was erected in the forest for CO₂ flux and meteorological measurements. The mean temperature, solar global radiation and monthly total precipitation are 17.8 and 16.9 °C, 488.7 and 535.8 W m⁻², 147.9 and 123.2 mm, respectively for 2010 and 2011 growing seasons (from June to September).

A Relaxed Eddy Accumulation (REA) system (Guenther and Hills, 1998; Baker et al., 1999; Greenberg et al., 2003) was used to collect air samples for estimating BVOC fluxes. The REA sampler segregated the sample flow, according to the vertical wind velocity measured by a sonic anemometer, into air samples consisting of updrafts and downdrafts that were collected separately into stainless steel cartridges filled with Tenax GR and Carboxograph 5TD. During each 100 ms period (i.e., 10 Hz), the measured vertical wind speed and direction was used to determine which cartridge to fill.

REA fluxes were estimated for thirty minute periods, corresponding to sample collection times for statistically meaningful samples (Guenther and Hills, 1998, Baker et al., 1999, Greenberg et al., 2003). The REA system, including a three-dimensional sonic anemometer (RM Young, Traverse City, Michigan, USA, Model 81000) measuring at 10 Hz, was located at the end of a 2-m boom positioned on a platform at a height of 32 m above ground level and approximately 8 m above the top of the canopy. The anemometer signal was sent to a data logger (Campbell Scientific, Logan Utah, USA, Model CR1000), which controlled fast solenoid valves that directed samples to either updraft or downdraft cartridges. When vertical wind speeds were below a threshold value ($\pm 0.6 \text{ m s}^{-1} \sigma_w$, where σ_w is the standard deviation of the vertical wind speed from the previous thirty minute period), sample air was collected on a third (neutral) cartridge. The ozone filter consisted of a glass fiber filter (Pall Corporation, USA) that was impregnated with potassium iodide. Lab. experiments showed that these filters can sufficiently remove ozone (<5 ppbv) from an ozone-rich air stream (100 ppbv) for approximately 35–40 Liters of sampled air, and that there are no significant losses of the major terpenes (α -pinene, β -pinene, limonene) when using a KI ozone filter. Filters were changed in the field well before this limit.

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, b is an empirical coefficient, and C_{up} and C_{down} are the concentrations of the BVOCs species of interest in the up and down cartridges, respectively. The empirical coefficient, b , was determined from the sensible heat flux measured with the sonic anemometer by conditionally sampling the sonic temperature and then inverting Equation (1) to determine b .

Solar global (Q) and direct radiation (D) were measured at the top of a building, located at the Changbai Mountain Forest Ecology Research Station. PAR (Photosynthetically Active Radiation) was measured with a LI-190SA Quantum Sensor with a relative error of less than $\pm 5\%$. The radiation sensors are about 1 km away from the measurement tower. The sampling frequency of solar radiation is 1 Hz. Solar scattered radiation (S) is derived from $Q - D$. Meteorological parameters (temperature, humidity) were also measured at the meteorological observation station (1.5 meters height) in the region of the Changbai Mountain Forest Ecology Research Station during the growing seasons in 2010 and 2011. The REA system also measures air virtual temperature. All solar radiation sensors were examined every morning before sunrise and cleaned as needed. More detailed information about the solar radiation system is given by Bai (2012).

Air samples were stored in a refrigerator at about 5 °C, and shipped to a laboratory at the National Center for Atmospheric Research (NCAR) in Boulder, CO, U.S.A. for analysis. During the shipping, all cartridges were sealed in a small and cold refrigerant box that was covered by aluminum foil paper. All cartridges were analyzed within 20–25 days after the collection. Samples were analyzed by thermally desorbing the adsorbent cartridges (Markes Unity Series 1 Thermal Desorber) onto a gas chromatograph equipped with both flame ionization and mass selective detectors (Agilent, GC7890 and MSD5975C). The procedures for sample analyses and calibrations have been described by Duhl et al. (2013) and Greenberg et al. (1999a, 1999b). Single concentration measurements have an uncertainty between 8–15% (Greenberg et al., 1999a) and the total uncertainty of the REA BVOC flux measurement techniques is about 25% (Guenther et al., 1996; Lamb et al., 1996).

Measurements were made in the 2010 and 2011 growing seasons during the experimental periods given in Table 1. The

sample numbers used for analyses of isoprene and monoterpenes were 14 and 18 for period A, 13 and 19 for period B, 12 and 17 for period C, 21 and 20 for period D, 19 and 18 for period E, 21 and 20 for period F, 17 and 17 period G, respectively. On some days samples were collected only at noon. On other days samples were collected every 3 hours from sunrise to sundown for a total of five samples. A total of 150 and 200 air samples were collected enabling estimates of 60 and 87 BVOC emissions in 2010 and 2011 growing seasons, respectively. Approximately 14% of the samples were not used in the analysis of isoprene fluxes in 2011 and monoterpene fluxes in 2010 and 2011 due to GC analytical problems and to eliminate periods of very low heat flux ($<0.01 \text{ m s}^{-1} \text{ K}$) or σ_w ($<0.1 \text{ m s}^{-1}$) which result in inadequate turbulence for valid flux measurements. Inadequate separation of isoprene from an unknown interfering compound resulted in a higher fraction of samples (35%) that could not be used to estimate isoprene fluxes in 2010. Table 1 indicates the number of samples that were used for each time period.

Table 1. BVOC emission flux sampling periods in summer 2010 and 2011

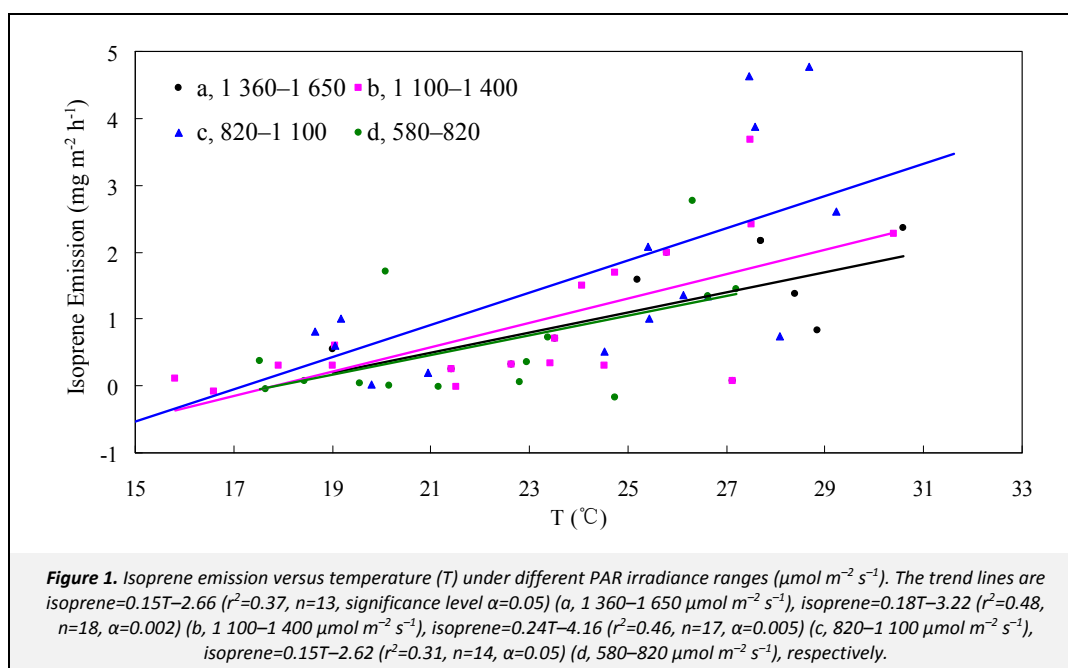
Year	Experimental Periods			
2010	A: 28 June– 9 July	B: 19 July– 30 July	C: 12 Aug.– 25 Aug.	
2011	D: 19 June– 30 June	E: 10 July– 16 July	F: 22 July– 29 July	G: 5 Sept.– 8 Sept.

