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A statistical approach for estimating representative emission rates of biogenic volatile organic compounds and their determination for 192 plant species/genera in China

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Abstract. To obtain more and accurate biogenic volatile organic compound (BVOC) emission rates for more plant species in China and further improve the accuracy of emission rates used in BVOC emission inventories, we conducted field measurements and developed a statistical approach for estimating representative emission rates. We performed field measurements of BVOC emissions from 50 plant species at nine locations in China using our established semi-static enclosure system. The emissions of 102 VOCs, including isoprene, α-pinene, β-pinene, and other VOC species, were analyzed with a custom-built online gas chromatography-mass spectrometry/flame ionization detector system. From the results, broadleaf trees were the greatest potential emitters of isoprene, while needle-leaf trees emitted more pinene. Shrubs had lower isoprene and pinene emission potentials, but higher emission potentials for other VOCs. Methyl methacrylate, isopropylbenzene, isopentane, acetone, ethane, propane, toluene, and xylene were the dominant species among other VOCs, probably with high emission intensities. Therefore, their emissions should be considered in future global and regional BVOC estimation studies. Next, we summarized our field measurements along with reported emission rates from China and abroad. The emission intensity categories were produced based on statistics, with more detailed categories, accurate emission rate intervals and representative rates compared to previous studies. The results showed that the BVOC emission intensities of plants displayed different categories, such as lowest, lower, low, moderate, high, higher, and highest. The isoprene emission rate intervals and representative rates were: lowest, 0.08–0.11 and 0.1 μg C gdw^{-1} h^{-1}; lower, 0.9–1.3 and 1.0 μg C gdw^{-1} h^{-1}; low, 5.2–6.5 and 5.8 μg C gdw^{-1} h^{-1}; moderate, 13.1–15.3 and 14.4 μg C gdw^{-1} h^{-1}; high, 31.1–37.0 and 33.6 μg C gdw^{-1} h^{-1}; higher, 67.2–75.1 and 70.1 μg C gdw^{-1} h^{-1}; and highest, 135.1–157.6 and 142.5 μg C gdw^{-1} h^{-1}. The monoterpene emission rate intervals and representative rates were: lowest, 0.08–0.11 and 0.1 μg C gdw^{-1} h^{-1}; lower, 0.17–0.22 and 0.2 μg C gdw^{-1} h^{-1}; low, 0.5–0.7 and 0.6 μg C gdw^{-1} h^{-1}; moderate, 1.2–1.5 and 1.4 μg C gdw^{-1} h^{-1}; high, 2.8–3.3

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and 3.0 μg C gdw^{-1} h^{-1}; and higher, 11.1–14.9 and 12.6 μg C gdw^{-1} h^{-1}. Using these established emission intervals, we determined the isoprene and monoterpene emission rates for 192 plant species/genera in China, including 30 dominant tree species, 149 shrub and grass genera, and 13 crop species. These estimations would be further improved by integrating larger quantities of rigorous field measurements from China in the future.

Keywords
BVOC; isoprene; monoterpene; semi-static enclosure system; emission rate; emission interval

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1 Introduction

China suffers from serious haze events and photochemical pollution, with enhanced atmospheric oxidation (Lou et al., 2010; Li et al., 2014; Xue et al., 2014; Huang et al., 2014; Zhang et al., 2015). Isoprene and monoterpenes are important precursors of tropospheric ozone (O_3) and secondary organic aerosol (SOA) (Guenther et al., 1999; Carslaw et al., 2010; Nozière et al., 2011; Sartelet et al., 2012). Therefore, it is essential to establish accurate isoprene and monoterpene emission inventories to support accurate air quality evaluations and effective decision-making regarding air pollution control in China.

It has been reported that simulated SOA and O_3 concentrations in air quality models are usually much lower than observations, especially in polluted regions and during pollution events (Hodzic et al., 2010). For example, SOA might be underestimated by 0–75% in models over an entire year in China (Jiang et al., 2012). This limitation of air quality models might be caused by underestimated emission inventories, especially biogenic volatile organic compound (BVOC) emission inventories. In the simulation evaluations, the input China's isoprene and monoterpene emissions produced by the Model of Emissions of Gases and Aerosols from Nature (MEGAN) were 9.3–16.85 and 4.49–4.9 Tg C yr^{-1}, respectively, which resulted in underestimations of SOA, O_3, and ambient isoprene concentrations in China (Fu et al., 2007, 2012; Geng et al., 2011; Jiang et al., 2012). Current BVOC emission inventories in China were varied, with isoprene ranging from 4.1 to 20.7 Tg C yr^{-1} and monoterpenes ranging from 1.8 to 4.9 Tg C yr^{-1} (Guenther et al., 1995; Klinger et al., 2002; Yan et al., 2005; Tie et al., 2006; Fu and Liao, 2012; Li et al., 2012; Li et al., 2013; Li and Xie, 2014; Stavrakou et al., 2014). Several studies greatly underestimated isoprene and monoterpene emissions in China. The uncertainties arose from emission rates, leaf biomass, vegetation cover data, meteorological variables, and emission algorithms. Underestimated emission rates might have been used in these emission estimations, resulting in underestimations of isoprene and monoterpene emissions in China (Zheng et al., 2010; Situ et al., 2014).

It is both important and challenging to estimate isoprene and monoterpene emission rates accurately when developing emission inventories. The emission rate sources and estimations in previous inventories varied, resulting in different results for individual plant species among studies. In addition, emission rate measurements for specific plant species and regions in China are rare. Different studies reported distinguished values with large uncertainties due to the use of different sampling techniques and sample sizes (Guenther et al., 1994). Uncertainty exists when selecting one emission rate from a single measurement or the mean of all measurements as the representative emission rate for the specific plant. Even if the best available observations were screened or conducted according to the criteria proposed by Niinemets et al. (2011), it would be still necessary to find a straightforward method to determine one emission rate value for a plant species when

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compiling an emission inventory. Therefore, instead of assigning one observation for each plant species, some studies have used emission categories to determine emission intensities and rates (Guenther et al., 1994; Simpson et al., 1999; Klinger et al., 2002; Wang et al., 2007). In this method, discrete emission categories (e.g., negligible, low, moderate, and high) were defined based on the emission intensity of vegetation, with a representative rate and a range of ±50%. For each plant species, the emission rate was determined based on the tendency of the reported emission rates to fall within certain categories. This method improved the accuracy of the final emission rates to a large extent; however, it had several limitations. For example, the process of determining emission categories, representative emission rates, and ranges was not straightforward, and lacked theoretical evidence. Furthermore, some studies used both distinct emission categories and representative values, resulting in different emission rates for specific plants. Some studies used coarse classifications of emission intensity, which might underestimate emission rates of plant species with high emission potentials. Table 1 shows the different isoprene emission categories used in several studies and the resulting emission rates for some plants with high emission potentials. Thus, it is essential to have detailed emission categories and accurate representative values and ranges to estimate emission rates accurately. Especially in China, where has a large vegetated land area and high species diversity, it becomes particularly important by using local measurements of emission rates from plants. Chinese researchers have conducted BVOC emission measurements in China, including the above-canopy emission flux and branch or leaf-level emission rates (e.g., Bai et al., 1994; Bai et al., 2012, 2015; Bao et al., 2014; Guo, 2012; Zhao et al., 1996; Zhao et al., 2004). However, BVOC emission rate measurements in China are relatively uncommon and have often been conducted using static enclosure systems, which introduced large errors into the measurements (Niinemets et al., 2011). In addition, isoprene and monoterpenes have often been the only VOC species measured in China, and there is a lack of measurements for other VOCs.

In this study, firstly, to obtain more and accurate BVOC emission rates for specific plant species in China, we conducted field measurements using our established semi-static emission enclosure technology and analyzed emissions of 102 VOCs using a custom-built gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID) system. Secondly, to further improve the accuracy of the emission rates applied to the emission inventories, we developed a theoretically effective approach to estimate emission rates. We summarized our field measurements and reported emission rates from China and abroad to establish emission intensity categories to determine the emission rates of 192 plant species/genera. The emission category intervals for isoprene and monoterpene were produced separately based on statistics, and included more detailed categories, accurate emission rate intervals and representative rates than previous studies. We estimated plant-specific emission rates based on the established emission intervals, and compared our results of

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several tree species with previous researches. Finally, we evaluated the quality of our measurements and estimations of representative emission rates.

