Characteristics and chemical reactivity of biogenic volatile organic compounds from dominant forest species in the Jing-Jin-Ji area, China

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Abstract

Background: Biogenic volatile organic compounds (BVOCs) play an essential role in tropospheric atmospheric chemical reactions. There are few studies on BVOCs emission of dominant tree species in the Jing-Jin-Ji area. Based on the field survey, forest resources data and the measured standard emission factors, this paper used Guenther model in 1993 (G93) to estimate the emissions of BVOCs from dominant forest species (*Platycladus orientalis*, *Quercus variabilis*, *Betula platyphylla*, *Populus tomentosa*, *Pinus tabuliformis*, *Robinia pseudoacacia*, *Ulmus pumila*, *Salix babylonica*, *Larix gmelinii*) in the Jing-Jin-Ji area in 2017, analyzed their spatiotemporal emission characteristics and evaluated their amospheric chemical reactivity.

Results: Results showed that the total annual BVOCs emissions were estimated to be 70.8 Gg $C \cdot a^{-1}$, consisting of 40.5% (28.7 Gg $C \cdot a^{-1}$) isoprene, 36.0% (25.5 Gg $C \cdot a^{-1}$) monoterpenes, and 23.4% (16.6 Gg $C \cdot a^{-1}$) other VOCs. The emissions of *Platycladus orientalis*, *Quercus variabilis*, *Populus tomentosa* and *Pinus tabulaeformis* contributed 56.1%, 41.2%, 36.0% and 31.1%, respectively. In summer and winter, BVOCs emissions from the Jing-Jin-Ji area accounted for 61.9% and 1.8% of the annual total. Emissions from Chengde contributed to 28.8%, followed by Beijing, accounting for 24.9%, which was mainly distributed in the Taihang Mountains and the Yanshan Mountains. *Robinia pseudoacacia*, *Populus tomentosa*, *Quercus variabilis,* and *Pinus tabulaeformis* contributed higher BVOCs reaction activity.

Conclusions: Emissions peaked in summer (June, July, and August) and bottomed out

in winter (December, January, and February). Chengde contributed the most, followed by Beijing. *Platycladus orientalis*, *Quercus variabilis*, *Populus tomentosa*, *Pinus tabulaeformis* and *Robinia pseudoacacia* are the primary BVOCs emission and atmospheric reactivity contributors, the planting rates of these species with significant emissions or atmospheric reactivity of BVOCs should be considered for reduction.

Keywords

Biogenic volatile organic compounds (BVOCs); Isoprene; Monoterpenes; Jing-Jin-Ji area; Spatiotemporal characteristics; Chemical reactivity

1. Background

Biogenic volatile organic compounds (BVOCs) are low boiling point volatile organic compounds synthesized by secondary metabolic pathways in plants. Many vascular plants can discharge BVOCs into the atmosphere (Loreto and Schnitzler, 2010). Forest is one of the primary sources that emits BVOCs, which occupies about 70% of the total BVOCs amounts from vegetation. According to the estimation of some researchers, the annual emissions of BVOCs in the world was about 10^6 Gg $C \cdot a^{-1}$ (Guenther et al., 2012), accounting for more than 90% of the total world's non-methane volatile organic compounds (NMVOCs) emissions on ground, far exceeding the anthropogenic compounds (Guenther et al., 1995). Isoprene (the simplest 5-carbon isoprenoid, C_5H_8, 2-methyl 1,3-butadiene) is the highest emission component (Atkinson and Arey, 2003), and its annual emission is approximately 50% of the total annual global emissions of BVOCs with 412-601 Tg $C \cdot a^{-1}$ (Guenther et al. 2012). Monoterpenes are 10-carbon isoprenoids that account for about 15% of global BVOCs emissions with 32-157 Tg $C \cdot a^{-1}$ (Guenther et al., 2012). They are both synthesized by the MEP pathway (Loreto and Schnitzler, 2010). BVOCs are formed constitutively or after stress induction. Those components can raise plant tolerance to abiotic stressors such as high temperature, oxidative stress and biotic stressors such as competing plants and microorganisms (Loreto and Schnitzler, 2010; Filella et al., 2013).

BVOCs play an essential role in tropospheric atmospheric chemical reactions (Sartelet et al., 2012; Kulmala et al., 2013). They are main precursors of tropospheric

ozone and atmospheric aerosols, promoting the formation of secondary pollutants such as peroxyacetyl nitrate (PANs), secondary organic aerosols (SOA), particulate matter (PM), aldehydes and ketones (Claeys et al., 2004; Laothawornkitkul et al., 2009). In detail, isoprene breakdown is known to produce ozone when reacting with NO_x (Fehsenfeld et al., 1992), while monoterpenes and sesquiterpenes can contribute to the formation of cloud condensation nuclei, thus providing formation place of secondary organic aerosols (Claeys et al., 2004), further affecting the local or global climate.

The Jing-Jin-Ji area, located on the North China Plain, is the core of north China and the most developed city cluster in China. With the rapid development of the economy, and the acceleration of urbanization, the problem of air pollution is becoming more and more serious. This area has been plagued by severe photochemical pollution and haze for many years (Tang et al., 2009; Han et al., 2013). Zhao et al. (2013) showed that the hourly average concentration of $PM_{2.5}$ in Beijing could reach 318 $\mu g/m^3$ on hazy days. Cities in Hebei province suffer more severe air pollution (Wang et al., 2012). Chen et al. (2013) reported that the Jing-Jin-Ji area's ozone mixing ratio was very high from May to September, causing strong photochemical reactions. Zhao et al. (2020) also reported that during 2014-2018, ozone concentration in the Jing-Jin-Ji area showed an upward trend, the average annual level rose by 4.90 $\mu g/m^3$. Ghirardo et al. (2016) found that the contribution of BVOCs released by vegetation to SOA generation in Beijing increased by two times during 2005-2010. Many types of research have shown that in the Jing-Jin-Ji area, especially in summer, the role of BVOCs in ozone formation cannot be

ignored (Ran et al., 2011; Xie et al., 2008). This caused severe impacts on human health, economic development, ecological environment, and climate change (Sicard et al., 2017). Considering the particular geographical location, diverse vegetation composition, and the enormous influence of BVOCs on ozone and secondary aerosols, it is crucial to clarify the BVOCs emitted from dominant forest species in the Jing-Jin-Ji area.

