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Emission patterns of biogenic volatile organic compounds from dominant forest species in Beijing, China

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ABSTRACT

Biogenic volatile organic compounds (BVOCs) have significant effects on atmospheric chemistry, ozone formation and secondary organic aerosol formation. Considering few investigations about BOVCs emissions in north China where is facing serious air pollution in recent years, emissions of various BVOCs from 24 dominant forest species in Beijing were measured from June to September in 2018, using a dynamic headspace sampling method. More than one hundred BVOCs in the collected samples were identified by using an automatic thermal desorption-gas chromatography/mass spectrometry, and their emission rates based on leaf biomass were calculated. Isoprene and monoterpenes were verified to be the dominant BVOCs emitted from the tree species, accounting for more than 50% of the total BVOCs. Generally, broad-leaved species displayed high isoprene emission rates, especially the *Platanus occidentalis* (21.36 μg/(g·hr)), *Robinia pseudoacacia* (11.55 μg/(g·hr)), and *Lonicera maackii* (9.17 μg/(g·hr)), while coniferous species emitted high rates of monoterpenes, such as *Platycladus orientalis* (27.18 μg/(g·hr)), *Pinus griffithii* (23.11 μg/(g·hr)), and *Pinus armandii* (7.42 μg/(g·hr)). High emission rates of monoterpenes from the broad-leaved species of *Buxus megistophylla* (13.07 μg/(g·hr)) and *Ligustrum vicaryi* (5.74 μg/(g·hr)), and high isoprene emission rate from the coniferous tree of *Taxus cuspidata* (5.86 μg/(g·hr)) were also observed. The emission rates of sesquiterpenes from each tree were usually 10–100 times smaller than those of isoprene and monoterpenes. Additionally, relatively high emission rates of oxygenated volatile organic compounds and other alkenes than isoprene and monoterpenes were also found for several tree species.

Introduction

Biogenic volatile organic compounds (BVOCs) emitted from vegetation are one of the main precursors of ozone and secondary organic aerosols (SOA), which have a significant effect on the deterioration of regional air quality (Faiola et al., 2015; Ghirardo et al., 2016; Kiendler-Scharr et al., 2009; Wyche et al., 2014). OH-initiated degradation of BVOCs produces RO_2 radicals, followed by the conversion of NO to NO_2, resulting in the accumulation of O_3 (Wayne, 2000; Atkinson and Arey, 2003; Lei and Zhang, 2004; Lelieveld et al., 2008). BVOCs also lead to the formation of SOA through the reactions producing the compounds of lower vapor pressures (Claeys et al., 2004; Joutsensaari et al., 2005; Meskhidze and Nenes, 2006). The SOA can indirectly affect global sunlight irradiation acting as cloud condensation nuclei and directly affect climate by scattering solar radiation (Laothawornkitkul et al., 2009).

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BVOCs contribute 90% of the global non-methane volatile organic compounds (NMVOCs) (Guenther et al., 2012). In the developed urban areas, the contribution of BVOCs to the generation of O_3 and SOA should not be ignored (Calfapietra et al., 2013; Mo et al., 2018; Ramasamy et al., 2016), although the emission of VOCs from human sources (AVOCs) is large. Compared with AVOCs, atmospheric concentrations of BVOCs in polluted areas are relatively low, but due to their extremely high reactivity BVOCs can make significant contribution to secondary oxidants (Sahu et al., 2016).

A large number of BVOCs emissions studies have been carried out, recognizing that plants can emit isoprene, monoterpenes, sesquiterpenes, and Oxygenated volatile organic compounds (OVOCs), among which isoprene and monoterpenes are the strongest species of BVOCs emitted by plants (Acton et al., 2016; Aydin et al., 2014; Bourtsoukidis et al., 2014; Kalogridis et al., 2014; Morrison et al., 2016). The emission flux of isoprene is mainly affected by photosynthetically active radiation (PAR) and temperature, while those of monoterpenes are mainly affected by temperature (Guenther et al., 1991, 1993). Based on a large number of BVOCs exchange flux measurement results, Guenther et al. (1993) summarized the formulas of emissions of isoprene and monoterpenes along with PAR and temperature, and widely used in the estimation of total BVOCs emissions. However, in addition to temperature and PAR, there are many factors that affect BVOCs emissions, such as plant leaf age, drought forcing, pollutant stress, etc. There are still great uncertainties in the estimation of BVOCs emissions. In addition, there are many kinds of plant species, with different emission components and emission intensity. However, the species with observed results are limited.

Compared with Europe and the United States, researches on emissions of common tree species in China are not enough to support the current air quality action. Most of the research has been mainly focused on isoprene and monoterpenes, with little attention to sesquiterpenes and OVOCs. In northern China, Wang et al. (2003) screened to estimate the emission rates of isoprene and monoterpenes for 23 kinds of typical plants in Beijing area. Although this work measured isoprene and monoterpene emissions from plants, but did not describe sesquiterpenes and OVOCs emissions. Chen et al. (2009) carried out investigations to determine the emission rates of BVOCs from eight major forestation tree species in Shenyang. The results showed that emission rates of BVOCs from *Populusalba* × *P. berolinensi* and *Salix babylonica* were 97.6 and 18.24 μg/(g·hr), which were significantly higher than those of other six tree species. In summary, the emission characteristics of isoprene and monoterpenes in BVOCs has been widely studied, but there are few results about the emission characteristics of sesquiterpenes and other volatile organic compounds.