2 Methodology

2.1 Field measurements

2.1.1 Enclosure system

We established a semi-static enclosure system to sample BVOC emissions from plants (Zimmerman, 1979; Lamb et al., 1985). This method improved the limitations of static enclosures, was simple to operate, and had lower environmental variations within the sampling chamber during the enclosure due to the induction of a large amount of zero air as a diluent into the enclosure within a short enclosure time (~10 min or less). Figure 1 shows a schematic of the semi-static enclosure system. To achieve a low residence time with a high enough concentration of BVOCs for sensitive chemical analysis, we used a branch enclosure. A polyvinylfluoride (PVF, Tedlar) bag with a 400-L volume (90 cm width × 160 cm length) was selected to enclose a healthy branch of a plant. The Tedlar bag was 50 μm thick, and was 90–95% transparent to photosynthetically active radiation (PAR) (Ortega et al., 2008). There was no production or adsorption of VOCs in the bag. The chamber was a rectangular bag with one open end and one port for the sampling line. The open end was sealed tightly with a Velcro strap around the trunk side of the branch, together with a temperature sensor and a zero air tube placed along the branch. The bag was carefully placed over the branch to minimize contact of the bag with foliage. After enclosing, the chamber was relatively airtight and had a certain volume of air inside the bag. The port of the bag was connected to fused-silica-lined SUMMA polished stainless steel canisters (3.2 L) with a polytetrafluoroethylene (PTFE, Teflon) tube for instantaneous sample collection. The canisters were cleaned with nitrogen (N_2) and evacuated to < 10 mtorr before sampling (Liu et al., 2008). The zero air was provided by the portable cylinder with synthetic air (79% N_2 and 21% O_2). The temperature inside the enclosure was measured using an HMP155A probe (Vaisala, Inc., Vantaa, Finland). PAR was measured with a quantum sensor (LI-190SB; LI-COR Biosciences, Inc., Lincoln, NE, USA). Owing to limitations of the field experiment, rotameters were used to monitor and control the flow rate of the zero air. Considering its relatively low accuracy, the flow rate had to be measured and calibrated with a primary air flow calibrator (Gilian Gilibrator-2; Sensidyne, Inc., St. Petersburg, FL, USA) at the beginning and end of each experiment.

To sample BVOCs using the semi-static branch enclosure system, after enclosing, ambient air was collected quickly as the background sample. Then, the bag was purged with zero air at a flow rate of 10 L min^{-1} for ~6 min. Next, the air flow rate was decreased to 2 L min^{-1} and the purge was continued for an additional ~3 min, which was expected to allow the air in the bag to be well mixed. Finally, air in the bag was collected as the emission sample. During the experiment, the start and end times of enclosure and each air purge stage were recorded, and temperature and PAR were monitored

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every minute. All leaves on the enclosed branch were collected and transported to the laboratory and weighed after drying at 70°C for 48 h. We assumed that the air in the bag had been mixed well in the enclosure, and that the volume and VOC concentration were constant during the emission sample collection. After the experiments, we confirmed that the enclosure had been relatively airtight, and the total volume of the residual air in the bag at the beginning of enclosure and the purged zero air was not large enough to cause gas to leak from the bag.

2.1.2 Analysis

The canister samples were transported to the laboratory for analysis as soon as possible to avoid loss of BVOCs due to their high reactivities. The analyses of the sampled VOCs were performed on a custom-built online GC-MS/FID (TH-PKU 300B; Wuhan Tianhong Instruments Co., Wuhan, China) (Liu et al., 2009; Yuan et al., 2012, 2013; Li et al., 2014, 2015). The two-channel system used dual columns and dual detectors to analyze C2–C11 VOCs simultaneously. It combined electronic refrigeration technology and the GC-MS/FID system to concentrate and analyze the VOC samples. The refrigeration system had an initial temperature of –160°C, which was achieved by compressing air. For each sample, 300 mL of air was concentrated when passing through the instrument at a flow rate of 60 mL min^{-1} after water and carbon dioxide removal. Then, the highly focused VOCs were quickly desorbed at 110°C by heating and transferred to the GC column for separation. The C2–C4 alkanes and alkenes were separated on a non-polar capillary column (PLOT-Al_2O_3, 15 m × 0.32 mm ID × 3 μm; J&W Scientific, Folsom, CA, USA) and quantified with FID. The C4–C10 compounds were separated on a semi-polar column (DB-624, 60 m × 0.25 mm ID × 1.4 μm; J&W Scientific) and quantified with a quadrupole MS detector.

For the quantification of C2–C4 hydrocarbons by FID, we used the external standard method. Meanwhile, we used the internal standard method for the GC/MS quantification of VOCs, using four compounds as internal standards: bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5, and bromofluorobenzene. Table 2 summarizes the full list of the 103 VOC species identified and quantified using certified VOC mixture standards: 56 nonmethane hydrocarbons (Environmental Technology Center, Ottawa, Canada), 63 compounds of TO-15 (Linde Electronics and Specialty Gases, Stewartsville, NJ, USA), and α- and β-pinene (KIN-TEK Laboratories, Inc., La Marque, TX, USA). The calibrations were performed using five to six concentrations, ranging from 0.4 to 10 ppbv with three standard gas mixtures. The correlation coefficients for the calibration curves were mostly > 0.99 for the VOCs. The precision of the system for VOCs ranged from 0.5% to 4%. The detection limits of the GC-MS/FID system for the various tested compounds were in the range of 0.01–0.09 ppbv.

2.1.3 Calculation of Emission rate

For each enclosure experiment, after determining the background and emission sample VOC

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concentrations, the emission rate was calculated with Equation (1):

$$ER = \frac{C \times (V + V_0) - C_0 \times V_0}{\Delta t \times B} \quad (1)$$

where ER is the emission rate (μg gdw^{-1} h^{-1}) of the VOC species under the experimental temperature and PAR conditions; C and C_0 are the VOC species concentrations (μg m^{-3}) in the emission and background samples, respectively; V is the total volume (m^3) of zero air purged into the enclosure bag; V_0 is the volume of dead air (i.e., residual air in the bag after enclosing but before purging zero air, m^3); Δt is the total enclosure time (h); and B is the dry weight (g dw) of the leaves on the enclosed branch.

In this study, we assumed that plants emitted no or negligible acetylene, so that the mass of acetylene in the background and emission sample was constant. Therefore, we estimated V_0 with Equation (2):

$$V_0 = \frac{V}{(C_b/C_s) - 1} \quad (2)$$

where C_b and C_s are the acetylene concentrations (μg m^{-3}) in the background and emission samples, respectively.

2.1.4 Sampling sites and plant species

We collected emission rate field measurements using the semi-static branch enclosure system at nine locations in China from May to October in 2014 and 2016. The sites were located in Beijing (Peking University, Jiufeng Mountain, Yunmeng Mountain, Wuling Mountain, and Beijing Gardening Research Institute), Hubei (Yunwu Mountain and Maan Mountain, Wuhan), and Sichuan (Longquan Mountain, Chengdu) provinces. To avoid excessive oxidation and loss of reactive compounds in the canisters, most locations were set far from anthropogenic sources. Mature and healthy plants and branches were selected for the BVOC emission measurements. The age of trees was not recorded due to lack of investigation and guidance from professionals. Table 3 lists the measured plant species at each location, including trees, shrubs, and vines. In total, we performed 67 experiments of 50 plant species. Due to the limitation of experiment equipment and field conditions, each plant species had one or two replicates of samples for BVOC emissions.

We selected sampling periods with no precipitation, low wind speed, higher visibility, and temperature and PAR close to the standard (i.e., temperature = 30°C, PAR = 1000 μmol m^{-2} s^{-1}). All the field measurements were conducted during the daytime, usually from ~10:00 am to 15:00 pm. Each enclosure experiment usually lasted for ~10 min. In most cases, the average temperature was 26–33 ℃ and PAR was 600–1300 μmol photons m^{-1} s^{-1}. For each enclosure experiment, the temperature variation in the bag was typically < 2 ℃.