The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGANv2.1) and other BVOC emission models provide inputs to regional air quality and global earth system models by combining an estimate of the emission capacity of a landscape, that is based on landcover variables, with an estimate of emission activity that may be related to variations in landcover, weather and other factors (Guenther et al., 2012). MEGAN is a canopy scale model and has an emission capacity that represents the expected emission at a standard set of conditions defined by Guenther et al. (2012), i.e., at an above canopy temperature of $30 \text{ }^\circ\text{C}$ and PAR of $1500 \mu\text{mol m}^{-2} \text{ s}^{-1}$ (Note: $1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$ is typically used as a standard condition for leaf level measurements and $1500 \mu\text{mol m}^{-2} \text{ s}^{-1}$ is used by Guenther et al. (2012) for canopy scale measurements). Emissions observed under experimental conditions are adjusted using emission activity algorithms to account for deviations from standard conditions during the sampling period. PAR and temperature are widely recognized as the

key factors controlling the emissions of isoprene and monoterpenes (Guenther et al., 1991; Penuelas and Llusia, 2001; Bai et al., 2006). For this study, we first ran MEGANv2.1 on a global scale using the default parameters and driving variables described by Guenther et al. (2006, 2012). In addition, we ran a single point version of MEGAN using site specific landcover and environmental conditions. We compared the observed canopy fluxes with the model predictions to investigate the ability of MEGANv2.1 to estimate isoprene and monoterpene emissions in this region. We examined both emission factors, the magnitude of the emission at standard conditions, and the variability associated with changes in environmental conditions.

3. Results and Discussion

Temperature, PAR and other parameters are often highly correlated which makes it difficult to investigate their individual influences under field conditions. To address this, we selected data subsets with a small range of PAR (or T) in order to investigate the relationship between terpenoid emissions and T (or PAR) within that range. We have used only the larger dataset from 2011 for this purpose. To reveal interactions between BVOC emissions with PAR (or T) as possible, observational data with low solar angle were not used for the analysis, because of the relatively large observational errors of solar radiation sensors and low VOC emission rates. Figure 1 shows the relationship between isoprene emission and temperature under different PAR irradiance ranges at $1360\text{--}1650$ (a), $1100\text{--}1400$ (b), $820\text{--}1100$ (c), and $580\text{--}820$ (d) ($\mu\text{mol m}^{-2} \text{ s}^{-1}$), respectively. The relationship between isoprene emission and temperature under PAR irradiance at $290\text{--}505$ ($\mu\text{mol m}^{-2} \text{ s}^{-1}$) is not shown, because only 4 groups of dataset can be found. Isoprene emission increased with temperature throughout the observed temperature range of about $16 \text{ }^\circ\text{C}$ to about $31 \text{ }^\circ\text{C}$. An emission increase of $\sim 16\%$ per $^\circ\text{C}$ was calculated for the four PAR condition subsets (situations a, b, c and d), which is similar to model predictions and observations from other sites (Bai et al., 2006; Guenther et al., 2012). The correlation coefficients (r^2) range from 0.31 to 0.48 for these three PAR data subsets. Based on the measurements, the response of isoprene emissions to temperature in different but narrow PAR ranges were linear, the best fits have been found, implying the nonlinear response of isoprene emissions to temperature in narrow PAR ranges turns to be linear.



The response of monoterpene emissions to temperature is shown in Figure 2, where the observations are categorized by PAR conditions. An increase of 0.5% to 1.5% per degree was observed for all PAR categories. These results suggest that the algorithms used in the MEGAN emission models are a reasonable approach for modeling terpenoid response to temperature and they are used below to normalize observed emissions to standard conditions. The increasing rates of isoprene with temperature were much higher than for monoterpenes at all PAR ranges (comparing Figure 1 and Figure 2), showing the strong temperature dependence for isoprene. As our observations did not suggest a strong light dependence, we also calculated the emission factor to account for light variations. If we did assume that isoprene emissions are light dependent and adjust emissions using the MEGAN (Guenther et al., 2012) light dependence algorithm and parameters then the estimated isoprene emission factor is 18% higher.