In order to prevent sand storm and improve the ecological environment, China, especially in the Beijing-Tianjin-Hebei region, the government has carried out large-scale afforestation activities. With the Man-made Three Northern Regions Shelter Forest project, the Beijing-Tianjin Sandstorm Source Control Project, and the Taihang Mountain Greening Project, the forest area in northern China continues to expand. According to data from the forestry survey, forest stock volume in Beijing increased 21.76 percent from 2010 to 17.477 million cubic meters in 2017. The dominant species planted were *Pinus tabulaeformis, Platycladus orientalis, Pinu armandii, Sabina chinensis, Robinia pseudoacacia, Sophora japonica, Carpinus turczaninowii, Quercus aliena* and *Acer truncatum*. Most of these trees emit BVOCs. This may lead to an increase in the emission of BVOCs from forest vegetation, which will have an impact on air quality. Especially in Beijing, a place with serious air pollution, the ground-level ozone and fine particulate matter ($PM_{2.5}$) have been the primary pollutants over the past few years and have caused a severe impact on human health

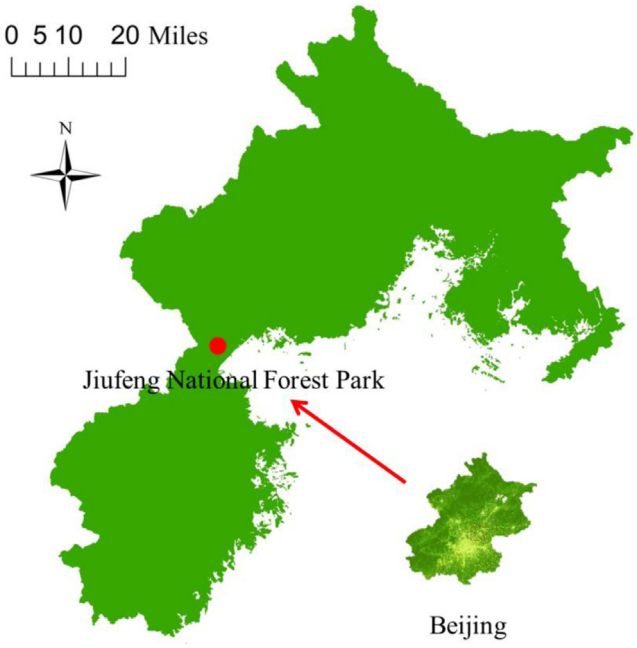

Fig. 1 – Location of the research area.

(An et al., 2016; Gao et al., 2018; Ren et al., 2017; Shao et al., 2009; Zhang et al., 2017). The contribution from the reacted isoprene in Beijing to HCHO formation was estimated to be in the range of 0.35–2.45 ppbV from April to October, which accounted for 4.6%–11.5% of ambient HCHO (Pang et al., 2009). And Li et al. (2015) carried out measurements of 56 non-methane hydrocarbons (NMHCs) and 12 carbonyls during the summer. Isoprene contributed 11.61%-38.00% of the total reactivity of measured volatile organic compounds (VOCs).

There are more than 60 kinds of forest tree species in Beijing, including more than 30 kinds of common tree species, in which only about 10 kinds of tree species have been tested emission rate data. The lack of emission rate of common tree species increases the uncertainty of emission estimation results and makes it more difficult to predict and control the air pollution. In this paper, the dominant species of forest vegetation in Beijing were selected for the study of BVOCs emissions. The dynamic headspace method and automatic thermal desorption-gas chromatography/mass spectrometry (ATD-GC/MS) were used to monitor the compounds and the emission rates of BVOCs from tree species. This result provides a detailed reference for the effective selection and configuration of tree species to effectively prevent and control atmospheric pollution.

1. Materials and methods

1.1. *Location of BVOCs flux measurements*

BVOCs emission fluxes from 24 tree species were measured in the Jiufeng National Forest Park (116°28′E, 39°54′N, Fig. 1) from June to September in 2018. The park is located in the northwest side of Beijing, with an area of 832.04 hectares fully covered by various vegetations.

1.2. *Collection of air samples for BVOCs flux measurements*

As temperature and PAR are two key factors affecting BVOCs emissions, a dynamic system was designed to make sure that the temperature and PAR in the enclosure bag covered

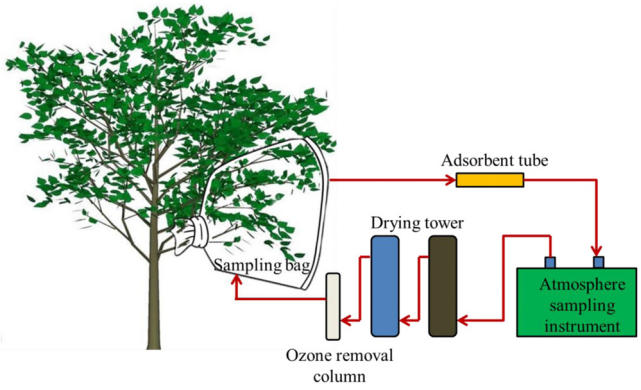

Fig. 2 – Process of the dynamic headspace sampling.

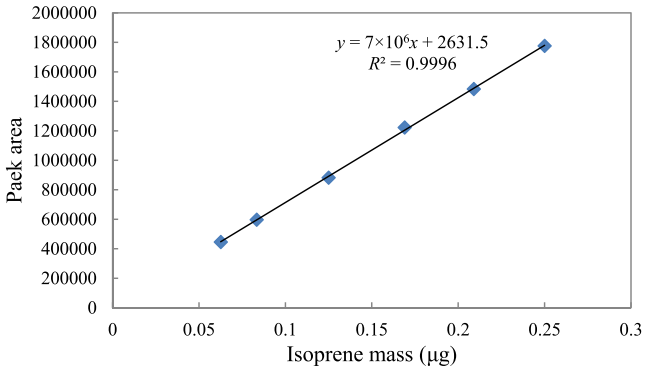

Fig. 3 – Standard curve of isoprene concentration calculation.