2.2 Data processing

In this study, the emission rates measured using the semi-static branch enclosure system were taken at

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the branch level and were derived under the experimental environmental conditions, such as temperature and radiation. Therefore, first, we normalized the results to standard conditions (i.e., temperature = 30°C; PAR = 1000 μmol photons m^{-2} s^{-1}). Owing to a lack of definite response curves, the results were normalized with a Guenther et al. algorithm developed by Guenther et al. (1993). We assumed this to be a reasonable approximation when temperature deviated within 26–33 ℃ and PAR deviated within 600–1300 μmol photons m^{-2} s^{-1} (Niinemets et al., 2011). Then, we converted the branch-level emission rates into leaf-level emission rates for future applications in canopy environment models to estimate BVOC emissions. The branch-level isoprene emission rates were converted into leaf-level emission rates by multiplying by 1.75 (Guenther et al., 1994; Guenther et al., 1996). Conversions were unnecessary for monoterpenes and other VOCs, due to their lower light dependence and a lack of available data.

To estimate representative emission rates, we summarized our field measurements, as well as a large number of measurements from China and abroad. The data from other studies collected under different environment conditions were normalized to standard conditions using the algorithm mentioned above. To minimize errors introduced by this extrapolation, we only included measurements conducted during the day in summer or growing season under temperature and light similar to the standards to obtain normalized emission rates of the studied plant species/genera. The reported isoprene emission rates were also measured at the branch or leaf level. Normalized leaf-level emission rates were also determined from branch-level rates using the method described above.

Before estimating the emission intervals and representative emission rates, we hypothesized that the VOC emission mechanisms were similar among species, and that their emissions were random. All available normalized leaf-level isoprene and monoterpene emission rates from all studied trees, comprising > 400 and 300 individual values, respectively, were separately analyzed.

3 Measurement of BVOC emission

Table 3 lists by sampling location the plant species, vegetation type, and measured leaf-level emission rate normalized to standard conditions. These are the first reported emission measurements of 102 VOC species. Owing to limited space, we only included the individual emission rates of the three most important VOC species, isoprene, α-pinene, and β-pinene, while the other VOC species were summarized as a single group (i.e., other VOCs). Notably, several plant species had higher potential emissions of other certrain VOC species than isoprene and pinene, such as *Aceracede*, *Fraxinus chinensis Roxb.*, *Quercus variabilis*, *Phoebe zhennan S. Lee*, *Paulownia Sieb.*, and most shrub species.

Of the studied plants, broadleaf trees were the greatest potential emitters of isoprene, while needle-leaf trees emitted more pinene. Shrubs had lower isoprene and pinene emissions, but higher emissions of other VOCs. In addition, 29 of the 39 broadleaf tree species emitted isoprene (i.e.,

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emission rate > 0.1 μg C gdw^{-1} h^{-1}). In general, deciduous broadleaf trees had higher isoprene emission intensities than evergreen broadleaf trees. *Broussonetia papyrifera (Linn.) L'Hér. ex Vent.* was the strongest emitter of isoprene, with an emission rate of 838.62 μg C gdw^{-1} h^{-1}. *Phyllostachys aureosulcata f. spectabilis*, a species of subfamily Bambusoideae, had a high emission potential of 187.73 μg C gdw^{-1} h^{-1}. *Styphnolobium japonicum*, *Populus tomentosa Carr.*, *Platanus orientalis*, and *Quercus wutaishanica* were all high isoprene emitters, producing > 60 μg C gdw^{-1} h^{-1}. However, *Quercus variabilis* was considered to have no or little isoprene emissions. The isoprene emission rates of needle-leaf trees and shrubs were mostly < 0.3 μg C gdw^{-1} h^{-1}. Only 3 of the 14 needle-leaf trees emitted isoprene, while all of these species emitted pinene. Among them, *Metasequoia glyptostroboides*, *Pinus tabulaeformis Carr.*, and *Axodiaceae* had especially high pinene emissions. Notably, one broadleaf tree species, *Liquidambar formosana Hance*, had considerable α- and β-pinene emission rates of 707.12 and 2542.13 μg C gdw^{-1} h^{-1}, respectively. In addition, the shrub *Cotinus coggygria Scop.* was a high pinene emitter. Owing to a large amount of compounds, the totaled emission rates of other VOCs might be high despite lower emissions of individual VOCs. For example, *L. formosana* was the highest emitter of other VOCs (90.44 μg C gdw^{-1} h^{-1}), followed by *Pteroceltis tatarinowii Maxim.* (23.68 μg C gdw^{-1} h^{-1}). For most shrub species, other VOCs contributed the most to their total VOC emission potentials. The other VOCs were dominated by light alkanes, alkenes, aromatics, and straight-chain alkanes, as well as some carbonyls, while halohydrocarbons were minimally emitted. For example, alkanes accounted for 43% of the total other VOC emissions in *L. formosana*. Meanwhile, 34% of other VOC emissions in *Q. wutaishanica* were attributed to alkenes. Aromatics accounted for 51% of other VOC emissions in *M. glyptostroboides*. In general, oxygenated compounds accounted for a greater proportion of the other VOCs in broadleaf tree species (> 50% for most trees) than in needle-leaf trees. Methyl methacrylate, isopropylbenzene, isopentane, acetone, ethane, propane, toluene, and xylene were the dominant components of the other VOCs, some of which had high emission intensities (> 10 μg C gdw^{-1} h^{-1}). Future studies should include these VOC species when measuring BVOC emissions, and they should be considered in global and regional BVOC emission estimates.

4 Estimation of representative emission rates

4.1 Emission rate intervals

The frequency distributions of the measured emission rates using all available data for isoprene and monoterpenes for trees are shown in Figure 2. The emission potentials differed greatly among plant species, resulting in a wide range of emission rates. The isoprene emission rates ranged from 0 to 500 μg C gdw^{-1} h^{-1}, while those of monoterpenes fell predominantly within 0–100 μg C gdw^{-1} h^{-1}, with a sparse distribution of higher emission rates. According to the distribution, we divided the emission range of isoprene (x-axis of Fig. 2(a)) into four groups, 0–1, 1–10, 10–100, and 100–500 μg C gdw^{-1}

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h^{-1}, which were further divided into 20 equivalent intervals separately. Similarly, three groups were evident in the monoterpene emission range (x-axis of Fig. 2(b)), 0–1, 1–10, and 10–100 μg C gdw^{-1} h^{-1}, which were further divided into 10 equivalent intervals each. Then, we counted the frequencies of values in each interval.

The plant emission rates were inconsistent, but regular in distribution, falling into different intensity levels (Fig. 2). Based on these distributions, we defined seven categories for isoprene emission rates (lowest, lower, low, moderate, high, higher, and highest), and six categories for monoterpene emission rates (lowest, lower, low, moderate, high, and higher). We included more emission rate categories than those in previous studies. First, we estimated a range of emission rates for each category according to the distribution, and counted the values in each interval. Table 4 lists the statistical frequency, mean, and standard deviation (SD) of emission rates and main plant species distributed in each category. The lowest isoprene emission category had the most isoprene emission rate measurements (42% of the total), while the higher category comprised 19% of the total measurements, and other categories each comprised only 7–9% of the total. The largest number of plants, including *Tilia*, *Paulownia Sieb.*, *Betula*, *Quercus Suber*, and most needle-leaf trees, were in the lowest isoprene emission category. Future studies should perform more emission measurements of plants in the lower and high isoprene emission categories. For monoterpenes, emission rates were uniformly distributed in the six emission categories, with frequencies of 15–20%. Future studies should perform more intensive measurements of plants in the low and lowest monoterpene emission intensity categories.

Based on the statistics listed in Table 4, the measured values displayed dispersed distributions (i.e., large SDs relative to the mean) in each emission rate range. If the mean were considered to be the representative emission rate for each emission category, large uncertainties would be introduced into the emission rate estimations of individual plants. Therefore, we considered additional statistics for all the values in each emission rate range separately, which each had a normal distribution. Using the *t*-test, we determined the 95% confidence interval (CI) of each range, which we considered to be the final emission rate interval for each emission category (Table 5). Table 5 lists the statistically valid sample sizes included after the *t*-test. Values from the initial estimated emission rate range that fell outside the new interval were eliminated due to possible measurement errors, resulting in smaller SDs. The means of the new intervals were considered as the representative emission rates for each emission category (isoprene: 0.1, 1.0, 5.8, 14.4, 33.6, 70.1, and 142.5 μg C gdw^{-1} h^{-1}; monoterpenes: 0.1, 0.2, 0.6, 1.4, 3.0, and 12.6 μg C gdw^{-1} h^{-1}).