At present, estimates of BVOCs emissions from plants have been made through various studies using different methods, including models and land cover and meteorological data. The results of the Jing-Jin-Ji area from different models and input parameters at home and abroad are different (Kilnger et al., 2002; Song et al., 2012; Li et al., 2016). Given that most of the previous estimates roughly divided the forest species into several plant functional types (PFT), using the global average emission rates and biomass density of each vegetation type, ignoring the differences between plant species and regions (Xia and Xiao, 2019). Besides, most of the studies used the recommended values of emission factors in the literature or select the measured values of adjacent areas, without the local measured primary data, which may not be representative enough (Song et al., 2012; Zhang et al., 2018). Different regions with different environments will cause different release rates of BVOCs. Besides, few reports are relevant to the measured emission rates of dominant forest species in the Jing-Jin-Ji area, and a systematic comparison of the BVOCs emissions of them is also lacking. In this study, we selected *Platycladus orientalis, Quercus variabilis, Betula platyphylla, Populus tomentosa, Pinus tabuliformis, Robinia pseudoacacia, Ulmus pumila, Salix*

babylonica, Larix gmelinii as the dominant forest species in the Jing-Jin-Ji area. Based on field vegetation investigation and measured forest species emission rates, this paper used Guenther model in 1993 (G93) (Guenther et al., 1993) to estimate the BVOCs emissions from dominant forest species in the Jing-Jin-Ji area, and analyze their spatiotemporal distribution characteristics and chemical reactivity, so as to make a more localized emission inventory, further eliminate its uncertainty.

2. Materials and Methods

2.1 Site description

Jing-Jin-Ji area is located in the North China Plain (**Figure 1**), including Beijing, Tianjin, and Hebei (36° 05 '- 42 ° 40' N, 113 ° 27 '- 119 ° 50' E), with a total area of about 21.72 ha. This area is bordering the Bohai Sea in the east, Tai-hang Mountains in the West and Yanshan Mountains in the north, 735 km long from north to south, and 576 km wide from east to west, with various terrains, and warm temperate continental monsoon climate. The annual average temperature is 0-13℃, and the average yearly precipitation is 300-800 mm. There are various vegetation types in this area, including forest, shrub, grassland, and so on. The sampling sites were all selected in the forest parks with abundant plant resources in this study area, and the experiment was conducted on bright days.

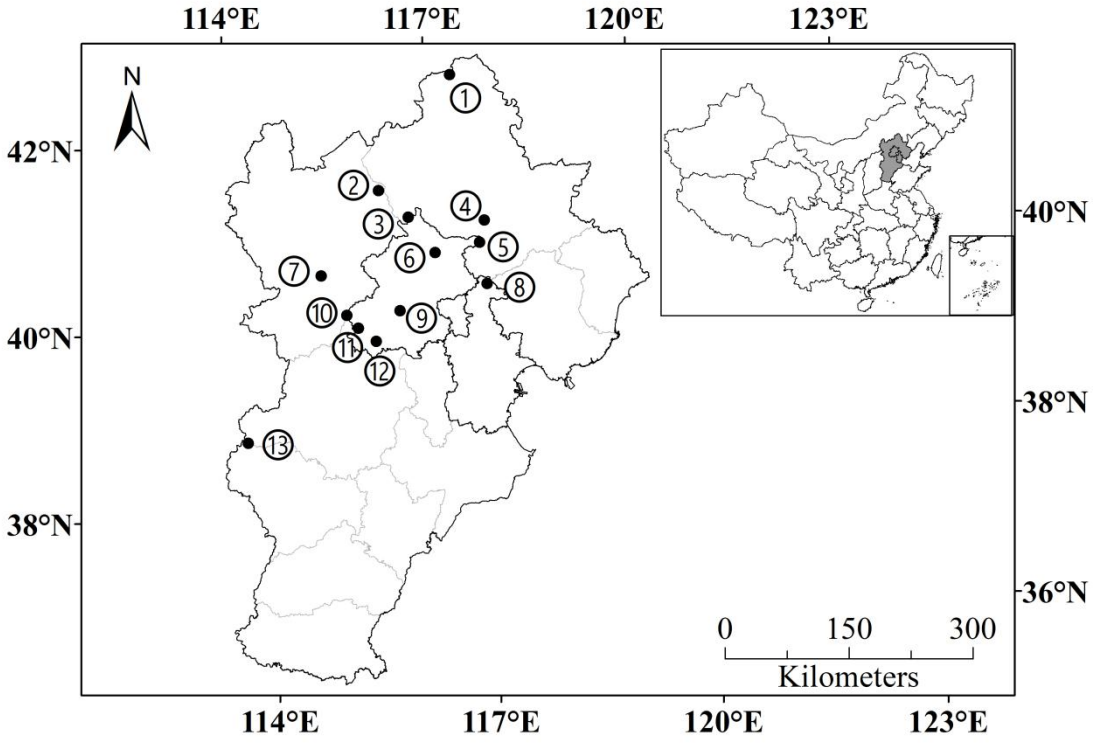

Figure 1. The site locations of the Jing-Jin-Ji area

The sampling sites (solid circles) identified as follows: ①Saihanba National Forest Park ②Heilongshan National Forest Park ③Labagou Primeval Forest Park ④Baicaowa National Forest Park ⑤Wuling Mountain Scenic Spot ⑥Yunmengshan National Forest Park ⑦Huangyangshan Forest Park ⑧Tianjin Jiulongshan National Forest Park ⑨Xishan National Forest Park ⑩Xiaolongmen National Forest Park ⑪Baihuashan National Nature Reserve ⑫Shangfangshan National Forest Park ⑬Wuyuezhai Scenic Spot

2.2 BVOCs emission estimation model

Guenther series models were widely used to estimate the BVOCs emission. Guenther combined with the latest experimental data deduced the G93 algorithm in 1993