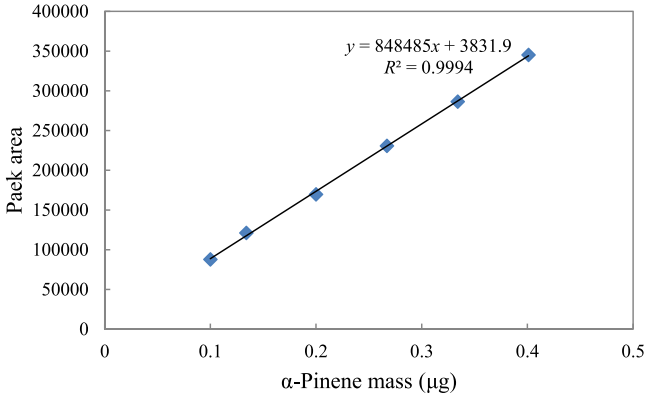

Fig. 4 – Standard curve of α-pinene concentration calculation.

a branch of a tree approached to those of the ambient air. As shown in Fig. 2, the dynamic system includes an enclosure bag, an absorbent tube, a pump, two drying towers, and an ozone removal column. The enclosure bag (10 L) is made of Teflon film with PAR transparency of ~100%. The absorbent tube (tubetype: stainless steel tube, Camsco company, USA) is filled with Carbograph 2 60/80 mesh, Carbograph 1 40/60 mesh and Carbosieve SIII 60/80 mesh for capturing BVOCs emitted from the branch of the tree. The pump (LaoDong QC-1S, Beijing Municipal Institute of Labor Protection, China) was used for cycling the air in the system to avoid temperature increase in the enclosure bag through reduction of the air duration in it. Due to the transpiration of the leaves, the two drying towers were separately filled with activated carbon particles and indicator silica gel to reduce the relative humidity in the enclosure and thus make sure the flow rate of the cycling air is stable. The ozone removal column is from Agela Technologies (Cleanert KI: 1.4 g/2.5 mL, Agela Technologies, China).

The granular activated carbon was heated at 160°C for more than 5 hr in an oven and then was allowed to naturally cool in the oven before being filled in the gas drying tower. Adsorbent tube was activated at 270°C for 120 min under a nitrogen purge of 100 mL/min (purity: $N_2 \geq 99.9992\%$). Subsequently, the tube was immediately sealed and stored in a desiccator equipped with activated carbon at 4°C for 10 days before the measurements.

Two healthy branches in a middle-aged tree, showing no disease, no evidence of animal foraging, or other reasons for missing leaves, were selected for the investigation with collection of four samples in two consecutive days. The air flow rates of the inlet and outlet for the sampling bag were both 150 mL/min, and the sampling period of each adsorption tube was one hour. All the gas in the bag was pumped out before sampling, and then the clean air filtered by the drying tower and ozone removal column was pumped in. Sampling date, temperature and PAR are shown in Table 1.

After sampling, the plant leaves in the sampling bag were taken and dried in the laboratory, then weighed to obtain the dry weight of the leaves.

1.3. *Automatic thermal desorption GC/MS*

The automatic thermal desorption conditions were as follows. The adsorbent tube was analyzed in a thermal resolver at 260°C for 5 min, and most of the organic matter in the tube was released. The thermally resolved substances were then adsorbed onto the cold trap (-25°C) and condensed. The substance was heated rapidly from 260 to 300°C (rate of temperature increase was 40°C/sec), and the material thermally resolved from the cold trap was transferred to a chromatograph for separation analysis. The following conditions were used for the chromatographic analysis. The column model was DB-5MS. The temperature of the column was controlled by program, the heating process was divided into three stages, from 40 to 160 and 270°C, each of which maintains a time of 2, 2 and 3 min, and the heating rate was 4°C/min. The mass spectrometer was equipped with an electron ejection ionization method with energy of 70 eV and a scanning atomic mass range of 30–500 amu.

BVOCs were identified based on retention time and mass-to-nuclear ratio of GC/MS spectral characteristic ions with the help of National Institute of Standards and Technology (NIST) data, and quantified by standard gas mixtures (Figs. 3 and 4). The standard gas used in the experiment was Photochemical Assessment Monitoring Stations (PAMS) (Spectra/Linde: 57) and the standard gas (*n*-hexane 12.3 ppmV, isoprene 12.7 ppmV, α-pinene 10.3 ppmV, β-pinene 10.8 ppmV, α-phellandrene 8.45 ppmV, 3-carene 10.6 ppmV, myrcene 8.19 ppmV, α-terpinene 7.12 ppmV, limonene 10.1 ppmV, γ-terpinene 7.81 ppmV, and ocimeme 7.68 ppmV) made by the National Institute of Metrology, China, which was quantitatively diluted into a summa canister with a gas distributor and then adsorbed onto the adsorbent tube for analysis. The standard curve was drawn by taking the mass as the abscissa and the peak area as the ordinate. The BVOCs emission rates of the measured tree species were obtained by qualitative and quantitative analysis, according to the following formula:

$$V_S = \frac{Q_S}{m \times t} \quad (1)$$

where V_S (μg/(g·hr)) is the chemical substance emission rate of plant, Q_S (μg) is the total mass of the chemical substance

Table 1 – Sampling dates and average environmental conditions during the samplings in 2018.

Binomial name	Date (mm/dd)	Ambient T (°C)	Inside bag T (°C)	PAR (μmol/(m^2·sec))
Pinus tabulaeformis	09/03–09/04	29.4	33.1	1963
Pinus griffithii	07/20–07/21	24.8	26.4	630
Pinus armandii	06/07–06/08	27.8	34.6	1362
Taxus cuspidata	06/15–06/16	24.3	25.6	369
Sabina chinensis	06/12–06/14	30.2	30.5	201
Platycladus orientalis	08/25–08/26	31.6	34.2	1606
Amygdalus triloba	06/12–06/14	27.8	34.6	839
Ulmus pumila	06/21–06/23	41.6	44.1	1537
Buxus megistophylla	07/13–07/14	28.1	29.7	542
Lonicera maackii	06/20–06/22	29.8	32.3	637
Ligustrum vicaryi	07/18–07/19	26.4	28.1	399
Phyllostachys propinqua	06/21–06/23	29.2	42.7	1461
Tilia japonica	06/14–06/16	28.1	29.5	1678
Magnolia biondii	06/14–06/16	28	29.5	301
Quercus aliena	06/19–06/20	31.5	34.5	259
Acer truncatum	06/19–06/20	31.5	34.5	521
Liriodendron chinense	06/16–06/19	35.2	36.7	652
Carpinus turczaninowii	06/20–06/21	33.5	35.3	1262
Salix matsudana	08/23–08/25	31.7	32.5	538
Populus tomentosa	08/26–08/27	32.4	34	969
Robinia pseudoacacia	09/05–09/06	30.1	32.8	1206
Sophora japonica	07/05–07/07	32.3	34.4	362
Koelreuteria paniculata	07/27–07/29	26.3	27.6	320
Platanus occidentalis	08/18–08/19	27.4	30.5	1230

T: temperature; PAR: photosynthetically active radiation.

in the obtained adsorbent tube, m (g) is the dry weight of the inner leaf in the sampling bag, and t (hr) is the sampling time.