It should be noted that future studies integrating more emission measurements with different intensities would create more detailed categories, accurate emission rate intervals and representative rates. Thus, the accuracy in the estimation of representative emission rates for each plant would be

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improved much with enhanced rigorous measurements.

4.2 Determination of emission rates for 192 plants

The plant-specific emission rates were estimated based on the established emission intervals and representative emission rate. Emission rates were determined for each tree species based on the tendency of their measured emission rates to fall within each emission interval. Each plant was assigned the representative rate of the emission interval in which most rates fell. The normalized emission rates from a number of studies fell within a single interval for more than 70% of the 30 tree species/genera studied. When the reported rates fell within more than one category, the tree genus/species was assigned to the interval with the most rates. There were no occasions where reported rates fell equally into several intervals.

We analyzed the emission rates reported in China and abroad separately. It was a priority to apply the domestic measurements. The data from other countries would be selected when there was a lack of domestic data. When the determined emission rate obtained from domestic and foreign studies for one plant differed, and when there are much more measurements abroad than in China, such as measurements for *Eucalyptus* and *Picea*, the mean of two representative rates was considered as the emission rate. We assigned plant species with no measurements the same emission interval as that of measured species of the same family or genus. When there were no measurements for a family or genus, the plant species was assigned to the lowest emission category for isoprene and monoterpenes, with representative emission rates of 0.1 μg C gdw^{-1} h^{-1} (Klinger et al., 2002).

Table 6 lists the estimated emission rates based on measurements from domestic and foreign studies and the final values of leaf-level emission rates for the 30 dominant tree species in this study. The final values for each plant species/genera were determined from the estimated domestic and foreign emission rates according to the principle described above. Broadleaf trees, such as *Quercus*, *Populus*, bamboo, and *Eucalyptus*, had higher or high isoprene emission rates. Meanwhile, needle-leaf trees, such as *Pinus*, *Abies*, and *Cupressus*, had higher monoterpene emission potentials. Similarly, the normalized isoprene and monoterpene emission rates of 149 shrub and grass genera and 13 crop species were determined based on the measurements from our study and those from other studies conducted in China (Wang et al., 2002; Wang et al., 2003b; Zhao et al., 2004; He et al., 2005; Bai and Baker, 2006; Xie et al., 2007; etc.), and abroad (Guenther et al., 1994; Geron et al., 2006; Simon et al., 2006; etc.) (Tables 7 and 8). In Table 7, only the average emission rates for 54 families of shrubs and grass are displayed due to space limitations. Overall, the emission potentials of crop, shrub, and grass were much lower than those of forest tree species; however, rubber had higher isoprene and monoterpene emission rates.

4.3 Comparison of representative emission rates

Previous studies of BVOC emission inventories in China applied a traditional method based on the

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use of emission categories to estimate emission rates, which lacked theoretical evidence in determining emission categories, representative emission rates, and ranges. Distinct emission categories and representative values were applied, resulting in different emission rates for specific plants. Table 9 lists the isoprene emission categories and determined emission rates of some dominant tree species with higher emission potentials. In addition, previous studies used coarse emission intensity classifications (usually three to six classes) (Klinger et al., 2002; Yan et al., 2005; Wang et al., 2007), while we defined seven categories for the isoprene emission rates. Their use of fewer categories could result in underestimation of emission rates for plants with higher emission potentials. For example, the emission rate estimates of *Eucalyptus*, *Quercus*, *Populus*, and bamboo were much lower in previous studies than in our study (Klinger et al., 2002; Yan et al., 2005; Wang et al., 2007), which could result in an underestimation of 4.9–7.8 Tg C yr^{-1} for isoprene emissions in China, estimated using the methodologies described in Li et al. (2013) and Li and Xie (2014). It should be noted that different data sources contributed to differences in the determined emission rates among studies. In the future, we will perform more measurements for further improvement of the approaches and accuracy of estimating representative emission rates.

5 Evaluation

Accurately estimating representative BVOC emission rates is a challenging but critical step for constructing emission inventories. However, efforts have been made to develop an accurate emission rate database. Niinemets et al. (2011) presented a fairly thorough discussion on estimations of isoprenoid emission capacities from enclosure studies. They reviewed sources of uncertainties in the emission rate estimates, including measurement techniques (focusing on dynamic enclosure systems), calculations, extrapolations to standard emissions, and averaging. They first proposed a standardized protocol for the measurements and calculations and standardized the examination and screening of emission rate data from numerous reports before developing the emission rate database. This review helped the developers of emission factor databases to select and process original observations successfully. However, there might be still a large number of available varied emission rate data for one given plant species, while no data existing for some certain species. Therefore, it was necessary to determine an accurate representative value as the emission rate for application in the BVOC emission inventory estimates. Here, our established reasonable statistical method for determining species-specific representative emission rates, with production of more detailed emission intensity categories, accurate emission rate intervals and representative rates, should work effectively. Certainly, the foundation of our method was the evaluation and screening based on the quality of the emission rate observations and the use of reliable extrapolations, as suggested by Niinemets et al. (2011). First, they recommended that only two quality classes (quantitative measurements and semi-quantitative measurements) associated with dynamic systems could be used to construct BVOC emission

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inventories. Meanwhile, non-quantitative measurements (i.e., those conducted using static enclosure systems or possibly semi-static and some dynamic systems) should not be used in BVOC modeling. In our study, the summarized reported emission rate measurements from abroad were mainly derived from dynamic open systems. While those in China were measured using simple static systems, primarily due to a lack of other measurements, which should only be used in emission rate estimates when there are no other available observations for a region. The errors introduced due to extrapolation were minimized and within a reasonable range, as discussed in Section 2.2.

In this study, we focused on gaining a comprehensive understanding of BVOC emissions from plants in China and exploring scientific methods for the accurate estimation of plant species-specific representative BVOC emission rates based on reliable original emission rate observations.

6 Conclusions

We performed field measurements of BVOC emissions from 50 plant species, including 36 trees and 14 shrubs, at nine locations in China using our established semi-static enclosure system. Emission rates of 102 VOC species (i.e., isoprene, α-pinene, β-pinene, and other VOC species) from 67 experiments were determined by analyzing with a custom-built online GC-MS/FID system. Of the studied plants, broadleaf trees were the greatest potential emitters of isoprene, while needle-leaf trees emitted more pinene. Shrubs had lower isoprene and pinene emissions, but higher emissions of other VOCs. Overall, deciduous broadleaf trees had higher isoprene emission intensities than evergreen broadleaf trees. *B. papyrifera* was the strongest emitter of isoprene, with a normalized leaf-level emission rate of 838.62 μg C gdw^{-1} h^{-1}. One broadleaf tree species, *L. formosana*, had considerable α- and β-pinene emission rates of 707.12 and 2542.13 μg C gdw^{-1} h^{-1}, respectively. Overall, shrubs emitted more other VOCs than isoprene and pinene. Other VOC species, including methyl methacrylate, isopropylbenzene, isopentane, acetone, ethane, propane, toluene, and xylene, were the dominant components even with high emission intensities. It was suggested that future studies should consider their emissions in global or regional estimations of BVOCs.