Taking 2011 data as an example, the relationship between terpenoid emissions and PAR, for narrow temperature ranges, indicated no significant correlation in most cases (coefficient of determination r^2 between 0.04 to 0.45). The linear increasing rates of isoprene emission with PAR were 0.0004 (18–20 °C), 0.0003 (20–22 °C), 0.0006 (22–24 °C), 0.0018 (24–26 °C), 0.0007 (26–28 °C), -0.0018 (28–31 °C), respectively. These variation patterns (low rate at low temperature ranges and higher rate at high temperature ranges) indicated a typical exponential function up to 24–26 °C, though most correlations were small at each narrow temperature region. Model G93 was also used to estimate isoprene [i.e., $C_i = I/(I_s \times C_T)$] responses to PAR in narrow temperature ranges and compared with the measurements (Guenther et al., 1993). In addition, the best fit functions are given here. For example, isoprene = 0.0019PAR - 0.7133 ($r^2 = 0.575$, $n = 5$) for measured and isoprene = 0.0035PAR - 1.3576 ($r^2 = 0.599$, $n = 5$) for G93 in 25–26 °C; isoprene = $1.3289e^{0.0002PAR}$ ($r^2 = 0.025$, $n = 4$) for measured and isoprene = $2.1335e^{0.0002PAR}$ ($r^2 = 0.018$, $n = 4$) for G93 in 26–27 °C; isoprene = $5.5764e^{-0.0009PAR}$ ($r^2 = 0.043$, $n = 8$) for measured and isoprene = $7.6802e^{-0.0009PAR}$ ($r^2 = 0.045$, $n = 8$) for G93 in 27–28 °C; isoprene = -0.0032PAR + 6.017 ($r^2 = 0.385$, $n = 4$) for measured and isoprene = -0.0037PAR + 6.963 ($r^2 = 0.394$, $n = 4$) for G93 in 28–29 °C. Generally, the responses of isoprene emission to PAR at narrow temperature ranges indicate good agreement for G93 and these measurements. The response of measured isoprene emission to temperature at a narrow PAR range (from 840 to 1 100, its average = $914.2 \mu\text{mol m}^{-2} \text{s}^{-1}$) was analyzed and isoprene emission = $2 \times 10^{-4} \times e^{0.34857T}$ (Figure 3a, $r^2 = 0.65$, $n = 10$). Seven out of twelve of the data categories were around noon, i.e., from 9:00 to 15:30. This exponential function is similar as reported by Harley et al. (1998). Similarly, the G93 simulated isoprene emissions (I/C_T) to temperature at the same narrow PAR range ($840\text{--}1\ 100 \mu\text{mol m}^{-2} \text{s}^{-1}$) was isoprene emission = $2 \times 10^{-4} \times e^{0.34887T}$ (Figure 3a, $r^2 = 0.65$, $n = 10$), which is close to the measured response. The averaged ratio of simulated to measured isoprene emission was 1.013 in the range of from 0.995 to 1.025. So, the G93 model simulates isoprene response to temperature very well. Under this situation, model G93 was also used to simulate normalized isoprene emission [i.e., $I_s = I/(C_i \times C_T)$] and its response to temperature was isoprene = $0.0076e^{0.21717T}$ ($r^2 = 0.42$, $n = 10$), which is close to the observational relationship (Figure 3b). These two curves displayed realistic and close response of isoprene emission to PAR and temperature under a little wider PAR and T ranges. The small difference between the response curves (and isoprene responses to PAR) may be caused by: (1) emission differences in leaf scale and canopy scale, (2) other factors, such as water vapor, precipitation, atmospheric conditions (e.g., S/Q) that influence the emission; plant information (such as plant species, tree age, etc.) associated with emission. All these plant and atmospheric factors are not considered in G93, and may need to be considered in future models. In more detail, isoprene emission at standard conditions ($T_s = 303.15 \text{ K}$ and $\text{PAR} = 1\ 000 \mu\text{mol m}^{-2} \text{s}^{-1}$) was estimated by using model G93 and above measurements, and was $3.04 \text{ mg m}^{-2} \text{h}^{-1}$. Similarly, monoterpene

emissions at a standard condition was acquired and $0.36 \text{ mg m}^{-2} \text{h}^{-1}$, $\beta = 0.178$ by using G93 algorithm $M = M_s \exp[\beta(T - T_s)]$, M and M_s are monoterpene emissions at a temperature T (K) and a standard temperature T_s . It should be noted that all parameters varied in this narrow PAR range, e.g., relative humidity (46.4%–77.9%, average = 59.3%), water vapor (14.8–23.9, average = 20.2 hPa), S/Q (solar scattered radiation to solar global radiation, 0.11–0.68, average = 0.32). A higher correlation ($r^2 = 0.45$) was found only for the case of temperatures between 24 and 26 °C. In that case isoprene increased with increasing PAR in agreement with MEGAN model predictions. The lack of correlation with PAR for other conditions may be due to the relatively small number of observations and the heterogeneity of the forest which results in a different number of isoprene emitting trees for different wind conditions. An analysis of spatial variability of the flux footprint in this mixed forest of broad-leaved and Korean pine showed that 76% of the flux measurements came from the relatively homogeneous mixed broad-leaved and Korean pine forests to the northwest to southwest of the tower, and the source areas of the maximum footprint were located in the range of 100–400 m southwest (Zhao et al., 2005). Given the lack of observed correlation between terpenoid emissions and PAR at this site, we neglected the isoprene PAR response algorithms while calculating emission factors.

In 2011, the main terpenoid species observed as emissions from this forest were isoprene (4.78 – -0.05), α -pinene (0.54 – -0.37), β -pinene (0.13 – -0.12), camphene (0.12 – -0.04), carene (0.12 – -0.18), and limonene (0.15 – -0.24). The numbers in the parentheses are emission ranges, and emission unit is $\text{mg m}^{-2} \text{h}^{-1}$. Similarly, in 2010, the main observed emissions were isoprene (2.35 – -0.65), α -pinene (0.21 – 0), β -pinene (0.07 – 0), camphene (0.06 – 0), carene (0.05 – 0), and limonene (0.20 – 0). Table 2 and Figure 4 show average measured terpenoid emissions, PAR, and temperature (T). Other parameters are reported for current and future analysis: (1) S/Q , scattered radiation to solar global radiation, is an indicator of total amounts of atmospheric constituents in the atmosphere; (2) E' (water vapor pressure at the ground, hPa) describes water amount in the atmosphere and the dynamic exchange between atmosphere, plants, and soil.

Isoprene in 2010 summer comprised 79.1% (in average) of total terpenoid emissions, ranging from 73.7% in June/July to 93.6% in August. α -pinene, constituting 6.3% of total emissions, was the dominant monoterpene; the other terpenes each contributed less than 3.0%. In 2011 summer, isoprene consisted of 82.0% of total terpenoid emissions and ranged from 73.2% in September to 87.7% in July. In terms of fluxes, α -pinene was the dominant monoterpene, consisting of 12.2% of the total terpenoid flux. The remaining 5.8% was comprised of β -pinene, camphene, carene, and limonene. Generally, isoprene and monoterpenes displayed evident seasonal variations, i.e., higher in June and July.

Variations in isoprene and monoterpene emission fluxes, PAR and temperature in 2011 summer are shown in Figure 5. All of the variables tend to be correlated but not all of the time.

As expected, the diurnal pattern in isoprene and monoterpene emissions includes a morning increase, an afternoon maximum, and a decrease in the evening. Isoprene and monoterpene emission maxima tended to appear 1 to 3 hours later than maximum PAR and coincided with maximum temperature. The delay between maximum solar insolation and temperature is due to the process of solar energy transmitting to the surface, converting to longwave energy, and then heating the atmosphere through sensible and latent heating. This phenomenon has also been observed at other sites (e.g., Berninger, 1994; Bai et al., 2008). The stronger correlation between terpenoid emission maxima and temperature, rather than PAR, agrees with the general patterns discussed above.