1.4. *Standardization of emission factor*

In order to apply the results of this study to the calculation of emission inventory, the BVOCs emission rate of plants was standardized. The real-time emission rates of BVOCs of tree species can be calculated to the standard emission rate according to the G93 method (Guenther et al., 1993). The specific algorithm is as follows:

$$I = I_S \times C_L \times C_T \quad (2)$$

where, I and I_S (μg/(g·hr)) represent the emission rate of isoprene at a certain temperature T (K) in the presence of PAR (μmol/(m^2·sec)) and standard conditions (T = 303 K, PAR = 1000 μmol/(m^2·sec)), respectively, while C_L and C_T represent correction factors for light and temperature, respectively, obtained by Eqs. (3) and (4), shown below.

$$C_L = \alpha C_{L1} L / \sqrt{(1+\alpha^2 L^2)} \quad (3)$$

The α (0.0027) and C_{L1} (1.066) shown here in Eq. (3) are empirical constants, and L is the measured PAR value.

$$C_T = \frac{\exp(C_{T1}(T-T_S)/RT_ST)}{1+\exp(C_{T2}\ (T-T_M)/RT_S\ T)} \quad (4)$$

In Eq. (4), R (8.314 J/(K·mol)) is the gas constant, C_{T1} (95,000 J/mol), C_{T2} (230,000 J/mol) and T_M (314 K) are empirical constants, and T_S (K) is the measured temperature. According to the values of multiple sets of I and the values of C_T and C_L, the value of the standard emission rate can be obtained by a linear regression method.

The emission rate of monoterpenes was described by the G93 algorithm, which can be described by the following equation:

$$M = M_{TS}\exp(\beta(T-T_S)) \quad (5)$$

where M (μg/(g·hr)) is the monoterpene emission rate at a certain temperature T (K), and M_{TS} (μg/(g·hr)) is the emission rate of monoterpenes under standard conditions (T_S = 303 K), while β (0.09 K^{-1}) and T_S (303 K) are empirical constants. In the present study, β was used as 0.10 for monoterpenes and oxygenated BVOCs, and 0.17 for sesquiterpenes since these are used as the default parameters for The Model of Emissions of gases and Aerosols from Nature version vely, 2.1 (MEGAN2.1) (Guenther et al., 2012).

2. Results and discussion

2.1. *Standard emission rate*

According to their molecular formula, BVOCs detected from 24 tree species were divided into five groups: isoprene, monoterpenes, sesquiterpenes, other alkenes, and oxygenated volatile organic compounds. The emission rates based on leaf biomass were calculated. The standard emission rates were obtained according to the measured temperature and PAR. They are summarized in Table 2 and are consistent with the literature.

The broad-leaved species emitted high rate of isoprene, and coniferous tree species emitted high rate of monoterpenes. Several species with high isoprene emission rate were ranked according to their emission rate: *Platanus occidentalis* (21.36 μg/(g·hr)), *Robinia pseudoacacia* (11.55 μg/(g·hr)), *Lonicera maackii* (9.17 μg/(g·hr)), *Salix matsudana* (6.75 μg/(g·hr)), and *Phyllostachys propinqua* (6.31 μg/(g·hr)). Some coniferous trees also emitted a large amount of isoprene. For example, the isoprene emission rate of *Taxus cuspidata* was 5.86 μg/(g·hr), which ranks sixth among the 18 species from which isoprene emission can be detected. There were also other broad-leaved tree species that emitted smaller amounts of isoprene,

Table 2 – Emission rates of biogenic volatile organic compounds (BVOCs) in 24 dominant tree species in Beijing.