We established a statistical approach to estimate representative emission rates, based on a summary of our field measurements and reported emission rates from China and abroad. First, we produced isoprene and monoterpene emission intensity categories based on statistics. Tree species fell into various emission intensity categories, including lowest, lower, low, moderate, high, higher, and highest. The isoprene emission rate intervals and representative rates were: lowest, 0.08–0.11 and 0.1 μg C gdw^{-1} h^{-1}; lower, 0.9–1.3 and 1.0 μg C gdw^{-1} h^{-1}; low, 5.2–6.5 and 5.8 μg C gdw^{-1} h^{-1}; moderate, 13.1–15.3 and 14.4 μg C gdw^{-1} h^{-1}; high, 31.1–37.0 and 33.6 μg C gdw^{-1} h^{-1}; higher, 67.2–75.1 and 70.1 μg C gdw^{-1} h^{-1}; and highest, 135.1–157.6 and 142.5 μg C gdw^{-1} h^{-1}. The monoterpene emission rate intervals and representative rates were: lowest, 0.08–0.11 and 0.1 μg C gdw^{-1} h^{-1}; lower, 0.17–0.22 and 0.2 μg C gdw^{-1} h^{-1}; low, 0.5–0.7 and 0.6 μg C gdw^{-1} h^{-1}; moderate, 1.2–1.5 and 1.4 μg C gdw^{-}

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427 ^{1} h^{-1}; high, 2.8–3.3 and 3.0 μg C gdw^{-1} h^{-1}; and higher, 11.1–14.9 and 12.6 μg C gdw^{-1} h^{-1}. Compared
428 with previous studies, our emission rate categories were more detailed, and the emission rate interval
429 and representative rates were more accurate. They would be further improved by integrating more
430 field measurements in the future, which would be significant for reducing the uncertainty in the
431 determination of emission rate and estimation of emissions in BVOC emission inventories.
432 Based on the emission intervals, we determined emission rates for 192 plant species/genera,
433 including 30 dominant tree species, 149 shrub and grass genera, and 13 crop species. Broadleaf trees,
434 including *Quercus*, *Populus*, bamboo, and *Eucalyptus*, had higher or high isoprene emission rates.
435 Meanwhile, needle-leaf trees, including *Pinus*, *Abies*, and *Cupressus*, had higher monoterpene
436 emission potentials. The emission potentials of crops, shrubs, and grasses were much lower than those
437 of forest plants. Of the crop species, rubber had higher isoprene and monoterpene emission rates. In
438 our study, the isoprene emission rates of several tree species with high emission potentials were
439 higher than those in previous studies, which could explain why China's BVOC emissions have
440 frequently been underestimated much (Li et al., 2013; Li and Xie, 2014).
441 Despite our efforts to achieve reliable estimation of accurate representative BVOC emission rates
442 to construct an emission inventory, it is still necessary to establish a measured emission rate database
443 with minimal uncertainties. This would improve the accuracy of our estimations by integrating more
444 quantitative measurements, as suggested by Niinemets et al. (2011), and is especially important in
445 China. Besides, it is necessary to conduct measurements in different regions to obtain the
446 representative emission rates of plants in the whole China.
447
448
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675 **Figure and table captions:**

676 **Table 1.** Isoprene emission categories and determined emission rates of the dominant tree species in
677 China's emission inventories (μg C gdw^{-1} h^{-1}).

678 **Table 2.** 103 VOC species quantified with the GC-MS/FID system.

679 **Table 3.** Plant species sampled at each location, sampling time, and measured emission rates.

680 **Table 4.** Isoprene and monoterpene emission rate categories, emission rate ranges, statistics, and
681 distributed plant species in each category (μg C gdw^{-1} h^{-1}).

682 **Table 5.** Isoprene and monoterpene emission rate intervals and representative values (μg C gdw^{-1} h^{-1}).

683 **Table 6.** Normalized leaf-level isoprene and monoterpene emission rates for 30 dominant tree
684 genera/species in China (μg C gdw^{-1} h^{-1}).

685 **Table 7.** Averaged normalized leaf-level isoprene and monoterpene emission rates for 54 shrub and
686 grass families in China (μg C gdw^{-1} h^{-1}).

687 **Table 8.** Normalized leaf-level isoprene and monoterpene emission rates for 13 crop species in China
688 (μg C gdw^{-1} h^{-1}).

689 **Table 9.** Comparison of isoprene emission categories and determined emission rates between our
690 study and other studies (μg C gdw^{-1} h^{-1}).

691 **Figure 1.** Schematic of the semi-static branch enclosure system used in this study.

692 **Figure 2.** Frequency distribution of (a) isoprene and (b) monoterpene emission rates from forest trees.

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693 **Table 1.** Isoprene emission categories and determined emission rates of the dominant tree species in
694 China's emission inventories (μg C gdw^{-1} h^{-1}).

Emission categories	*Eucalyptus*	*Quercus*	*Populus*	Bamboo	Studies
0.1, 14, 70	-	56	22	5	Klinger et al., 2002
0.1, 1, 6, 8, 34, 60	-	60	60	0.5	Yan, 2005
0.1, 5, 10, 20, 40, 60	50	50	50	0.5	Wang, 2007

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695 **Table 2.** 103 VOC species quantified with the GC-MS/FID system.

Alkanes (28)		**Alkenes (13)**	**Aromatics (16)**	**Oxygenated VOCs (17)**	**Halocarbons (27)**	
Ethane*	2,3-Dimethylpentane	Ethylene*	Benzene	Acrolein	Chloromethane	1,1,2-Trichloroethane
Propane*	2,2,4-Trimethylpentane	Propene*	Toluene	Propanal	Vinylchloride	Tetrachloroethylene
Isobutane*	2,2-Dimethylbutane	trans-2-Butene*	Ethylbenzene	Acetone	Bromomethane	1,2-Dibromoethane
n-Butane*	2,3-Dimethylbutane	1-Butene*	m/p-Xylene	Methylacetate	Chloroethane	Chlorobenzene
Cyclopentane*	Methylcyclohexane	cis-2-Butene*	o-Xylene	Methyl tert-butyl ether	1,1-Dichloroethylene	Bromoform
Isopentane*	2,3,4-Trimethylpentane	1,3-Butadiene	Styrene	Methacrolein	Dichloromethane	1,1,2,2-Tetrachloroethane
n-Pentane*	2-Methylheptane	1-Pentene	Isopropylbenzene	Vinylacetate	1,1-Dichloroethane	1,3-Dichlorobenzene
n-Nonane	3-Methylheptane	trans-2-Pentene	n-Propylbenzene	n-Butanal	cis-1,2-Dichloroethylene	1,4-Dichlorobenzene
n-Heptane	2-Methylpentane	Isoprene	3-Ethyltoluene	Methylvinylketone	Chloroform	Benzylchloride
n-Hexane	3-Methylpentane	cis-2-Pentene	4-Ethyltoluene	Methylethylketone	1,1,1-Trichloroethane	1,2-Dichlorobenzene
n-Decane	3-Methylhexane	1-Hexene	1,3,5-Trimethylbenzene	Ethylacetate	tetrachloromethane	
Octane	2-Methylhexane	α-Pinene	2-Ethyltoluene	2-Pentanone	1,2-Dichloroethane	
Cyclohexane	2,4-Dimethylpentane	β-Pinene	1,2,4-Trimethylbenzene	n-Pentanal	Trichloroethylene	
Udecane	Methylcyclopentane	**Alkynes (1)**	1,2,3-Trimethylbenzene	3-Pentanone	1,2-Dichloropropane	
		Acetylene*	1,3-Diethylbenzene	Methylmethacrylate	Bromodichloromethane	
		Other (1)	1,4-Diethylbenzene	n-Hexanal	trans-1,3-Dichloropropene	
		Acetonitrile		n-Butylacetate	cis-1,3-Dichloropropene	

696 * quantified by FID detector

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697 **Table 3.** Plant species sampled at each location, sampling time, and measured emission rates.