158 (Guenther et al., 1993). It normalized the emission rate of BVOCs under various
159 environmental conditions as T=303 K, PAR=1000 mol·m^{-2}s^{-1}, and it matches the
160 estimation method of subdivision species selected in this paper. The BVOCs emitted by
161 dominant forest species were classified as isoprene, monoterpene, and other VOCs
162 (including alcohols, aldehydes, ketones, organic acids, low carbon alkanes and alkenes)
163 in this paper. According to the model of light and temperature effect proposed by G93,
164 the BVOCs emissions classified by forest species were estimated respectively. Specific
165 formulas are as follows:

166 $$\text{Isoprene: } I=I_S \times C_L \times C_{TI} \quad (1)$$

167 Where, I is the emission rate of isoprene (in C, μg·g^{-1}·h^{-1}) at a certain temperature T
168 (K) and PAR (μmol·m^{-2}s^{-1}), and I_S is the emission rate (standard emission rate) of
169 isoprene (in C, μg·g^{-1}·h^{-1}) under standard condition (T=303 K, PAR=1000 μmol·m^{-2}s^{-1});
170 C_L and C_{TI} are correction factors for light and temperature, respectively, and can be
171 obtained by equations (2) and (3):

172 $$C_L=\alpha C_{L1} L/\sqrt{1+\alpha^2 L^2} \quad (2)$$

173 Where, α(0. 0027) and C_{L1} (1. 066) are empirical constants, and L is PAR.

174 $$C_{TI}=\frac{\exp[C_{T1}(T-T_S)/RT_S T]}{1+\exp[C_{T2}(T-T_M)/RT_S T]} \quad (3)$$

175 Where, R is a gas constant (8.314 J·K^{-1}·mol^{-1}); Ts is the leaf temperature of the
176 standard state (303 K). C_{T1}(95000 J·mol^{-1}), C_{T2} (230000 J·mol^{-1}) and T_M (314 K) are
177 empirical constants.

178 The monoterpenes and other VOCs emission rates in algorithm G93 can be calculated

using equation (4) and (5):

$$M=M_{TS}C_{TM} \quad (4)$$

$$C_{TM} = \exp[\beta (T - Ts)] \quad (5)$$

Where M is the emission rate of monoterpene and other VOCs (in C, $\mu g \cdot g^{-1} \cdot h^{-1}$) at a certain temperature T (K); M_{TS} is the emission rate (basic emission rate) of monoterpene and other VOCs (in C, $\mu g \cdot g^{-1} \cdot h^{-1}$) under standard condition (Ts=303 K); C_{TM} are correction factors for temperature of monoterpenes and other VOCs; β (0.09 K^{-1}) are empirical constants.

Experimental results showed that the emission rate of isoprene is mainly controlled by leaf temperature and PAR. However, the main factor affecting monoterpenes and other VOCs emission by plants is temperature. Therefore, the emission estimation method of isoprene is:

$$E_{ISOP}=I_S \times B \times C_{TI} \times C_L \quad (6)$$

The emission estimation method of monoterpenes and other VOCs is:

$$E_{MONO},E_{OVOC}=M_{TS} \times B \times C_{TM} \quad (7)$$

Where, E_{ISOP} is the emission of isoprene (in C, μg); E_{MONO} and E_{OVOC} are the emissions of monoterpenes and other VOCs (in C, μg), respectively; and B is the leaf biomass (dry weight, g) of each species.

2.3 Determination of model parameters

2.3.1 Emission rates

BVOCs were collected by a dynamic headspace method combining the Tenax

adsorption tube and sampling pump. The volatile gases released by plants can be adsorbed in CAMSCO adsorption tubes filled with Tenax-TA adsorbents. Before sampling, the adsorption tubes were purged and activated for 2 hours under high-purity N_2, then wrapped in tin foil and stored under 4℃ cold storage for sampling. The sampling objects were healthy branches. Simultaneously, temperature, relative humidity and photosynthetic effective radiation were recorded with a hand-held meteorological instrument. After collection, the adsorption tube was stored in the refrigerator and analyzed within one week. BVOCs were adsorbed PE TurboMatrix (650ATD-Clarus600) and analyzed by thermal desorption gas chromatography-mass spectrometry (TCT-GC-MS, Agilent 6890, USA). The emission rates of dominant forest species in the Jing-Jin-Ji area were respectively calculated according to the following equation:

$$ER = \frac{m}{t \times M} \quad (8)$$

Where, ER is the emission rate of each forest species (in C, $\mu g \cdot g^{-1} \cdot h^{-1}$); m is the quality of BVOCs in adsorption tube (in C, μg); t is the sampling time (h); M is the leaf biomass of forest species (dry weight, g).

The standard emission factors of each forest species corrected by the light and temperature model were detailed in the other article of this research group (Fan, 2019).

2.3.2 Leaf biomass calculation

The Jing-Jin-Ji area's leaf biomass data were obtained based on the method of volume and yield conversion. The statistical method of subdividing species enables them to correspond to more appropriate emission factors and biomass, fully consider the

biomass difference of the same species in different regions. Based on the volumes obtained from the national forest resource inventory, the leaf biomass of the dominant forest species can be calculated as follows:

$$B=\frac{V\times D_T}{P_T}\times P_L \quad (9)$$

Where B is leaf biomass of forest species (dry weight, g); V is tree volume; D_T is the basic density of tree trunk (the ratio of absolute dry wood mass to raw wood volume); P_T and P_L are the proportion of stem and leaf in the total biomass of tree layer respectively. The data of P_T, P_L and D_T mainly came from literature (Wang et al., 2001). In this paper, the proportion of trunk density, leaf and stem biomass to the total biomass of dominant forest species in the Jing-Jin-Ji area were presented in **Table A.1**. Tree volumes data were mainly based on national forest resources survey data, checked and supplemented by forestry network and field survey.

2.4 Methods of chemical activity evaluation

Different BVOCs components have different chemical compositions and physical properties, thus the atmospheric chemical reaction capacity is different (Goldan et al., 2004). Studying the chemical reactivity of different BVOCs and their ability to generate ozone can provide a reference for the proposal of BVOCs control measures. This study adopted two methods, the maximum incremental reactivity (MIR) method and the ·OH reaction rate (L^{OH}) method, to comprehensively analyze the chemical activity of the BVOCs components of dominant forest species in the Jing-Jin-Ji area.