Binomial name	Emission rate (μg/(g·hr))					
	Isoprene	Monoterpenes	Sesquiterpenes	Other alkenes	OVOCs	Total BVOCs
Pinus tabulaeformis	0.98512 ± 0.3520	3.8294 ± 2.6055	0.0579 ± 0.0361	0.3015 ± 0.0900	0.0332 ± 0.0300	5.20712 ± 2.6311
Pinus griffithii	nd	23.106 ± 2.3454	8.1294 ± 1.0496	3.7537 ± 1.3167	2.8301 ± 1.2245	37.8192 ± 3.1362
Pinus armandii	0.006 ± 0.0000	7.4208 ± 0.3333	0.1936 ± 0.2343	0.1098 ± 0.0361	0.1447 ± 0.1091	7.8749 ± 0.4233
Taxus cuspidata	5.8629 ± 0.8613	nd	nd	0.0199 ± 0.0245	0.0518 ± 0.0678	5.9346 ± 0.8643
Sabina chinensis	0.002 ± 0.0000	5.4947 ± 1.4391	0.0047 ± 0.0000	0.0171 ± 0.0100	0.612 ± 0.0583	6.1305 ± 1.4403
Platycladus orientalis	1.6022 ± 1.2012	27.1768 ± 4.9461	0.0509 ± 0.0141	0.5093 ± 0.4438	0.0117 ± 0.0141	29.3509 ± 5.1092
Amygdalus triloba	nd	0.1081 ± 0.0374	nd	0.4437 ± 0.4022	0.612 ± 0.2404	1.1638 ± 0.4701
Ulmus pumila	0.0529 ± 0.0566	0.0496 ± 0.0000	nd	0.4881 ± 0.3908	0.1016 ± 0.0316	0.6922 ± 0.3961
Buxus megistophylla	nd	13.0742 ± 2.8077	nd	12.5472 ± 3.6905	2.6122 ± 0.8204	28.2336 ± 4.7092
Lonicera maackii	9.1668 ± 2.7301	nd	nd	0.3457 ± 0.1670	0.1416 ± 0.0806	9.6541 ± 2.7364
Ligustrum vicaryi	nd	5.7385 ± 1.9597	2.0682 ± 0.5710	6.673 ± 1.2941	3.2369 ± 1.7991	17.7166 ± 3.0130
Phyllostachys propinqua	6.3063 ± 1.5573	0.0836 ± 0.0600	0.0978 ± 0.0520	0.3639 ± 0.2431	0.1223 ± 0.0000	6.9739 ± 1.5782
Tilia japonica	nd	0.9795 ± 0.5427	nd	0.5035 ± 0.3917	0.087 ± 0.0693	1.5700 ± 0.6728
Magnolia biondii	3.4427 ± 1.1551	0.2455 ± 0.1404	0.0143 ± 0.0000	0.0872 ± 0.0300	0.0960 ± 0.0332	3.8857 ± 1.1644
Quercus aliena	2.4584 ± 1.1554	0.1200 ± 0.1217	nd	0.3029 ± 0.1536	0.1200 ± 0.0436	3.0013 ± 1.1727
Acer truncatum	0.0522 ± 0.0265	2.2944 ± 1.2999	0.0636 ± 0.0316	1.4019 ± 0.4253	0.3229 ± 0.0686	4.1350 ± 1.3700
Liriodendron chinense	nd	3.7300 ± 1.6139	nd	0.4583 ± 0.3266	0.1220 ± 0.3266	4.3103 ± 1.6484
Carpinus turczaninowii	0.2570 ± 0.0224	nd	0.1386 ± 0.1688	nd	0.0881 ± 0.0866	0.4837 ± 0.1910
Salix matsudana	6.7542 ± 1.2251	nd	nd	0.0888 ± 0.0557	0.1068 ± 0.0000	6.9498 ± 1.2263
Populus tomentosa	3.1089 ± 1.5459	4.8704 ± 1.9892	0.0099 ± 0.0000	0.5012 ± 0.2787	0.0151 ± 0.0000	8.5055 ± 2.5347
Robinia pseudoacacia	11.5502 ± 0.9063	0.4503 ± 0.4135	0.3828 ± 0.3064	2.9268 ± 1.2464	0.9267 ± 0.3040	16.2368 ± 1.6529
Sophora japonica	3.7609 ± 1.8298	0.0267 ± 0.0000	0.0059 ± 0.0000	0.0792 ± 0.0283	0.0943 ± 0.0490	3.9670 ± 1.8307
Koelreuteria paniculata	nd	1.7594 ± 0.3780	0.4928 ± 0.3114	5.1763 ± 0.6631	2.0267 ± 1.4832	9.4552 ± 1.6969
Platanus occidentalis	21.3621 ± 4.2042	4.3806 ± 0.5362	3.9050 ± 0.9696	7.4940 ± 1.1050	11.5062 ± 2.0705	48.6479 ± 4.9407

OVOCs: oxygenated volatile organic compounds; nd: not detected.

such as *Carpinus turczaninowii* (0.26 μg/(g·hr)), *A. truncatum* (0.05 μg/(g·hr)), *Ulmus pumila* (0.05 μg/(g·hr)).

P. orientalis (27.18 μg/(g·hr)), *Pinus griffithii* (23.11 μg/(g·hr)), *P. armandii* (7.42 μg/(g·hr)), and *S. chinensis* (5.49 μg/(g·hr)) are coniferous tree species with a large emission rate of monoterpenes. No monoterpenes were detected in *T. cuspidata* samples. The higher emission rate of monoterpenes emitted from broad-leaved species was observed in *Buxus megistophylla* (13.07 μg/(g·hr)) and *Ligustrum vicaryi* (5.74 μg/(g·hr)). Aydin et al. (2014) reported several tree species such as *Castanea sativa, Tilia argentea*, and *Populus tremula* had higher monoterpene emissions although they are broad-leaved species. High isoprene emissions were also observed for a few coniferous species such as *Abies nordmanniana* and *Picea orientalis*.

Fifteen tree species were detected to emit sesquiterpenes, and the largest emissions rates were *P. griffithii* (8.13 μg/(g·hr)), *P. occidentalis* (3.91 μg/(g·hr)) and *L. vicaryi* (2.07 μg/(g·hr)). The emission rates of sesquiterpenes from the remaining twelve species were less than 1 μg/(g·hr). Other alkenes were detected from 23 tree species, which had emission rates ranging from 0.01 μg/(g·hr) to 12.55 μg/(g·hr). OVOCs were detected in all 24 tree species, but only five tree species were detected emission rates higher than 1 μg/(g·hr), i.e., *Platanus occidentalis* (11.51 μg/(g·hr)), *ligustrum vicaryi* (3.24 μg/(g·hr)), *Pinus griffithii* (2.83 μg/(g·hr)), *Buxus megistophylla* (2.61 μg/(g·hr)) and *Koelreuteria paniculata* (2.03 μg/(g·hr)), respectively.

The photochemical ozone creation potential (POCP) of BVOCs is an important indicator used to evaluate the contribution of VOCs to atmospheric pollution. The POCP value is related to the reaction constant of BVOCs and the hydroxyl radical. The POCP of α-pinene, which has a large occupation in plant-derived monoterpenes, is about twice that of β-pinene (Jenkin et al., 2017). Therefore, the emission rate of BVOCs in plants should be measured separately, especially for high-emission and high-activity monoterpenes. Table 3 shows the monoterpenes emission rate in the study where emission is greater than 0.5 μg/(g·hr) and there are more than four trees that emit this monoterpene.

2.2. Components of BVOCs

The BVOCs components from the measured tree species according to the peak area standard algorithm are shown in Fig 5. The results indicate that isoprene and monoterpenes, the most common components of BVOCs, were detected from most tree species.

Some coniferous trees emitted large amount of monoterpenes, such as *P. armandii, S. chinensis, P. orientalis, P. tabulaeformis*, and *Liriodendron chinese*. Monoterpenes emitted from each of these tree species can account for more than 70% of its own total biogenic volatile organic compounds (TBVOCs) emissions.

For some broad-leaved species, the isoprene accounted for more than 90% of the TBVOCs, such as from *L. maackii, P. propinqua, S. matsudana* and *S. japonica*. Isoprene emitted from *Magnolia biondii* and *Q. aliena* accounted for more than 80% of its total emissions. Isoprene emissions from coniferous tree, *T. cuspidata*, accounted for more than 90% of the TBVOCs emissions.