No.	Plant species	Vegetation type [a]	Sampling time	Dry biomass of enclosed leaves (gdw)	Normalized leaf-level emssion rate [b] (μgC gdw^{-1} h^{-1})			
					isoprene	α-pinene	β-pinene	other VOCs [c]
Peking University, Beijing (116°18.30′E, 39°59.82′N)								
1	*Populus tomentosa Carr.*	dbt	19 Aug. 2014	50.85	140.99	-	-	0.29
2	*Platanus orientalis*	dbt	25 Aug. 2014	42.30	41.67	-	-	0.74
3	*Populus tomentosa Carr.*	dbt	8 Sep. 2014	57.92	67.96	0.02	0.04	6.58
4	*Sophora japonica*	dbt	2 Oct. 2014	54.7	29.16	0.02	0.05	4.83
5	*Phyllostachys aureosulcata f. spectabilis*	ebt	2 Oct. 2014	118.6	187.73	0.00	0.01	3.21
6	*Fraxinus chinensis Roxb.*	dbt	5 Oct. 2014	28.7	0.18	0.01	0.08	8.71
7	*Sabina chinensis (L.) Ant.*	ent	5 Oct. 2014	136.8	0.00	3.87	0.45	1.45
8	*Pinus bungeana*	ent	5 Oct. 2014	106.2	NA	2.70	4.68	2.92
Jiufeng Mountain, Beijing (116°5.02′E, 40°3.27′N)								
9	*Aceracede*	dbt	21 Sep. 2014	26.5	NA	NA	0.06	4.62
10	*Quercus wutaishanica*	dbt	21 Sep. 2014	64.3	67.16	NA	NA	2.17
11	*Pinus tabulaeformis Carr.*	ent	21 Sep. 2014	95.5	0.07	17.78	188.50	3.49
12	*Quercus variabilis*	dbt	21 Sep. 2014	106	0.03	0.07	0.46	1.66
Yunmeng Mountain, Beijing (116°42.33′E, 40°33.92′N)								
13	*Quercus variabilis*	dbt	7 Oct. 2014	60.9	NA	0.02	0.17	5.45
14	*Pinus tabulaformis*	ent	7 Oct. 2014	89.3	0.03	2.94	11.18	1.06
15	*Sophora japonica*	dbt	7 Oct. 2014	52.6	142.66	0.29	1.83	3.28
16	*Sabina chinensis (L.) Ant.*	ent	7 Oct. 2014	162.1	0.02	1.71	0.23	0.73
17	*Populus simonii*	dbt	7 Oct. 2014	18.3	46.93	0.12	0.31	10.33
18	*Crataegus pinnatifida*	dbt	27 July 2016	52.10	0.13	0.10	-	1.06
19	*Weigela florida（Bunge）A. DC.*	dbs	27 July 2016	23.53	0.02	0.29	-	6.12
20	*Quercus aliena Bl.*	dbt	27 July 2016	77.82	40.79	0.16	-	2.22
21	*Corylus heterophylla Fisch*	dbs	27 July 2016	22.14	1.72	0.29	-	13.59
22	*Betula platyphylla Suk.*	dbt	27 July 2016	20.41	NA	20.42	-	9.10
23	*P. thomsoni*	dv	27 July 2016	8.86	NA	NA	-	6.65

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24	*Picea meyeri Rehd. et Wils.*	ent	27 July 2016	82.41	0.05	1.13	-	1.05
25	*Pirus, i, f.*	dbt	27 July 2016	23.23	0.23	0.03	-	1.07
26	*Juglans mandshurica Maxim*	dbt	27 July 2016	49.24	0.12	15.20	-	1.89
27	*Lespedeza bicolor Turcz.*	dbs	28 July 2016	21.15	0.29	NA	-	10.34
28	*Fraxinus chinensis Roxb.*	dbt	28 July 2016	20.63	0.16	0.12	-	4.85
29	*Acer mono Maxim*	dbt	28 July 2016	26.77	0.42	NA	-	1.15
30	*Deutzia grandiflora Bunge*	dbs	28 July 2016	9.11	20.56	0.52	-	9.80
Wuling Mountain, Beijing (117°25.97′E, 40°37.85′N)								
31	*Populus tomentosa Carr*	dbt	8 Oct. 2014	23.8	40.59	0.02	0.10	6.86
32	*Salix matsudana*	dbt	8 Oct. 2014	18.4	15.45	0.02	0.07	5.31
Beijing Gardening Research Institute, Beijing (116°28.56′E, 39°58.99′N)								
33	*Salix matsudana f. pendula.*	dbt	19 May 2016	64.85	28.62	0.05	-	3.27
34	*Pinus tabulaeformis Carr.*	ent	19 May 2016	326.64	0.00	41.02	-	0.37
35	*Cotinus coggygria Scop.*	dbs	19 May 2016	28.01	0.02	154.26	-	2.50
36	*Aesculus chinensis Bunge*	dbt	19 May 2016	95.45	NA	5.16	-	0.94
37	*Forsythia viridissima Lindl*	dbs	20 May 2016	34.15	0.08	0.02	-	4.95
38	*Malus 'Sparkler'*	dbt	20 May 2016	53.34	0.03	1.05	-	2.04
39	*Buxus megistophylla Levl.*	dbs	20 May 2016	43.11	NA	NA	-	0.59
40	*Cerasus sp.*	dbt	20 May 2016	51.53	0.02	0.38	-	0.92
41	*Salix matsudana Koidz.*	dbt	20 May 2016	36.19	27.08	0.56	-	6.32
42	*Sabina chinensis (L.) Ant.*	ent	20 May 2016	108.35	0.08	18.64	-	3.05
43	*Syringa oblata Lindl.*	dbs	20 May 2016	32.08	0.26	3.35	-	6.12
Yunwu Mountain, Wuhan (114°15.11′E, 31°12.15′N)								
44	*Pteroceltis tatarinowii Maxim.*	dbt	23 Oct. 2014	15.9	1.87	2.65	10.90	23.68
45	*Cunninghamia*	ent	23 Oct. 2014	183.7	0.03	1.11	0.18	0.92
46	*Metasequoia glyptostroboides*	ent	23 Oct. 2014	47.9	0.18	46.53	6.42	3.47
47	*Platycladus orientalis*	ent	23 Oct. 2014	100.7	2.20	9.32	0.95	1.66
48	*Cinnamomum bodinieri Levl.*	ebt	23 Oct. 2014	32.8	1.55	1.92	4.50	3.85
Maan Mountain, Wuhan (114°26.25′E, 30°31.43′N)								
49	*Phoebe zhennan S. Lee*	ebt	24 Oct. 2014	36.1	0.05	0.10	0.08	4.03
50	*Cinnamomum bodinieri Levl.*	ebt	24 Oct. 2014	47.8	0.19	0.54	1.32	2.24

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51	*Fraxinus chinensis Roxb.*	dbt	24 Oct. 2014	39.5	0.39	0.34	0.36	1.68
52	*Pinus massoniana*	ent	24 Oct. 2014	81.3	0.02	5.55	14.89	2.94
53	*Liquidambar formosana Hance*	dbt	24 Oct. 2014	25.2	30.13	707.12	2542.13	90.44
54	*Quercus wutaishanica*	dbt	24 Oct. 2014	99.8	76.71	NA	NA	0.88
55	*Paulownia Sieb.*	dbt	24 Oct. 2014	54.2	NA	0.17	0.09	2.40
Qingcheng Mountain, Chengdu (103°53'E, 30°51'N)								
56	*Cinnamomum bodinieri Levl.*	ebt	2 Sep. 2016	30.9	NA	NA	-	1.39
57	*Metasequoia glyptostroboides*	ent	2 Sep. 2016	21.3	NA	181.26	-	4.08
58	*Phyllostachys viridis*	ebt	2 Sep. 2016	13.4	12.30	23.47	-	5.40
59	*Phoebe zhennan S. Lee*	ebt	2 Sep. 2016	21.8	0.14	33.83	-	3.28
60	*Osmanthus fragrans*	dbs	2 Sep. 2016	61.4	0.17	3.78	-	2.43
61	*Alangium chinense (Lour.) Harms*	dbs	2 Sep. 2016	39.9	0.16	1.07	-	1.50
Longquan Mountain, Chengdu (104°28'E, 30°56'N)								
62	*Ligustrum lucidum*	ebs	6 Sep. 2016	19.3	0.05	1.60	-	6.72
63	*Platanus orientalis*	dbt	6 Sep. 2016	34	96.52	0.33	-	2.80
64	*Broussonetia papyrifera (Linn.) L'Hér. ex Vent.*	dbt	6 Sep. 2016	19.1	838.62	0.45	-	4.80
65	*Rhus chinensis Mill.*	dbs	6 Sep. 2016	45.3	52.54	NA	-	1.40
66	*Axodiaceae*	ent	6 Sep. 2016	54.6	0.75	77.62	-	0.81
67	*Pittosporum tobira*	ebs	6 Sep. 2016	20.4	NA	15.85	-	1.38

[a] dbt: deciduous broadleaf tree; ent: evergreen needle-leaf tree; ebt: evergreen broadleleaf tree; dbs: decidous broadleaf shrub; ebs: evergreen broadleleaf shrub; dv: decidous vine.