Ozone formation potential (OFP) can be used to evaluate the potential of BVOCs

242 released into the atmosphere under optimal reaction conditions to participate in
243 generating ozone, so as to measure the reactivity of different BVOCs components
244 (Carter, 1991). Its value is obtained by multiplying the emission of each component by
245 the corresponding MIR factor, as shown in equation (10):

246 $$OFP_i = \mathrm{MIR_i} \times C_i \quad (10)$$

247 Where OFP_i is the ozone generation potential of each component (μg/m^3); $\mathrm{MIR_i}$ is
248 the maximum incremental response factor of each component (gO_3/gVOCs) (Carter,
249 2008); C_i is the mass concentration of each component (μg/m^3).

250 The chemical reaction of the troposphere during the daytime is mainly OH radicals
251 (·OH). Volatile organic compounds first react with ·OH, and then respond with O_2 and
252 NO_X under light conditions to generate new free radicals and initiate a chain reaction.
253 The first reaction is a key step that determines the atmospheric photochemical reaction
254 chain's speed, so the consumption rate of ·OH can be used to evaluate the
255 photochemical activity of BVOCs. Its value is obtained by multiplying the atmospheric
256 molecular concentration of the component with the ·OH reaction rate constant, as
257 shown in equation (11):

258 $$L_i^{OH} = \mathrm{K_i^{OH}} \times [BVOCs]_i \quad (11)$$

259 Where L_i^{OH} is the consumption rate of each component to atmospheric ·OH (s^{-1});
260 $\mathrm{K_i^{OH}}$ is the reaction rate constant between each component and atmospheric ·OH
261 (cm^3·molecule^{-1}s^{-1}) (https://kinetics.nist.gov/kinetics/index.jsp); $[BVOCs]_i$ is the
262 atmospheric molecular concentration of every component (molecule·cm^{-3}).

3. Results and discussion

3.1 Emission budgets and compositions of BVOCs

BVOCs emitted from dominant forest species were divided into isoprene, monoterpenes, and other VOCs (OVOCs) (**Table 1**). The total annual emission of BVOCs from dominant trees in the Jing-Jin-Ji area was estimated to be 70.8 Gg C·a^{-1}, including 40.5% (28.7 Gg C·a^{-1}) isoprene, 36.0% (25.5 Gg C·a^{-1}) monoterpenes, and 23.4% (16.6 Gg C·a^{-1}) other VOCs, respectively.

Monoterpenes including α-pinene, β-pinene, β-myrcene, limonene, 3-carene and so on. Different forest species can produce various components of BVOCs. **Figure 2** shows each component and proportion of BVOCs emitted by nine dominant species in the Jing-Jin-Ji area. Among them, the main component emitted by some broadleaf trees such as *Betula platyphylla*, *Quercus variabilis*, and *Salix babylonica* is isoprene. Except for isoprene, some broadleaf trees like *Populus tomentosa*, *Robinia pseudoacacia, Ulmus pumila* and most coniferous trees like *Platycladus orientalis*, *Pinus tabuliformis*, and *Larix gmelinii* can release monoterpenes such as α-pinene, β-pinene, β-myrcene, limonene, and so on. **Figure A.1** shows that *Quercus variabilis*, *Populus tomentosa* are significant isoprene emitters among those forest species, contributing 41.2% and 31.1%, respectively, while *Platycladus orientalis* and *Pinus tabuliformis* are significant emitters of monoterpenes, providing 56.1% and 36.0%, respectively. Therefore, the above four forest species are the main contributors to BVOCs in the Jing-Jin-Ji area, about 19.3 Gg C·a^{-1} of *Platycladus orientalis*, 14.0 Gg C·a^{-1} of *Quercus variabilis*, 13.4 Gg C·a^{-1} of

284 *Populus tomentosa* and 12.2 Gg C·a^{-1} of *Pinus tabuliformis*, accounting for 27.2%,
285 19.8%, 18.9% and 17.2% of total BVOCs emissions from dominant forest species,
286 respectively (**Table 1**).

287 **Table 1.** The annual emissions of BVOCs from dominant forest species in the
288 Jing-Jin-Ji area (t C·a^{-1})

Forest species	Isoprene	α-pinene	β-pinene	β-myrcene	limonene	3-carene	[1]OVOCs	[2]TVOCs	Proportion
Platycladus orientalis	70.0	7591.2	318.2	1185.1	765.1	4446.0	4885.1	19260.6	27.2%
Robinia pseudoacacia	3375.0	209.7	150.4	57.4	90.5	32.5	1191.4	5107.0	7.2%
Betula platyphylla	2131.1	14.9	0.0	0.0	0.0	0.0	2232.4	4378.3	6.2%
Quercus variabilis	11818.3	0.0	0.0	0.0	0.0	0.0	2184.3	14002.6	19.8%
Salix babylonica	1637.2	0.0	0.0	0.0	0.0	0.0	190.7	1827.9	2.6%
Populus tomentosa	8934.9	464.7	48.4	279.3	255.2	2.7	3383.8	13368.9	18.9%
Pinus tabuliformis	707.7	3254.4	22.1	4041.9	1854.7	11.0	2263.0	12154.8	17.2%
Ulmus pumila	28.1	17.9	0.0	20.2	0.0	0.0	193.3	259.6	0.4%
Larix gmelinii	0.1	276.3	114.5	0.0	0.0	0.0	79.8	470.7	0.7%
Total	28702.3	11829.1	653.5	5583.9	2965.5	4492.2	16603.7	70830.2	100.0%
Proportion	40.5%	16.7%	0.9%	7.9%	4.2%	6.3%	23.4%	100.0%	-