In addition to isoprene and monoterpenes, a certain amount of OVOCs were detected from broad-leaved species. For example, OVOCs emitted from *Amygdalus triloba* accounted for more than 50% of its TBVOCs emissions. More than 20% of OVOCs in TBVOCs were detected in other broad-leaved species (*Koelreuteria paniculata, P. occidentalis*).

Among the 24 tree species, the relative content of other alkenes in the seven trees of *A. triloba, U. pumila, B. megistophylla, L. vicaryi, TIlia. japonica, A. truncatumm* and *K. paniculata* were more than 20%. Sesquiterpenes were detected from 15 tree species, and the largest sesquiterpenes emission tree species were *P. griffithii, C. turczaninowii* and *L. vicaryi*.

Alpha-pinene (α-pinene) were detected in 18 trees species. The α-pinene emitted from seven tree species accounted for more than 50% of the amount of monoterpenes emitted from

Table 3 – Emission rate of each monoterpene components from partial tree species.

Binomial name	Emission rates (μg/(g·hr))				
	α-Pinene	β-Pinene	Limonene	γ-Terpinene	Ocimene
Pinus tabulaeformis	2.2487	0.6842	0.5163	nd	nd
Pinus griffithii	10.3650	7.5422	3.7944	nd	nd
Pinus armandii	5.1829	2.0855	nd	nd	nd
Sabina chinensis	nd	nd	2.6018	1.4168	nd
Platycladus orientalis	0.8715	10.1792	9.7836	1.2132	nd
Buxus megistophylla	3.1207	4.2628	nd	nd	0.9185
Ligustrum vicaryi	1.1828	1.3456	nd	nd	2.3420
Tilia japonica	0.8563	nd	nd	nd	nd
Acer truncatum	nd	nd	0.8212	0.8217	nd
Liriodendron chinense	nd	0.9755	1.0242	0.8275	nd
Populus tomentosa	1.8721	0.7370	1.2267	nd	nd
Koelreuteria paniculata	1.1836	nd	nd	nd	nd
Platanus occidentalis	2.8855	nd	nd	nd	0.2893

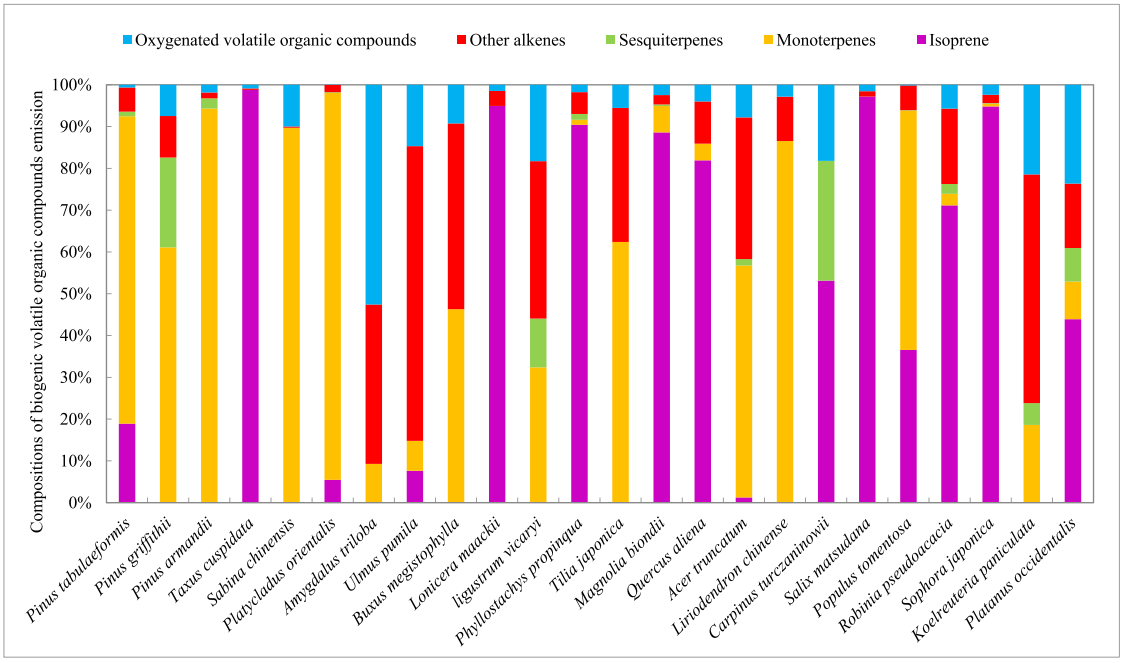

Fig. 5 – Compositions of biogenic volatile organic compounds emission from 24 dominant tree species in Beijing.

each species. The amounts were 59% for *P. tabulaeformis*, 70% for *P. armandii*, 82% for *P. propinqua*, 87% for *T. japonica*, 65% for *Q. aliena*, 67% for *K. paniculata* and 66% for *P. occidentalis*.

There were fifteen tree species that emitted terpinene, of which eleven species emitted α-terpinene, four tree species emitted γ-terpinene and one species emitted α-terpinene. The tree species emitted terpinene that accounted for the large proportion of monoterpenes emissions were *M. biondii* (61%), *A. triloba* (49%), *A. truncatum* (36%), *S. chinense* (26%) and *L. chinense* (28%).

The emission of limonene was detected in 11 tree species, which were ranked according to their proportion in monoterpenes emissions as *U. pumila* (72%), *S. chinensis* (47%), *A. truncatum* (36%), *P. orientalis* (36%) and *L. chinense* (26%).

The emission of bate-pinene (β-pinene) was detected in eleven species, *P. orientalis* (37%), *P. griffithii* (33%), *B. megistophylla* (33%), *P. armandii* (28%) and *L. vicaryi* (23%).

In addition, there were also tree species that mainly emitted other monoterpenes. For example, myrcene emitted by *R. pseudoacacia* reached 63% of the total amount monoterpenes discharged. Among all of the tree species that detected monoterpenes emission, there were six species with more than seven components of monoterpenes, which were *P. tabulaeformis, P. griffithii, B. megistophylla, A. truncatum, L. chinense*, and *P. tomentosa*.