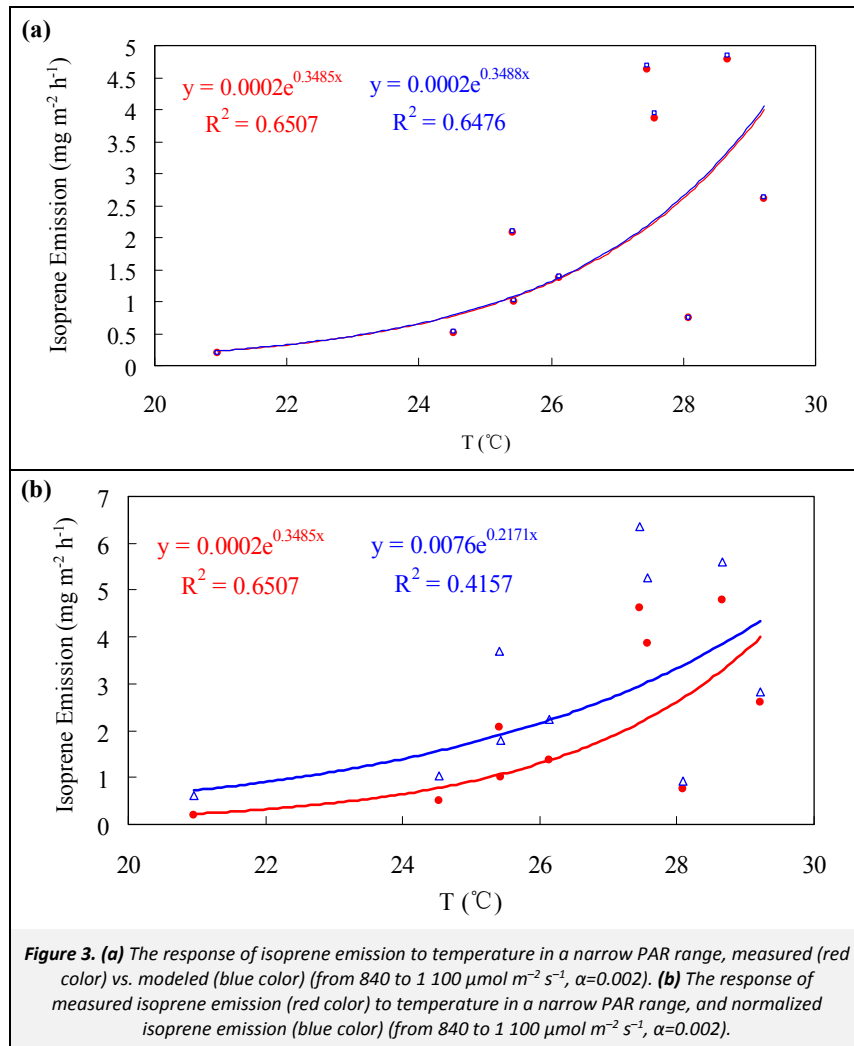
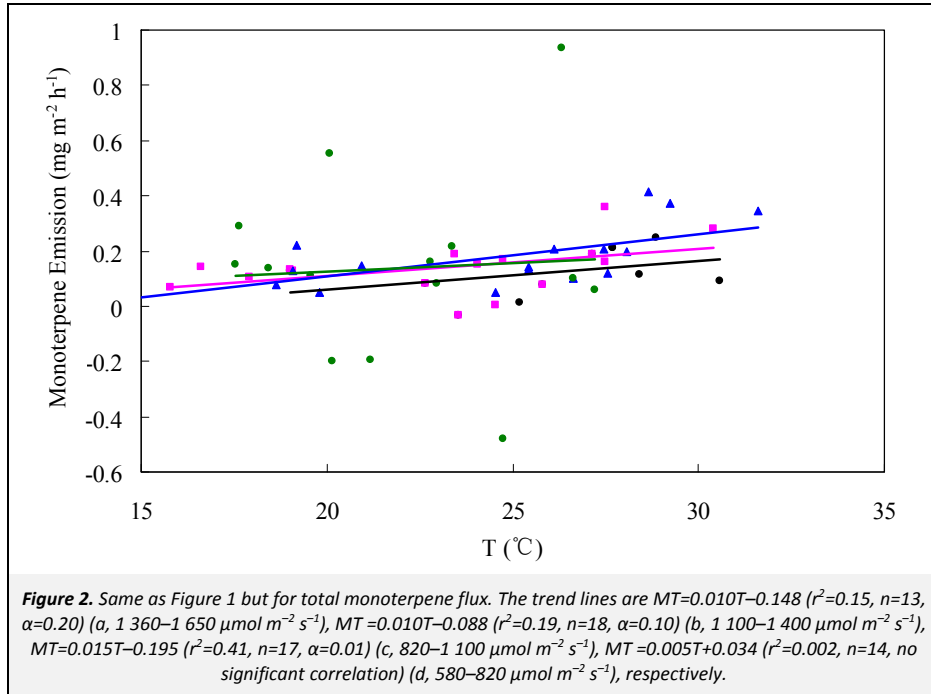


Table 2. Average terpenoid fluxes ($\text{mg m}^{-2} \text{h}^{-1}$), PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$), and temperature ($^{\circ}\text{C}$) during the experimental periods described in Table 1

	A (28 June–9 July, 2010)	B (19 July–30 July, 2010)	C (12 August–25 August, 2010)	D (19 June–30 June, 2011)	E (10 July–16 July, 2011)	F (22 July–29 July, 2011)	G (5 September–8 September, 2011)
Isoprene	0.624	1.024	0.472	1.28	1.06	0.918	0.181
α -pinene	0.065	0.076	0.052	0.092	0.058	0.094	0.049
β -pinene	0.019	0.020	0.017	0.013	0.008	0.010	0.005
Camphene	0.014	0.024	0.014	0.021	0.006	0.016	0.009
Carene	0.016	0.016	0.015	0.002	0.008	0.016	0.002
Limonene	0.026	0.057	0.027	0.014	-0.011	0.164	-0.007
Monoterpene	0.185	0.246	0.132	0.196	0.063	0.205	0.061
PAR	817.7	937.8	896.9	997.5	693.0	757.8	762.1
T	21.3	24.7	23.9	23.5	23.5	24.3	17.2
S/Q	0.78	0.59	0.53	0.35	0.18	0.29	0.46
E'	19.5	22.0	19.2	15.4	20.3	21.6	12.3

