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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 (mg m^{-2} 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 mg m^{-2} h^{-1} for total monoterpenes and 4.3 mg m^{-2} 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 O_3 formation in the troposphere (e.g. Chameides et al., 1988; Monson and Holland, 2001; Atkinson and Arey, 2003). Organic peroxy (RO_2) and HO_2 radicals formed during the photooxidation of biogenic and anthropogenic VOCs react with NO to form NO_2. The photo-dissociation of NO_2 then leads to net O_3 formation. By influencing OH radical and O_3 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°–46°N, 126°–131°E) and compare them with MEGANv2.1 model simulations of BVOC emission. The forest area (42°–46°N, 126°–131°E) is about 5.7×10^5 km^2, 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°24'N, 128°6'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 CO_2 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 Carbograph 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 (±0.6 m s^{-1} σ_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:

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

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 ±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