Sesquiterpenes commonly detected were caryophyllene, farnesene, cedrene, isocaryophillene, while other alkenes commonly found were 1,3,8-*p*-menthatriene, diisoamylene, azulene, 6-tridecene, 6-dodecene, *o*-cymene and 7-tetradecene. The most common and significant components of OVOCs emitted by plants were tested to be cyclopropaneethanol, acetic acid, cyclodecanol, 2-ethylhexanol, cyclodecanol, 1,1-dodecanediol diacetate and *cis*-3-hexenyl acetate.

2.3. Discussion

2.3.1. Discussion of emission rate

The standard emission rates reported in the research show wide ranges even for the same plant species (Table 4). Several common tree species such as *R. pseudoacacia, P. tabulaeformis*

Table 4 – Comparison of calculated standard emission rates with the literature.

Binomial name	Emission rates (μg/(g·hr))		References
	Isoprene	Monoterpenes	
Robinia pseudoacacia	14	0.2	Guenther et al., 1994
Robinia pseudoacacia	79.71	nr	Wang et al., 2002
Robinia pseudoacacia	37.3	2.3	Wang et al., 2003
Robinia pseudoacacia	12.40	0.07	Aydin et al., 2014
Robinia pseudoacacia	17.80	nr	Khedivea et al., 2017
Robinia pseudoacacia	11.55	0.45	This study
Sophora japonica	0.42–2.3	nr	Mu et al., 1999
Sophora japonica	85.88	nr	Wang et al., 2002
Sophora japonica	52.5	1.9	Wang et al., 2003
Sophora japonica	3.76	0.027	This study
Pinus tabulaeformis	0.4	19	Wang et al., 2003
Pinus tabulaeformis	nr	1.76	Chen et al., 2019
Pinus tabulaeformis	0.99	3.83	This study
Platanus orientalis	139	0.3	Guenther et al., 1994
Platanus orientalis	0.3–49	nr	Mu et al., 1999
Platanus orientalis	25.2	0.1	Wang et al., 2003
Platanus orientalis	27.0	0.03	Aydin et al., 2014
Platanus orientalis	45	nr	Khedivea et al., 2017
Platanus acerifolia	10.1	nr	Wang et al., 2002
Platanus occidentalis	21.36	4.38	This study
Salix matsudana	35	<0.1	Guenther et al., 1994
Salix	6.5	nr	Mu et al., 1999
Salix chaenomeloiddes	58.81	nr	Wang et al., 2002
Salix babylonica	132.91	nr	Wang et al., 2002
Salix matsudana	70.2	3.7	Wang et al., 2003
Salix matsudana	6.75	nd	This study
Koelreuteria paniculata	<0.1	0.4	Wang et al., 2003
Koelreuteria paniculata	nd	1.76	This study
Platycladus orientalis	nd	0.3	Guenther et al., 1994
Platycladus orientalis	<0.1	2.2	Wang et al., 2003
Platycladus orientalis	1.60	27.18	This study
Populus	70	0.1	Guenther et al., 1994
Populus	6.1	nr	Mu et al., 1999
Populus tomentosa	271.62	nr	Wang et al., 2002
Populus	105.8	0.2	Wang et al., 2003
Populus deltoides	4.72	0.07	Aydin et al., 2014
Populus tremula	22.40	0.22	Aydin et al., 2014
Populus tomentosa	3.11	4.87	This study
Quercus aliena	70	0.2	Guenther et al., 1994
Quercus aliena	32.1	7.8	Wang et al., 2003
Quercus glandulifera	222.17	nr	Wang et al., 2002
Quercus fabri	43.12, 61.73, 211.12	nr	Wang et al., 2002
Quercus petraea	0.08	0.02	Aydin et al., 2014
Quercus cerris	9.63	0.01	Aydin et al., 2014
Quercus aliena	2.46	0.12	This study

nr: not reported; nd: not detected.

and *P. orientalis* that are naturally grown in most areas of the world were investigated by many studies (Aydin et al., 2014; Chen et al., 2019; Guenther et al., 1994; Khedivea et al., 2017; Mu et al., 1999; Wang et al., 2003, 2002). These studies provided an opportunity to compare the standard emission rates in different areas or by using different measurement methods.

In this study, the isoprene emission rate of *R. pseudoacacia* was 11.6 μg/(g·hr), and 17.8 and 12.4 μg/(g·hr) in Khedivea et al., 2017 and Aydin et al., 2014, respectively. The monoterpenes standard emission rate of *R. pseudoacacia* in this study was 0.5 μg/(g·hr), while Aydin et al. (2014) reported it as 0.1 μg/(g·hr). Comparing the isoprene and monoterpenes emission rates of *R. pseudoacacia* among three studies, it can be found that the difference in the isoprene and monoterpene emission rates reported in this study and the study by Aydin et al. (2014) were smaller, and there was a significant difference in the rate of isoprene emissions in the study conducted by Khedivea et al. (2017). In addition, a large difference was seen between the isoprene emission rate between this study and the study by Khedivea et al. (2017) for *P. orientalis*. This study conducted measurements of isoprene emission rates from *R. pseudoacacia* on early-September 2018, but Aydin et al. (2014) and Khedivea et al. (2017) did measurements on mid-August 2012 and late-October in 2014. The difference in leaf age may also result in a difference of BVOCs emission rates. Compared with this study, Wang et al. (2002) showed that the isoprene emission rate of tree species was generally high. This difference may be due to different research sites with different soil nutrition. The Taihu Basin belongs to the south China. Under the influence of climate, the isoprene emission rate of plants was generally high. The results of Wang et al. (2003) showed that emission rates of plant iso-

Table 5 – OH reactivity of biogenic volatile organic compounds (sec^{-1}) in 24 dominant tree species in Beijing.