[b] normalized to the standard condition (i.e., temperature=30℃; PAR=1000 μmol photons m^{-2} s^{-1}) and transferred to the leaf-level emission rate from the branch-level one; "-" means no measurement, "NA" means emission was not detected.

[c] including 99 quantified VOC compounds excluding isoprene, α-pinene, β-pinene, and acetylene.

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703 **Table 4.** Isoprene and monoterpene emission rate categories, emission rate ranges, statistics, and
704 distributed plant species in each category (μg C gdw^{-1} h^{-1}).

Compound	No.	Emission category	Ranges	Frequency	Mean	SD	Plant species
Isoprene	I	lowest	0−0.5	163	0.1	0.11	*Tilia*, *Paulownia Sieb.*, *Betula*, *Quercus Suber*, most needle-leaf trees
	II	lower	0.5−3	27	1.1	0.38	*Axodiaceae*
	III	low	3−9	31	5.7	1.51	*Casuarina equisetifolia L.*, *Picea*
	IV	moderate	9−20	34	14.2	2.48	-
	V	high	20−50	31	34.1	8.81	*Eucalyptus*
	VI	higher	50−90	73	67.4	9.20	*Populus*, Bamboo, *Quercus liaotungensis*
	VII	highest	90−200	32	129.2	33.74	-
Monoterpene	I	lowest	0−0.1	71	0.1	0.04	*Cunninghamia*, most broadleaf trees
	II	lower	0.1−0.3	50	0.2	0.05	*Larix*, *Quercus*, *Betula*
	III	low	0.3−0.9	38	0.6	0.18	*Cupressus*
	IV	moderate	0.9−2	47	1.3	0.28	*Axodiaceae*
	V	high	2−4	63	3.5	1.14	*Pinus*[a], *Abies*, *Cupressus*, *Picea*, *FJP*[b], *Eucalyptus*
	VI	higher	10−30	33	16.9	6.25	-

705 [a] *Pinus* includes *Pinus koraiensis*, *Pinus densiflora*, *Pinus sylvestris var. mongolica Litv.*, *Pinus*
706 *thunbergii*, *Pinus tabulaeformis*, *Pinus armandi*, *Pinus massoniana*, *Pinus yunnanensis*, *Pinus kesiy*,
707 *Pinus densata.*
708 [b] FJP: *Fraxinus mandshurica*, *Juglans mandshurica Maxim*, *Phellodendron amurense.*

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709 **Table 5.** Isoprene and monoterpene emission rate intervals and representative values (μg C gdw^{-1} h^{-1}).

Compound	Emission category	Emission rate interval	Valid sample size	Mean	SD
Isoprene	lowest	0.08−0.11	58	0.1	0.003
	lower	0.9−1.3	13	1.0	0.10
	low	5.2−6.5	15	5.8	0.38
	moderate	13.1−15.3	7	14.4	0.52
	high	31.1−37.0	5	33.6	1.46
	higher	67.2−75.1	27	70.1	1.59
	highest	135.1−157.6	8	142.5	5.07
Monoterpene	lowest	0.08−0.11	51	0.1	0.004
	lower	0.17−0.22	34	0.2	0.01
	low	0.5−0.7	19	0.6	0.06
	moderate	1.2−1.5	19	1.4	0.11
	high	2.8−3.3	33	3.0	0.09
	higher	11.1−14.9	13	12.6	1.00

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710 **Table 6.** Normalized leaf-level isoprene and monoterpene emission rates for 30 dominant tree genera/species in China (μg C gdw^{-1} h^{-1}).

Species/genera	In China			Abroad			Final value	
	Isoprene	Monoterpene	References[a]	Isoprene	Monoterpene	References[a]	Isoprene	Monoterpene
Eucalyptus	70.1	3.0	15	33.6	3.0	1,2,10,13,14,23,25	50.0	3.0
Tilia	0.1	0.1	3,15,17	1.0	0.2	5,10,11	0.1	0.1
Betula	0.1	0.2	3,15,17,21	0.1	0.2	1,2,10,13,23	0.1	0.2
Quercus	70.1	0.2	Our study,15,16,17,18,20,21	70.1	0.2	1,2,7,10,13,19,22,23	70.1	0.2
Casuarina equisetifolia L.	5.8	0.1	8,21	70.1	0.1	1, 2	5.8	0.1
Phoebe zhennan S. Lee	0.1	0.1	Our study,15	-	-	-	0.1	0.1
FJP[b]	0.1	3.0	Our study,15	-	-	-	0.1	3.0
Paulownia Sieb.	0.1	0.1	Our study,12,15	-	-	-	0.1	0.1
Populus	70.1	0.1	Our study,4,6,15,17,24	70.1	0.1	1,10,13,23	70.1	0.1
Bamboo	70.1	0.1	Our study,15,16,18,20,21	70.1	0.2	5,10,26	70.1	0.1
Cupressus	0.1	3.0	Our study,15,18,21	0.1	0.6	1,2,9,10,13	0.1	3.0
Abies	0.1	3.0	15	0.1	3.0	1,2,10,13,23	0.1	3.0
Axodiaceae	1.0	1.4	Our study,21	-	-	-	1.0	1.4
Cunninghamia	0.1	0.1	Our study,8	0.1	-	26	0.1	0.1
Larix	0.1	0.2	17,18,21	0.1	1.4	11,13,18,23	0.1	0.2
Pinus[c]	0.1	3.0	Our study,6,15,18,21,24	0.1	3.0	1,2,10,13,23,26	0.1	3.0
Tsuga	-	-	-	0.1	0.2	1,2,9,10	0.1	0.2
Keteleeria	-	-	-	-	-	-	0.1	3.0
Picea	5.8	3.0	15	14.4	3.0	1,2,10,11,19,27	10.0	3.0

711 [a] References: 1: Geron et al., 1994; 2: Guenther et al., 1994; 3: Zhang et al., 1994;4: Bai et al., 1995; 5: Guenther et al., 1996; 6: Zhao et al., 1996; 7:
712 Kesselmeier et al., 1997; 8: Bai et al., 1998; 9: Drewitt et al., 1998; 10: Kesselmeier and Staudt, 1999; 11: Isebrands et al., 1999; 12: Mou et al., 1999;
713 13: Simpson et al., 1999; 14: He et al., 2000; 15: Klinger et al., 2002; 16: Wang et al., 2002; 17: Wang et al., 2003a; 18: Wang et al, 2003b; 19:
714 Stewart et al., 2003; 20: Zhang et al., 2003; 21: Zhao et al., 2004; 22: Simon et al., 2005; 23: Simon et al., 2006; 24: Chen et al., 2009; 25: Winters et

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al., 2009; 26: Chang et al., 2012; 27: Yassaa et al., 2012.

[b] *Pinus* includes *Pinus koraiensis*, *Pinus densiflora*, *Pinus sylvestris var. mongolica Litv.*, *Pinus thunbergii*, *Pinus tabulaeformis*, *Pinus armandi*, *Pinus massoniana*, *Pinus yunnanensis*, *Pinus kesiy*, *Pinus densata*.

[c] FJP: *Fraxinus mandshurica*, *Juglans mandshurica Maxim*, *Phellodendron amurense*.

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719 **Table 7.** Averaged normalized leaf-level isoprene and monoterpene emission rates for 54 shrub and grass families in China (μg C gdw^{-1} h^{-1}).