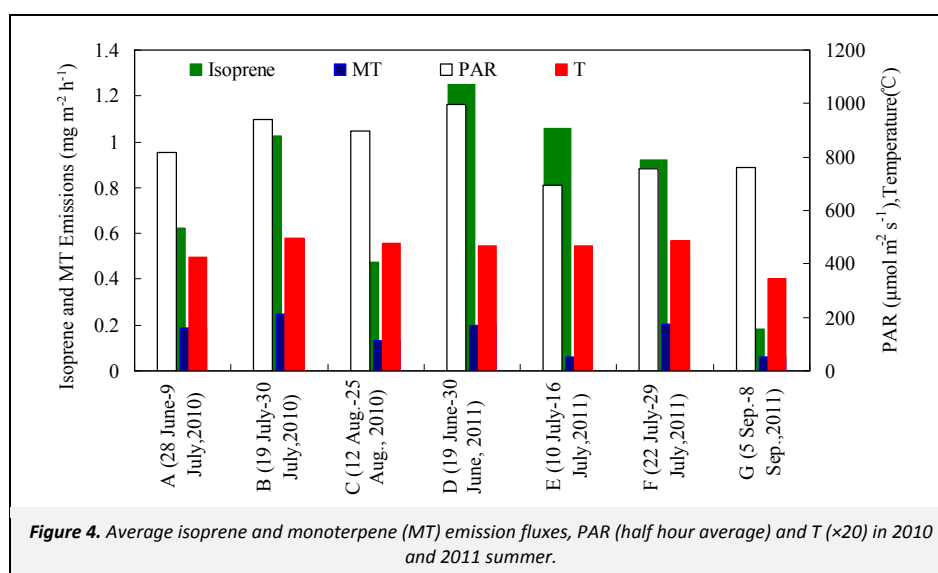


Table 2 shows that seasonal and interannual variations in terpenoid emissions were correlated with temperature which was generally correlated with PAR. Investigation of seasonal and interannual variations can be facilitated by comparing the average values for the sampling periods as compiled in Table 2. Table 3 shows the ratios of isoprene emissions, monoterpene emissions, PAR and temperature for the three sampling periods in 2010 and four sampling periods in 2011. We selected these observation periods in order to represent most of the whole growing seasons in 2010 and 2011. In general, mean monthly precipitations in 2010 and 2011 growing seasons (from June to September) were 147.9 and 123.2 mm, respectively. No significant drought was observed in Changbai Mountain region in 2011 growing season. Senescence occurred around the beginning of September for broadleaved trees. Isoprene flux was essentially constant all summer in 2011 until the last period (September) when it dropped concurrent with lower temperatures. In addition, the monthly precipitation decreased from 181.2 mm in Aug. to 48.2 mm in September, 2011. Monoterpene flux in 2011 was more variable and included a period of low emissions in summer. In both 2010 and 2011, seasonal variations in isoprene and monoterpene fluxes followed each other, and temperature, PAR, e.g., comparing late July 2010 (period B) to "late June" 2010 (period A) and late August 2010 (period C) to late July 2010 (period B); in addition, isoprene was more sensitive to PAR and T than monoterpenes. Isoprene and monoterpene fluxes were highest in late July 2010 as were temperature and PAR. Interannual variations could also be mainly explained by variations in PAR and temperature. Comparing late June 2011 (period D) to

late June 2010 (period A), isoprene and monoterpene emission both increased by 105.1% and 5.9%, respectively, along with an increase in PAR by 22.0% and temperature by 10.3%. Comparing late July 2011 (period F) to late July 2010 (period B), isoprene and monoterpene emission both decreased by 10.4% and 16.7%, respectively, along with a decrease in PAR by 19.2% and temperature by 0.4 $^{\circ}\text{C}$. Comparing late July 2011 (period F) to mid August 2010 (period C), there was an increase of isoprene and monoterpene fluxes by 99.5% and 55.3%, respectively, along with an increase in atmospheric water content (E') by 12.5% which may have led to increased water availability for plants. There was a slight temperature increase, 0.4 $^{\circ}\text{C}$, but this would not be expected to lead to such a large increase in emissions. In contrast, PAR decreased by -15.5%, S/Q decreased by -45.3%. A similar result was observed in the Inner Mongolia grassland (Bai et al., 2003), i.e., isoprene emission flux measured with a surface enclosure chamber (0.90 m \times 0.90 m \times 0.35 m) was highly correlated with water vapor content in a chamber ($r^2=0.62$, confidence level 0.001, $n=45$). These increases occurred even though there was a PAR decrease of 16% and stable T . Pegoraro et al. (2004) found increased isoprene emission with high vapor pressure deficit (VPD) under conditions of water stress. Potosnak et al. (2014) observed the influence of drought on whole canopy isoprene fluxes and concluded that mild drought will increase isoprene emissions, due to higher leaf temperatures driven by lower stomatal conductance, while stronger drought results in diminished isoprene emissions after photosynthetic declines. However, given that there was no drought observed at Changbai Mountain during this period, we know of no

mechanism that would lead higher atmospheric water vapor content to lead to higher emissions. Considering late August (period C) 2010 to late July 2010 (period B), isoprene and monoterpene fluxes were reduced by half and correlated with a water decrease, along with the stable PAR and *T*. Comparing late July 2011 (period F) to mid July 2011 (period E), the increase of *S/Q* corresponded to decreased isoprene emission, and a small increase in PAR, *T* and water. In addition to PAR, *T*, and water availability (e.g., Baker et al., 2005; Monson et al., 2007), other factors that have been shown to control BVOC emissions include CO₂ and stress (e.g., Harley et al., 1994; Monson et al., 2007; Fowler et al., 2009). During daytime, BVOC concentrations are controlled by BVOC emission, photochemical reactions and boundary layer dynamics. The utilization and consumption of UV and PAR by atmospheric constituents through OH radical are a basic energy source for BVOC photochemistry (Bai, 2009; Bai, 2011; Bai, 2012). The closer but different ratios of isoprene and monoterpenes concentrations in

different periods are likely due to differences in both emission and photochemistry.

To better understand “seasonal” effect to some extent (e.g. Grote et al., 2013), isoprene and monoterpene emissions in different periods at standard conditions (30 °C, 1 500 μmol m⁻² s⁻¹) were calculated using G93 and measured data in 2011, their averaged emission factors are shown in Table 4. Generally, the emission factors of isoprene and monoterpenes were the highest in June and lowest in September. Their emission factors varied with the “season”, the ratio of emission factor to their average was from 0.98 to 1.13 for isoprene and from 0.86 to 1.30 for monoterpenes, apart from G period, which was in autumn. i.e., the emission factor varied in the range of 15% for isoprene and 30% for monoterpenes. In addition, similar simulated seasonal effect of isoprene and monoterpene emissions can be seen in Figure 6a and 6b for 2010 growing season, Figure 6c and 6d for 2011 growing season.