289 [1]OVOCs: other VOCs; [2]TVOCs: total VOCs

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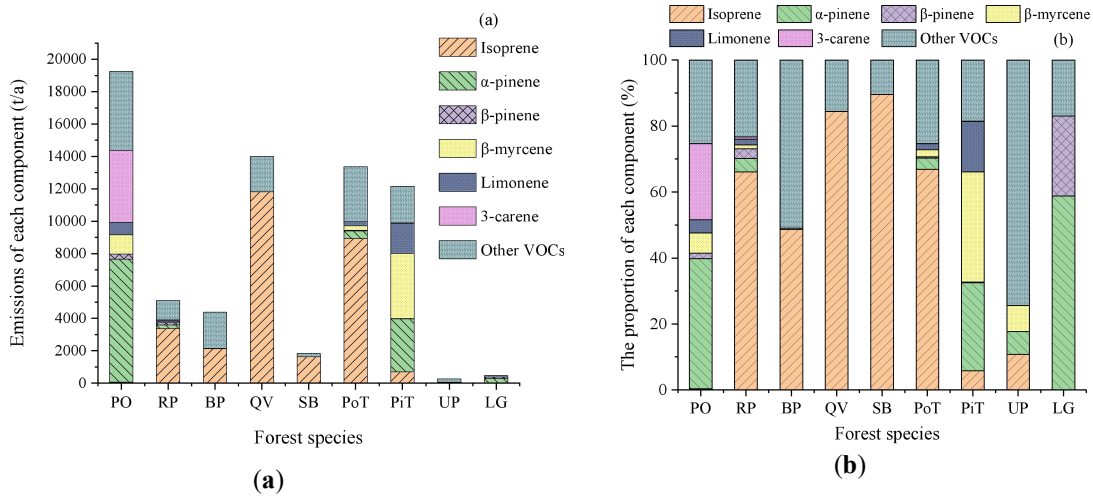
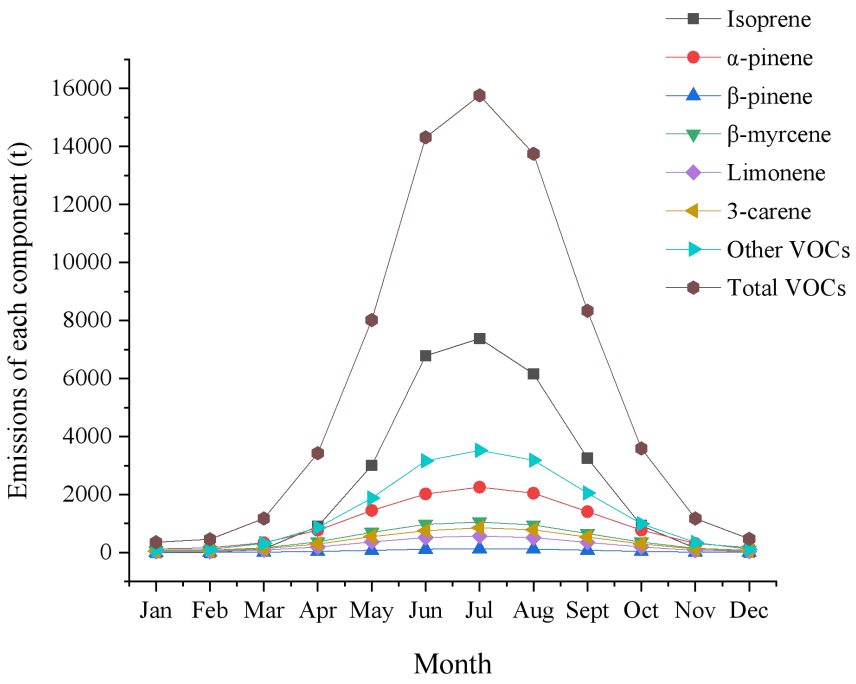


Figure 2. The BVOCs emissions (a) and proportion of each component (b) from dominant forest species in the Jing-Jin-Ji area (BP: *Betula platyphylla*; QV: *Quercus variabilis*; UP: *Ulmus pumila*; PoT: *Populus tomentosa*; RP: *Robinia pseudoacacia*; PO: *Platycladus orientalis*; PiT: *Pinus tabuliformis*; SB: *Salix babylonica*; LG: *Larix gmelinii*)

3.2 Monthly and Seasonal variations

Table A.2 and **Figure 3** indicates that the BVOCs emissions and compositions in the Jing-Jin-Ji area demonstrate significant monthly and seasonal variations. We can observe that the emissions of BVOCs show a distinct unimodal change with the month.



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303 **Figure 3.** The monthly BVOCs emissions from dominant forest species in the

304 Jing-Jin-Ji area (t)

305

306 Total BVOCs emissions peaked in July, with a total amount of 15.8 Gg C·a^{-1}, and

307 reach a minimum in January of about 0.4 Gg C·a^{-1}, with two orders of magnitude

308 difference. In January, the isoprene emission from vegetation hit its low point at 1.9 t

309 C·a^{-1} due to low temperature, the less sunlight, and the less biomass of leaves.

310 Accordingly, isoprene emissions hit its high point at 7.4 Gg C·a^{-1} in July, when

311 temperatures were high, sunlight was strong, and the foliar biomass was at the largest.

312 The isoprene emissions estimated in other months fluctuated between this maximum

313 and minimum. The same pattern occurred with monoterpenes' emissions and other

314 VOCs, they all reached their highest emissions in July and their lowest emissions in

January.

Overall, the total BVOCs emissions peaked in summer (June, July, and August) and bottomed out in winter (December, January and February). In spring, BVOCs emissions showed an upward trend, among which isoprene increased most significantly. Monoterpenes and other VOCs also increased, but not as much as isoprene, because of the greater influence of light and temperature on isoprene. The vegetation was still in the growing season in spring, the leaves were in the germination growth stage, leaf area was far less than mature leaves, and enzyme activity had not reached the highest level. Therefore, the spring BVOCs emissions only accounted for 17.8% of the whole year. In summer, the average daily temperature and sunshine time had significantly increased compared to that in spring, and the vegetation leaves had reached the mature stage, the leaf area had basically reached the maximum. The enzyme activity was also the highest. As a result, summer was the period of high BVOCs emissions, with the emissions getting 43.8 Gg $C \cdot a^{-1}$, accounting for 61.9% of the total annual emissions. In the autumn, the temperature difference was noticeable, and the leaves were also changed from the mature leaves to the decaying leaves. Therefore, BVOCs emissions showed a trend of decline in September, a sharp decrease in October, and basically stable in November. The total BVOCs emissions in autumn only accounted for 18.5%. Due to low temperatures and limited sun irradiation in winter, BVOCs emissions reached the lowest stage of the year, only accounting for 1.8%.