Family	Isoprene	Monoterpene	Family	Isoprene	Monoterpene	Family	Isoprene	Monoterpene
Liliaceae	1.0	0.6	Apocynaceae	0.1	0.2	Rosaceae	1.0	0.6
Cistaceae	0.1	0.1	Hamamelidaceae	1.0	0.2	Caprifoliaceae	0.1	0.2
Primulaceae	0.1	0.1	Crassulaceae	0.1	0.2	Cyperaceae	1.0	0.6
Goodeniaceae	1.0	0.2	Asteraceae	1.0	0.6	Caryophyllaceae	1.0	0.6
Lamiaceae	1.0	0.6	Plumbaginaceae	0.1	0.2	Rhamnaceae	0.1	1.6
Flacourtiaceae	1.0	0.2	Chenopodiaceae	1.0	0.6	Caesalpiniaceae	0.1	0.2
Euphorbiaceae	1.0	0.2	Gleicheniaceae	0.1	0.2	Myrtaceae	1.0	0.2
Juncaceae	0.1	0.1	Polygonaceae	0.1	0.6	Cactaceae	0.1	0.6
Fabaceae	1.0	0.2	Pandanaceae	2.0	0.6	Berberidaceae	1.0	0.2
Ericaceae	0.1	0.1	Ephedraceae	0.1	0.2	Convolvulaceae	0.1	0.2
Annonaceae	0.1	1.6	Verbenaceae	0.1	0.2	Salicaceae	1.0	0.2
Pteridiaceae	0.1	0.2	Coriariaceae	1.0	0.6	Ulmaceae	0.1	0.1
Tamaricaceae	1.0	0.2	Ranunculaceae	1.0	1.6	Iridaceae	0.1	0.2
Poaceae	1.0	0.6	Oleaceae	0.1	0.6	Rutaceae	1.0	0.6
Rhizophoraceae	1.0	0.2	Sphagnaceae	0.1	0.1	Restionaceae	0.1	0.1
Elaeagnaceae	1.0	0.2	Anacardiaceae	1.0	0.2	Myrsinaceae	0.1	0.2
Zygophyllaceae	0.1	0.2	Rubiaceae	1.0	0.6	Nyctaginaceae	0.1	0.2
Cupressaceae	0.1	1.6	Pinaceae	0.1	3	Betulaceae	0.1	0.2

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720 **Table 8.** Normalized leaf-level isoprene and monoterpene emission rates for 13 crop species in China
721 (μg C gdw^{-1} h^{-1}).

Species/genera	Isoprene	Monoterpene	Species/genera	Isoprene	Monoterpene
Tea	0.1	0.2	Rubber	1.0	3.0
Beans	0.1	0.1	Wheat	0.1	0.1
Fruit tree	0.1	0.6	Tobacco	0.1	0.1
Bast fibre plants	0.1	0.6	Oil plants	0.1	0.2
Cotton	0.1	0.2	Corn	0.1	0.2
Potatos	0.1	0.1	Cereal	0.1	0.2
Rice	0.1	0.1			

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722 **Table 9.** Comparison of isoprene emission categories and determined emission rates between our
723 study and other studies (μg C gdw^{-1} h^{-1}).

Emission categories	*Eucalyptus*	*Quercus*	*Populus*	Bamboo	Studies
0.1, 1.0, 5.9, 14.4, 34.7, 70.1, 144.4	50.0	70.1	70.1	70.1	This study
0.1, 14, 70	-	56	22	5	Klinger et al., 2002
0.1, 1, 6, 8, 34, 60	-	60	60	0.5	Yan, 2005
0.1, 5, 10, 20, 40, 60	50	50	50	0.5	Wang, 2007

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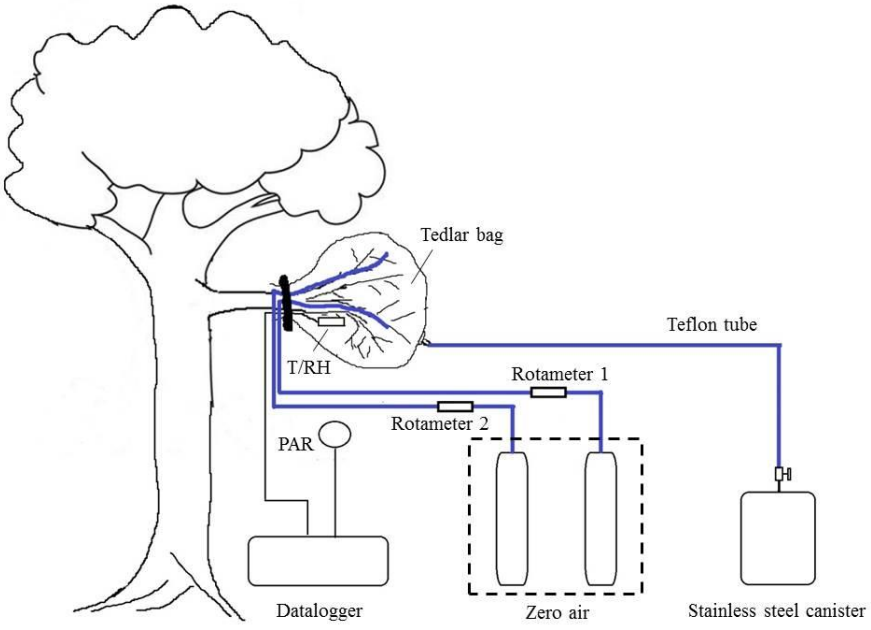

724

725 **Figure 1.** Schematic of the semi-static branch enclosure system used in this study. T/RH
726 means the temperature and relative humidity probe; PAR means light sensor; Blue lines
727 indicate the Teflon tubes. Rotameter 1 and 2 were used to monitor and control the flow rate of
728 10 L min^{-1} and 2 L min^{-1} at the two purging of zero air, respectively.

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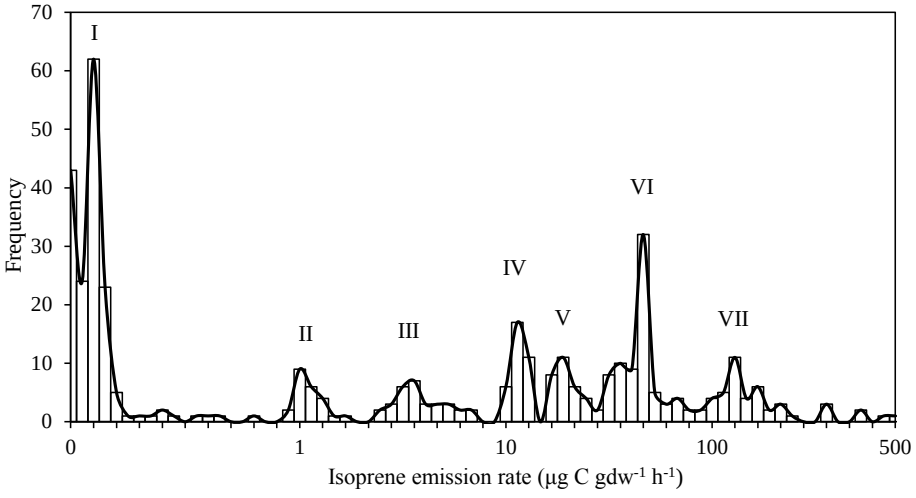
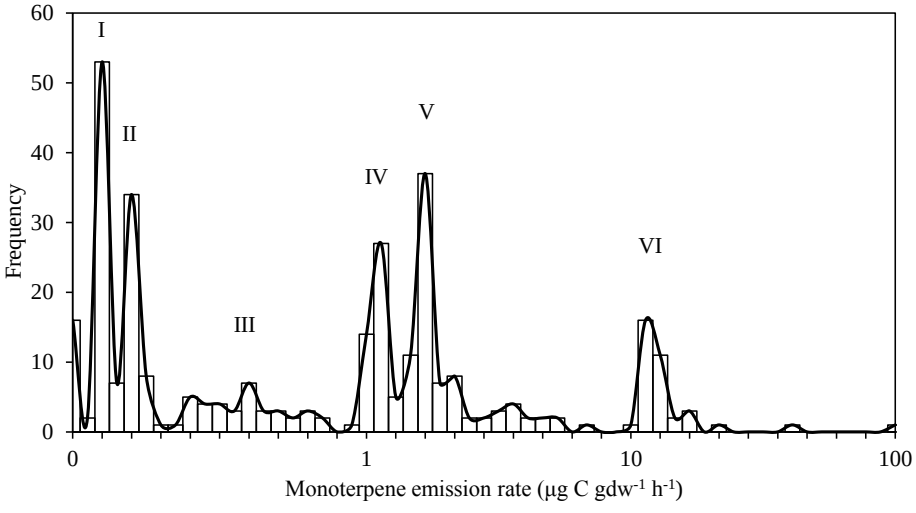


(a)



(b)

Figure 2. Frequency distribution of (a) isoprene and (b) monoterpene emission rates from forest trees.