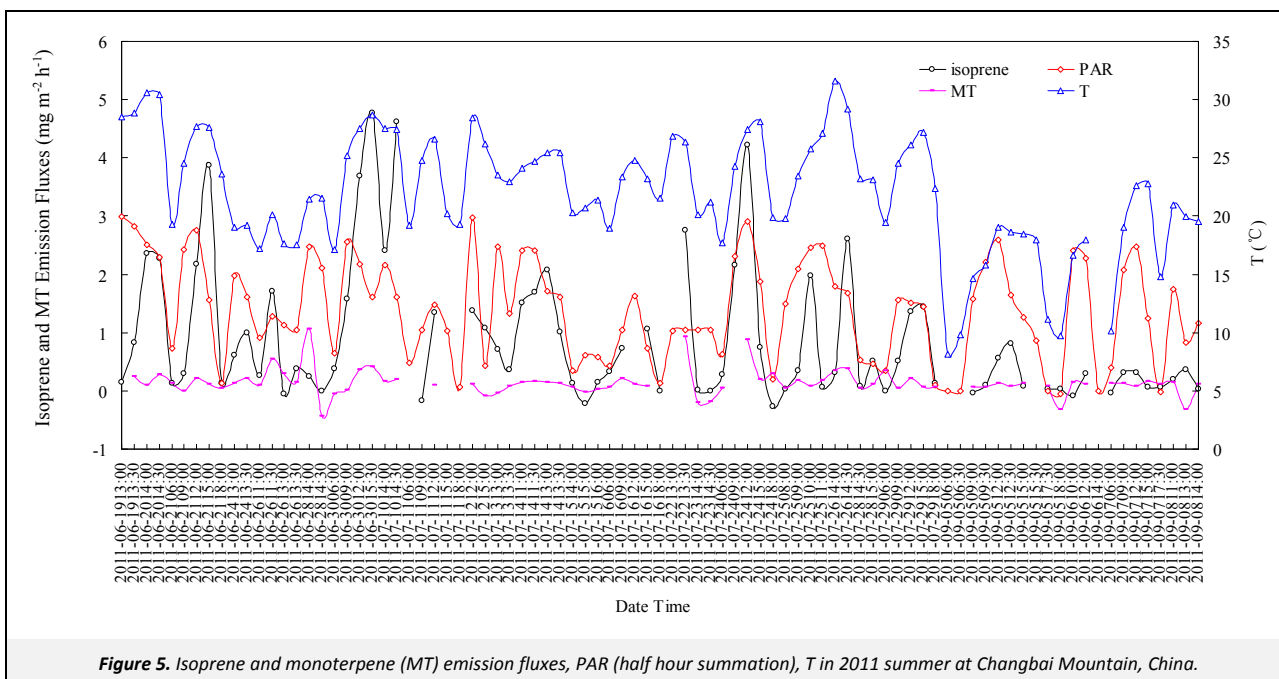


Figure 5. Isoprene and monoterpene (MT) emission fluxes, PAR (half hour summation), *T* in 2011 summer at Changbai Mountain, China.

Table 3. The ratios of averaged parameters between different time periods (A–early July (2010), B–late July (2010), C–mid August (2010), D–late June (2011), E–mid July (2011), F–late July (2011), G–early September (2011)). The ratios B/A, C/B, E/D, F/E, and G/F show seasonal variations while D/A, E/B and G/C, F/B, F/C show interannual variations

	Seasonal Variations					Interannual Variations				
	B/A	C/B	E/D	F/E	G/F	D/A	E/B	G/C	F/B	F/C
Isoprene	1.64	0.46	0.84	0.86	0.20	2.04	1.04	0.38	0.89	1.95
Monoterpenes	1.33	0.54	0.33	3.25	0.3	1.06	0.26	0.46	0.83	1.55
PAR (μmol m ⁻² s ⁻¹)	1.15	0.96	0.70	1.09	1.01	1.22	0.74	0.85	0.81	0.84
<i>T</i> (°C)	1.16	0.97	1.00	1.03	0.71	1.10	0.95	0.72	0.98	1.02
<i>S/Q</i>	0.76	0.90	0.51	1.61	1.59	0.45	0.31	0.87	0.49	0.55
E	1.13	0.87	1.32	1.06	0.57	0.79	0.92	0.64	0.98	1.13

Table 4. Emission factors (mg m⁻² h⁻¹) of isoprene and monoterpenes at standard conditions in 2011 summer

Experimental Periods	D: 19 June–30 June	E: 10 July–16 July	F: 22 July–29 July	G: 5 Sept.–8 Sept.	Average
Isoprene	3.889	3.364	3.456	2.367	3.443
Monoterpenes	0.458	0.325	0.304	0.306	0.353

Table 5 shows the emission fluxes of isoprene and monoterpenes measured at other sites in China. Our isoprene and monoterpene fluxes were 1.275 (4.775, maximum, the same hereinafter), 0.195 (1.061) $\text{mg m}^{-2} \text{h}^{-1}$, respectively, during 19 June to 30 June, 2010, ~6% lower for isoprene and ~50% higher for monoterpenes than the emissions measured by Karl et al. (2003) in a temperate forest in northern Michigan. The canopy isoprene flux at the Changbai site was higher than that measured in a rubber tree plantation in China during a wet season (Baker et al., 2005). At the Inner Mongolia grassland, isoprene emission fluxes measured by an enclosure chamber were 0.783, 0.624 and 0.377 $\text{mg m}^{-2} \text{h}^{-1}$ in June, August and September, 2002, respectively (Bai et al., 2003), averaging 0.594 $\text{mg m}^{-2} \text{h}^{-1}$ in the growing season (Table 5). In comparison with the results of the studies summarized by Unger et al. (2013), the isoprene flux observed at the Changbai site is higher than most other temperate forests although there are sites in Germany, U.S. and Canada that reported higher fluxes. It should

be noted that there are differences in measurement periods, plants, and atmospheric conditions (e.g., T , PAR, E , S/Q).

Isoprene and monoterpene emission fluxes at Dinghushan tropical forest, China were 0.03 (0.21) and 0.01 (0.31) $\text{mg m}^{-2} \text{h}^{-1}$, respectively, which were measured by REA technique during 17 Oct., 2010 to 30 March, 2011. Their details in measurements and evaluation of MEGAN are described by Situ et al. (2013). More BVOC emission measurements are needed at more sites and for local representative forests by REA technique, so as to acquire accurate BVOC emission data and then improve BVOC estimations in China (e.g., Li et al., 2013). More factors, including water vapor, SOA, scattering ability, e.g., S/Q factor, should be measured along with BVOC emission flux, because BVOCs are associated with photochemical formations of other gases, liquids, particles. An all-around point of view in investigating BVOC emission and their roles in GLP formation and energy transferring and consumption is very important (Bai, 2009; Bai, 2011; Bai, 2012).