3.3 Spatial distribution

To understand the spatial distribution of BVOCs emissions in the Jing-Jin-Ji area, we calculated the BVOCs emissions in 13 cities (Beijing, Tianjin, Baoding, Cangzhou, Chengde, Handan, Hengshui, Langfang, Qinhuangdao, Shijiazhuang, Tangshan, Xingtai, Zhangjiakou). As is shown in **Table A.3** and **Figure 4**, the BVOCs emission fluxes and compositions in the Jing-Jin-Ji area has an apparent spatial distribution. Given that Chengde and Beijing have high vegetation coverage, and the dominant species in Wuling Mountain Reserve and Saihanba Forest Farm in Chengde are *Betula platyphylla*, *Quercus variabilis*, *Populus tomentosa* and *Pinus tabulaeformis*, which have higher BVOCs emission rates. Therefore, Chengde contributed the most to the BVOCs emissions of dominant forest species in the Jing-Jin-Ji area, with a total emission of 20.4 Gg $C \cdot a^{-1}$, accounting for 28.8%, followed by Beijing, with a total discharge of 17.6 Gg $C \cdot a^{-1}$, accounting for 24.9%. The others were Baoding, Tangshan, Hengshui, Zhangjiakou, and so on. Due to the smaller city area and lower vegetation coverage, the emissions of Cangzhou (0.4 Gg $C \cdot a^{-1}$) and Langfang (0.5 Gg $C \cdot a^{-1}$) were less than others, which only account for 0.6% and 0.8%, respectively. In terms of compositions, as is shown in **Figure A.2**, Chengde has the largest isoprene emission with 7.7 Gg $C \cdot a^{-1}$, accounting for 26.8% of the total isoprene emissions released by dominant forest species in the Jing-Jin-Ji area, most probably due to the extensive vegetation coverage of deciduous trees with high isoprene emissions such as *Quercus variabilis*. Besides Chengde, Beijing had high emissions of monoterpenes (9.4 Gg $C \cdot a^{-1}$), accounting for 36.9% of the total monoterpenes emissions, which was mainly attributed to α-pinene

and β-myrcene from coniferous such as *Platycladus orientalis* and *Pinus tabuliformis,* which can also explain why Chengde's emissions are the highest in spring, summer, and autumn, but are exceeded by Beijing in winter. Chengde has the most substantial difference in emissions in winter and summer because the dominant forest species here are mostly deciduous trees. The low temperature and less sunshine in winter make the leaf biomass of deciduous trees emit less, thus significantly reducing emissions (**Figure 5)**. In general, the distribution of BVOCs emission fluxes is highly consistent with the distribution of vegetation.

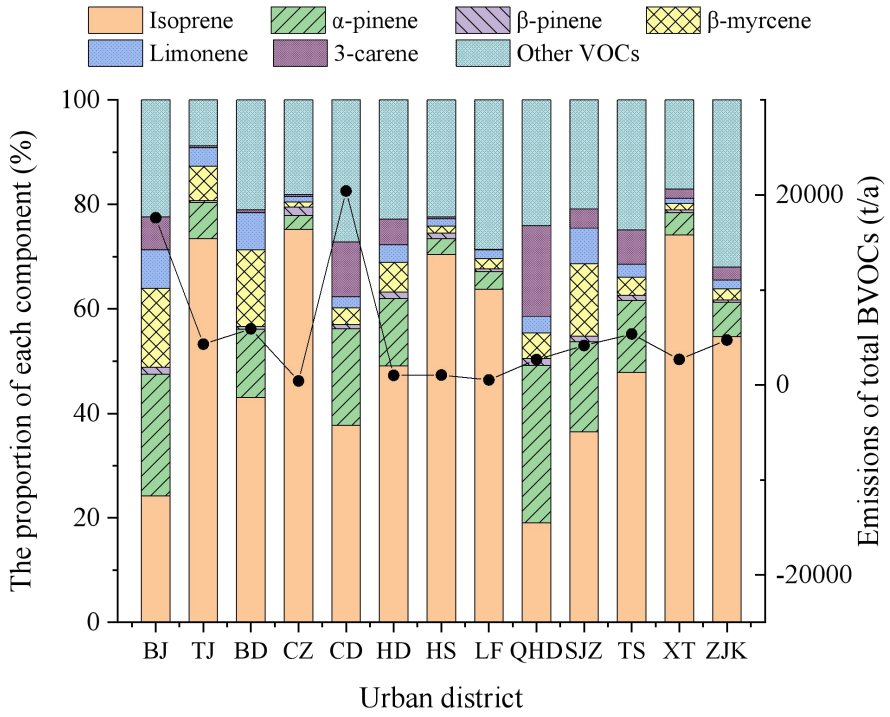


Figure 4. The BVOCs emissions (a) and proportion of each component (b) in each city in the Jing-Jin-Ji area

(BJ: Beijing; TJ: Tianjin; BD: Baoding; CZ: Cangzhou; CD: Chengde; HD: Handan; HS: Hengshui; LF: Langfang; QHD: Qinhuangdao; SJZ: Shijiazhuang; TS: Tangshan;

XT: Xingtai; ZJK: Zhangjiakou)