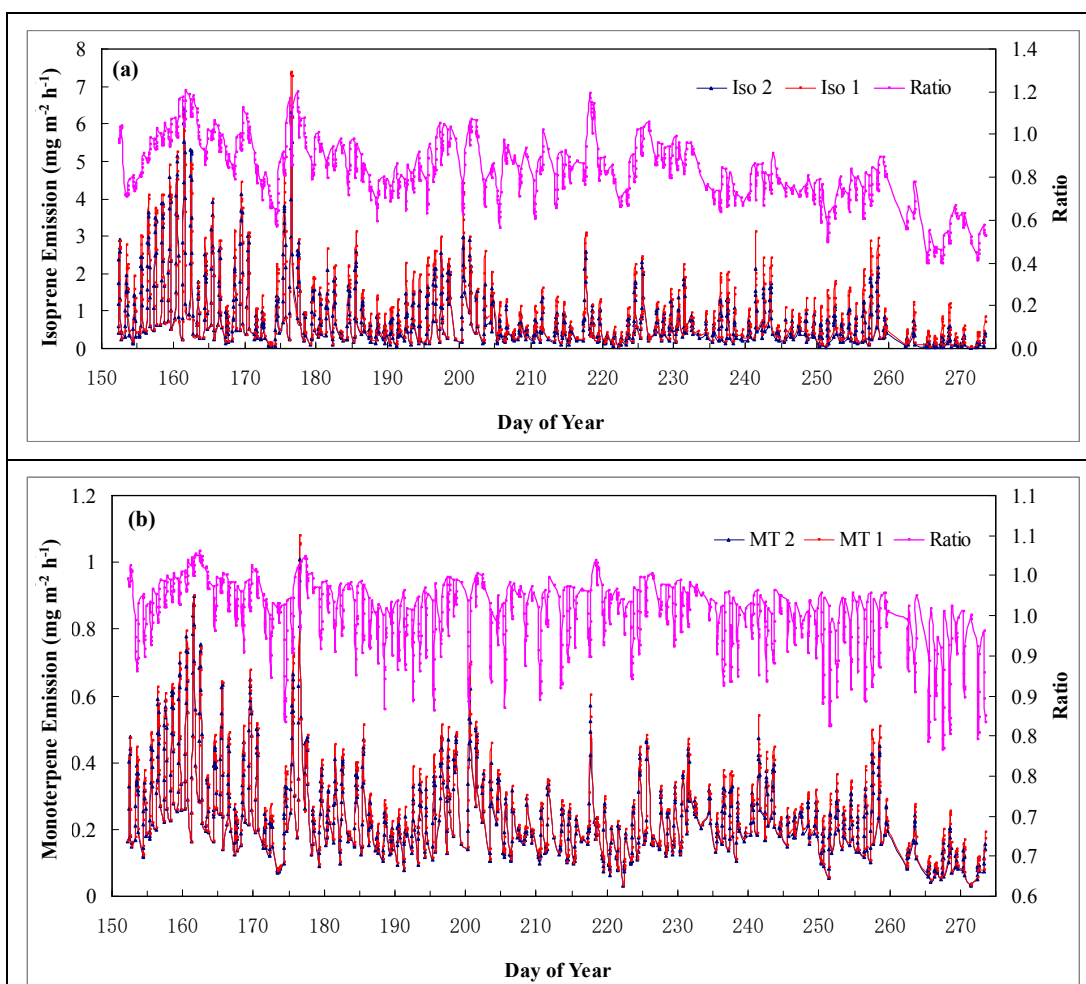


Figure 6. (a) MEGAN model results for Changbai Mountain forest for 2010, Case 1 (Iso 1): The simulated emissions depend on the instantaneous light and temperature, Case 2 (Iso 2): The simulated emissions depend on both the influence of the instantaneous light and temperature and the influence of the temperature and light of the past 10 days. The ratio of these two values (Iso 2/Iso 1) indicates the model's prediction of the influence of seasonal acclimation due to light and temperature. (b) Same as Figure 6a, but for monoterpenes (MT). (c) MEGAN model results for Changbai Mountain forest for 2011, Case 1 (Iso 1): The simulated emissions depend on the instantaneous light and temperature, Case 2 (Iso 2): The simulated emissions depend on both the influence of the instantaneous light and temperature and the influence of the temperature and light of the past 10 days. The ratio of these two values (Iso 2/Iso 1) indicates the model's prediction of the influence of seasonal acclimation due to light and temperature. (d) Same as Figure 6c, but for monoterpenes (MT).

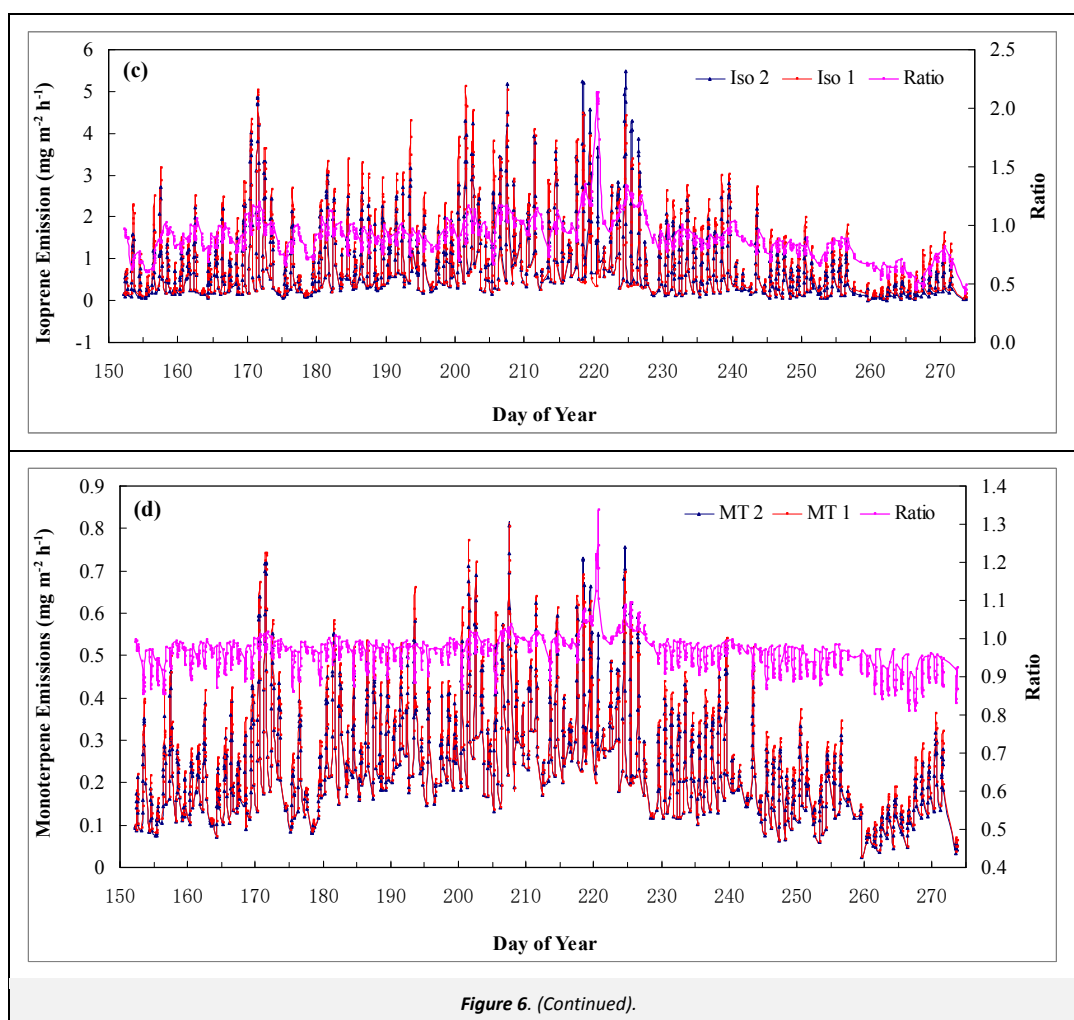


Figure 6. (Continued).