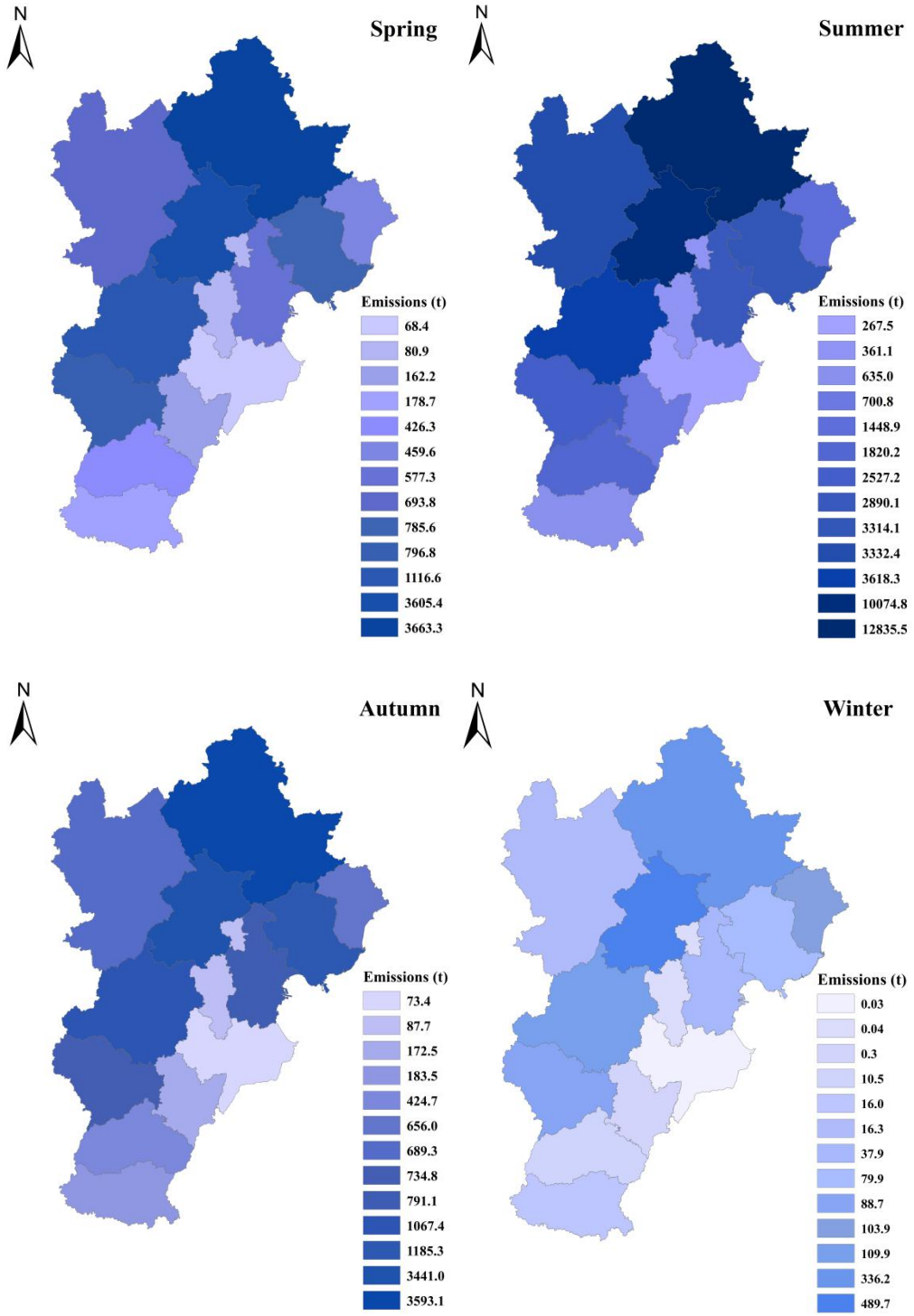


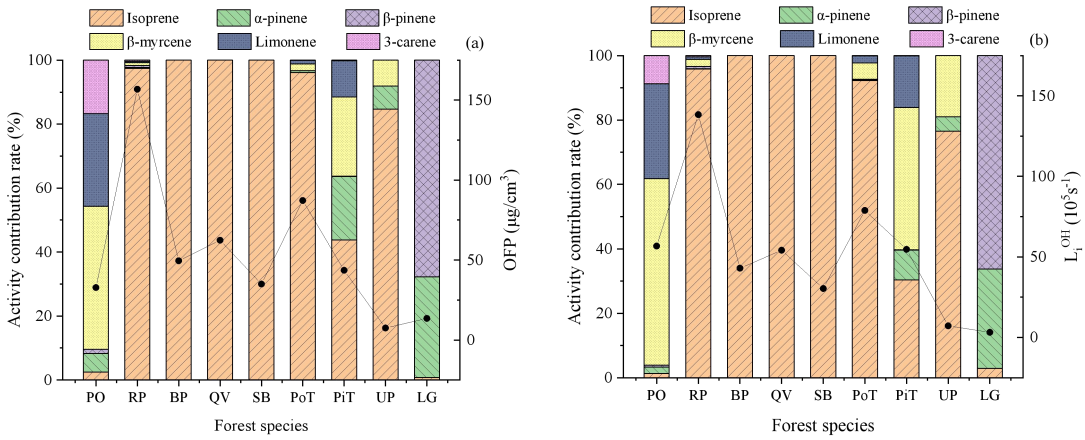
Figure 5. The seasonal BVOCs emissions distribution of dominant forest species in the Jing-Jin-Ji area

In order to visualize the spatial distribution of BVOCs in the Jing-Jin-Ji area more intuitively, this study also used the Model of Emissions of Gases and Aerosols from Nature (MEGAN), version 3.0 (Guenther et al., 2006) to estimate the BVOCs emissions in the Jing-Jin-Ji area with 3km*3km resolution in 2017. The localized forest species and emission factors were updated in MEGAN. **Figure A.3** shows the modeled annual emissions of isoprene, terpenes, other VOCs, and total VOCs. By comparing the results from MEGAN and G93 model, the BVOCs distributions show a similar pattern. MEGAN results show that the areas with high BVOCs emissions in Jing-Jin-Ji are mainly distributed in the Taihang mountains from southwest to northeast and the Yanshan mountains in the north, where primary BVOCs emitters such as *Betula platyphylla* or *Quercus variabilis* forests are the main vegetation types. The areas with low isoprene emission mainly occurred in southeast and northwest, where the main vegetation types were cultivated land and grassland. The emissions of isoprene in the study area ranged from 0.3 to 6 $t \cdot a^{-1} \cdot km^{-2}$. Compared to isoprene, the differences of terpenes are not significant, and the emissions in most areas ranged from 0.1 to 2 $t \cdot a^{-1} \cdot km^{-2}$. A similar distribution also occurred on other VOCs, and it ranged from 0.02 to 0.4 $t \cdot a^{-1} \cdot km^{-2}$. On the whole, Isoprene distributions were correlated with broad-leaved forests and shrubbery, and monoterpenes distributions were correlated with coniferous forests. The total BVOCs emitted by plants mainly concentrated in Chengde and Beijing, covering the Yanshan Mountains, and Baoding, located in the north of the Taihang Mountains.