Table 5. Mean and maximum (max) measurements of above canopy fluxes ($\text{mg m}^{-2} \text{h}^{-1}$) of isoprene and monoterpenes at sites in China

Sites	Isoprene		Monoterpene		Measuring Period	References
	Mean	Max	Mean	Max		
China subtropical forest		0.215		0.313	Oct., 2010 to March, 2011	Situ et al. (2013)
China tropical forest	1.0				July, 2002	Baker et al. (2005)
China Grassland	0.594				June–September, 2002	Bai et al. (2003)
China temperate forest	1.275	4.775	0.195	1.061	19 June to 30 June, 2010	This study

Only one of the five dominant tree species at this site, *Quercus mongolica*, has been identified as a high isoprene emitter by Kim et al. (2005) based on enclosure measurements in Korea. *Quercus mongolica* has a 17% contribution the total canopy cover at the site which results in an isoprene emission factor of $4.1 \text{ mg isoprene m}^{-2} \text{h}^{-1}$ using the scaling up procedures of Guenther et al. (2006). This falls within the range of the values, 3.5 to $5 \text{ mg isoprene m}^{-2} \text{h}^{-1}$, found in the global MEGANv2.1 emission factor database (Guenther et al., 2012) for a 50 km region surrounding the site. The MEGAN land cover for this site is a mixture of vegetation types but dominated by temperate broadleaf and needle leaf trees. The MEGANv2.1 estimates are based on a global database of emission factor measurements and China provincial forestry statistics (Guenther et al., 2012). Using the emission factors in the global MEGANv2.1 database, *Pinus koraiensis* is the dominant monoterpene emitter at the site although the broadleaf trees together contribute about 25% of the total monoterpene emission. An emission factor of $0.4 \text{ mg monoterpenes m}^{-2} \text{h}^{-1}$ is estimated using the site specific landcover data.

The isoprene and monoterpene emission rate observations shown in Table 2 were adjusted for temperature using the approach described in Guenther et al. (2006) to estimate emission factors representative of an above-canopy temperature of 30°C . All of the observations described in Table 1 were used for this analysis. The average emission factor was $4.3 \text{ mg m}^{-2} \text{h}^{-1}$ for isoprene and $0.32 \text{ mg m}^{-2} \text{h}^{-1}$ for total monoterpenes. These values are within 10% (for isoprene) and 20% lower (for total monoterpenes) than the MEGANv2.1 emission model estimates based on site-specific landcover data which is within the uncertainties of these measurements. For comparison with leaf level measurements reported in the literature, we determined the canopy average leaf-level emission rates required for MEGANv2.1 to predict the observed above canopy emission rate resulting in estimated leaf level values of $14.9 \mu\text{g (g dry weight)}^{-1} \text{h}^{-1}$ for isoprene and $0.64 \mu\text{g (g dry weight)}^{-1} \text{h}^{-1}$ for monoterpenes. The impact of changes in BVOC emissions on regional air quality is highly dependent on regional distributions of other emission sources. Regional modeling studies of air quality in China have

investigated the impact of BVOC emissions in several parts of China and have found that the impact of increasing BVOC emissions on ozone is relatively small, and can be positive or negative depending on levels of anthropogenic pollutants (e.g. Situ et al., 2013). The impact on particles can be considerably greater especially in polluted regions (e.g. Wang et al., 2005; Hallquist et al., 2009).

4. Summary and Conclusions

Whole ecosystem terpenoid emissions were measured using an REA technique in a temperate forest in the Changbai Mountains of Jilin province, China, during growing seasons in 2010 and 2011. Solar radiation and meteorological parameters were also measured. The dominant terpenoid BVOCs emitted from this temperate forest were isoprene (consisting of 82.0% in 2011 summer and 79.1% in 2010 summer) and α -pinene (12.2% in 2011 summer and 6.3% in 2010 summer) with β -pinene, camphene, carene and limonene contributing the remainder. During the summer of 2011, the mean (range) isoprene emission flux was 0.889 (–0.267 – 4.78) $\text{mg m}^{-2} \text{h}^{-1}$, with values of 0.143 (–0.435 to 1.06) for monoterpenes. The average (and maximum) of emission fluxes ($\text{mg m}^{-2} \text{h}^{-1}$) for individual monoterpenes were 0.074 (0.537) for α -pinene, 0.009 (0.133) for β -pinene, 0.013 (0.117) for camphene, 0.007 (0.123) for carene, and 0.013 (0.525) for limonene, respectively. During the summer of 2010, the mean (range) isoprene emission flux was 0.711 (–0.654 – 2.353) $\text{mg m}^{-2} \text{h}^{-1}$, with values of 0.190 (0.005 to 1.056) for monoterpenes. The emissions of isoprene and monoterpenes had evident diurnal variations with lower emissions in the morning and late evening and the highest emissions in midday. Maximum isoprene and monoterpene emissions occurred at about the same time as maximum temperature, and usually 1 to 3 hours later than the PAR maximum. Under realistic atmospheric conditions, good agreement between terpenoid emissions and temperature was obtained at narrow PAR ranges. The responses of isoprene and monoterpene emissions to PAR, or T , water vapor, S/D at different periods in 2010 and 2011 indicated isoprene is more sensitive to PAR and T than monoterpenes, interannual variations could be explained by variations in temperature, the increase of isoprene and monoterpene emissions was correlated with an increase in atmospheric water content. Most of the observed seasonal and interannual variations could be explained by changes in temperature. The MEGANv2.1 model can represent variations in isoprene and monoterpene emissions at a canopy scale to some extent. The total monoterpene emission factor (0.32 $\text{mg m}^{-2} \text{h}^{-1}$) is about 7% of the isoprene emission factor (4.3 $\text{mg m}^{-2} \text{h}^{-1}$). These emission factors agree well with the emission factor values in the global database used to drive the MEGAN biogenic emission model.

Acknowledgments

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