3.4 Chemical activity evaluation

The contribution of BVOCs to atmospheric chemical reaction not only depends on the level of its emission but also closely related to their chemical activity. Since the olefins with double bonds are more active ingredients, and the main BVOCs components released by dominant forest species in the Jing-Jin-Ji area are isoprene and monoterpenes, this study comprehensively analyzes the chemical activity of isoprene and monoterpenes by the maximum incremental reactivity (MIR) method and the ·OH reaction rate (L^{OH}) method. **Figure 6** shows the OFP and L_i^{OH} values and activity contribution rates of every dominant forest species. Overall, the activity contribution rate of isoprene and monoterpenes of each species calculated by the two methods is basically consistent. Among them, the OFP values of *Robinia pseudoacacia*, *Populus tomentosa* and *Quercus variabilis* obtained by the MIR method were higher, followed by *Betula platyphylla* and *Pinus tabuliformis*, and the OFP values of *Ulmus pumila* were the lowest. The forest species with higher L_i^{OH} value obtained by the L^{OH} method were *Robinia pseudoacacia*, *Populus tomentosa*, *Platycladus orientalis*, *Pinus tabuliformis* and *Quercus variabilis*, *Larix gmelinii* had the lowest L_i^{OH} value. The difference between the two methods is due to their different principles. L^{OH} method reflects the reactivity by calculating the ability of BVOCs and OH radical to produce RO_2, ignoring the influence of other subsequent reactions. Although the MIR method considers a series of responses of BVOCs, the lack of some MIR coefficients also affects the results. Based on the two approaches, *Robinia pseudoacacia*, *Populus tomentosa*, *Quercus*

variabilis and *Pinus tabulaeformis* are the dominant forest species that contribute higher BVOCs reaction activity in the Jing-Jin-Ji area. Among them, *Robinia pseudoacacia*, *Populus tomentosa* and *Quercus variabilis* have higher reactivity due to their higher isoprene activity contribution rate. The OFP and L^{OH} value of *Robinia pseudoacacia*, *Populus tomentosa*, *Quercus variabilis* were 156.76 μg/m^3 and 138.36×10^5, 87.19 μg/m^3 and 78.86 × 10^5, 87.19 μg/m^3 and 78.86 × 10^5, respectively. Similarly, *Pinus tabulaeformis* is attributed to its higher activity contribution rate of monoterpenes, especially β-myrcene, limonene, and α-pinene, so its OFP and L^{OH} value was 43.63 μg/m^3 and 54.67×10^5, respectively.



(**a**) (**b**)

Figure 6. The reaction activity and activity contribution rate of BVOCs of dominant tree species in the Jing-Jin-Ji area calculated by MIR method (a) and L^{OH} method (b)

4. Uncertainty in BVOCs emission estimates

As the release of BVOCs by vegetation is affected by multiple factors, the estimated emissions are uncertain to some extent. The primary sources of uncertainty in BVOCs

emission estimation are emission factors, leaf biomass, vegetation distribution, model algorithm, and meteorological parameters. Estimates of total BVOCs emissions released by vegetation on the ground in the Jing-Jin-Ji area have been studied using different algorithms and data sources. Different models and emission factors may get considerably different emissions (approximately doubling) (Carlton and Baker, 2011; Hogrefe et al., 2011). The vegetation type data measured from different remote sensing sources, the vegetation type data calculated by various methods of the same remote sensing data, and the vegetation type data of different years affect the BVOCs estimation results (Chen et al., 2018). In view of the above, the BVOCs emissions estimated in our study are based on the field vegetation investigation and measured forest species emission rates, further eliminating the uncertainties. However, as the sampling process was carried out in the outdoor environment, many environmental factors were difficult to control. The rapid reactivity of BVOCs will also affect the measurement of flux, and the analysis made by the GC-MS instrument may also have some measurement errors. Besides, the leaf biomass was mainly calculated by the biological parameters such as forest vegetation accumulation and trunk density, and so on. The measurement error of data used will affect the accuracy of leaf biomass calculation results. Furthermore, although the meteorological data used in this study is from the MODIS satellite published on the NASA website, there are some differences between the satellite data and the actual observation data, such as solar radiation and ground temperature. Future works need to focus on reducing those uncertainties.

5. Conclusions

The total annual emissions of BVOCs released from dominant forest species in the Jing-Jin-Ji area were estimated to be 70.8 Gg $C \cdot a^{-1}$. Isoprene, monoterpenes, and other VOCs contributed 40.5%, 36.0%, and 23.4%, respectively. As for monthly and seasonal variations, the emissions peaked in summer (June, July, and August) and bottomed out in winter (December, January, and February). This is also one of the reasons why summer is the season with the most severe ozone pollution. In terms of spatial distribution, the areas with high BVOCs emissions were mainly distributed in the Taihang Mountains and the Yanshan Mountains. Chengde contributed the most, followed by Beijing. These two places should strengthen the contribution of BVOCs to atmospheric ozone and particulate pollution. In terms of forest species, *Platycladus orientalis*, *Quercus variabilis*, *Populus tomentosa*, *Pinus tabulaeformis* and *Robinia pseudoacacia* are the primary BVOCs emission and atmospheric reactivity contributors. Therefore, when carrying out forest greening configuration and forest species selection in the future, these species with significant emissions or atmospheric reactivity of BVOCs should be avoided as much as possible.

Abbreviations

BVOCs: Biogenic volatile organic compounds; G93: Guenther model in 1993; NMVOCs: non-methane volatile organic compounds; PANs: peroxyacetyl nitrate ; SOA: secondary organic aerosols; PM: particulate matter; PFT: plant functional types; MIR:

maximum incremental reactivity; L^{OH}: ·OH reaction rate; OFP: Ozone formation potential; OVOCs: other VOCs; TVOCs: total VOCs

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Authors' contributions

Xiaoxiu Lun and Ying Lin conceived the study; Ying Lin participated in study design, field measurements, data processing and writing the manuscript; Xiaoxi Jing and Chong Fan took part in the field measurements; Wei Tang and Zhongzhi Zhang took part in the procedure of data processing. All authors contributed critically to successive drafts and gave final approval for publication.

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Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable requests.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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