Binomial name	Isoprene	α-Pinene	β-Pinene	γ-Terpinene	β-Terpinene	Limonene	4-Carene	Ocimene	Total
Pinus tabulaeformis	9.68×10^{1}	1.40×10^{1}	6.34×10^{0}		4.76×10^{-8}	9.62×10^{0}	8.60×10^{-1}		1.27×10^{2}
Pinus griffithii		1.07×10^{1}	1.16×10^{1}		1.19×10^{-8}	1.17×10^{1}			3.40×10^{1}
Pinus armandii	5.89×10^{-1}	1.66×10^{1}	9.97×10^{0}						2.72×10^{1}
Taxus cuspidata	5.76×10^{2}								5.76×10^{2}
Sabina chinensis	1.96×10^{-1}	2.13×10^{0}		1.50×10^{0}	2.98×10^{-8}	3.38×10^{1}			3.76×10^{1}
Platycladus orientalis	1.57×10^{2}	7.64×10^{-1}	1.33×10^{1}	2.59×10^{-1}		2.57×10^{1}			1.97×10^{2}
Amygdalus triloba		7.36×10^{0}			9.82×10^{-7}				7.36×10^{0}
Ulmus pumila	5.20×10^{0}		2.34×10^{0}		7.44×10^{-8}	5.14×10^{1}			5.90×10^{1}
Buxus megistophylla		5.69×10^{0}	1.16×10^{1}		3.55×10^{-7}		2.14×10^{0}	3.11×10^{-8}	1.94×10^{1}
Lonicera maackii	9.00×10^{2}								9.01×10^{2}
Ligustrum vicaryi		4.19×10^{0}	8.32×10^{0}		2.10×10^{-7}			1.81×10^{-7}	1.32×10^{1}
Phyllostachys propinqua	6.19×10^{2}	1.95×10^{1}							6.39×10^{2}
Tilia japonica		2.08×10^{1}							2.08×10^{1}
Magnolia biondii	3.38×10^{2}	5.68×10^{0}			1.21×10^{-6}				3.44×10^{2}
Quercus aliena	2.42×10^{2}	1.55×10^{1}				1.33×10^{1}			2.70×10^{2}
Acer truncatum	5.13×10^{0}	7.39×10^{-1}	5.41×10^{0}	2.08×10^{0}		2.55×10^{1}			3.89×10^{1}
Liriodendron chinense		2.37×10^{0}	3.98×10^{0}	1.59×10^{0}	3.40×10^{-9}	1.87×10^{1}		9.83×10^{-8}	2.66×10^{1}
Carpinus turczaninowii	2.52×10^{1}								2.52×10^{1}
Salix matsudana	6.63×10^{2}								6.63×10^{2}
Populus tomentosa	3.05×10^{2}	9.16×10^{0}	5.37×10^{0}		2.73×10^{-8}	1.80×10^{1}	6.64×10^{0}		3.45×10^{2}
Robinia pseudoacacia	1.13×10^{3}	4.75×10^{0}			1.01×10^{-7}	6.58×10^{0}			1.15×10^{3}
Sophora japonica	3.69×10^{2}	1.47×10^{1}			7.65×10^{-7}				3.84×10^{2}
Koelreuteria paniculata		1.60×10^{1}			3.89×10^{-7}				1.60×10^{1}
Platanus occidentalis	2.10×10^{3}	1.57×10^{1}			3.98×10^{-7}			2.93×10^{-8}	2.11×10^{3}

prene and monoterpene were consistent with this study. However, Wang et al. (2003) did not give sampling date, so further comparisons were not possible.

The differences in environmental/physiological factors and genetically induced metabolism may also cause differences of BVOCs emission. During sampling, the sampled branch was stored in a Teflon sampling bag which changed the external environment of the plant. The temperature inside the bag increased in the enclosed environment with the presence of light over a short period of time. Studies have shown that plants emit isoprene and monoterpenes to protect their photosynthetic organs from damage at high ambient temperatures, thereby reducing photosynthetic ability (Laothawornkitkul et al., 2009). Due to the temperature variation discussed here, the emission rates of isoprene and monoterpenes are affected, leading to result in errors.

2.3.2. *Photochemical impacts of BVOCs components*

OH reactivity (OH reaction rate constant is multiplied by the BVOCs emission rate) can reveal the relative importance of BVOCs emissions from each tree species on atmospheric chemistry. OH radical reactivity of BVOCs (Reactivity of BVOCs each gram dry weight per hour in 10 L of gas) in 24 dominant tree species are shown in Table 5. The OH radical reactivity of BVOCs emitted by three trees, *P. occidental*, *R. pseudoacacia* and *L. maackii* were the highest.

The reaction constants of isoprene, α-pinene, β-pinene, γ-terpinene, 3-carene and limonene with OH radicals are high compared with other BVOCs. Moreover, the emission rates of isoprene, α-pinene and β-pinene are high for most tree species. Therefore, the OH reactivity of tree species are mainly determined by the emission rates of isoprene, α-pinene and β-pinene.

The OH radical reactivity of BVOCs emitted by three trees, *P. occidental* (2.11×10^{3} sec^{-1}), *R. pseudoacacia* (1.15×10^{3} sec^{-1}) and *L. maackii* (9.01×10^{2} sec^{-1}) were the highest. According to the data from the forestry survey, in 2017, the stock volume of *Robinia pseudoacacia* in the forest vegetation of Beijing reached 1.0833 million cubic meters, which was the dominant species of forest vegetation in Beijing. Although the OH reactivity of *Pinus tabulaeformis* (1.27×10^{2} sec^{-1}) and *Platycladus orientalis* (1.97×10^{2} sec^{-1}) are not the largest, its stock volume of forest vegetation in Beijing in 2017 reached 5.722 and 5.344 million cubic meters, respectively. It is the dominant species of forest vegetation in Beijing. Therefore, *Pinus tabulaeformis*, *Platycladus orientalis* and *Robinia pseudoacacia* all contribute greatly to the production of ozone and SOA, which deserves further attention and research.

3. Conclusions

This study used dynamic headspace sampling and ATD-GC/MS to measure 24 dominant tree species of forest vegetation in Beijing from June to September in 2018. The results showed that the trees mainly emitted isoprene and monoterpenes. The broad-leaved species mainly emitted isoprene, and the coniferous species mainly emitted monoterpenes. In addition to isoprene and monoterpenes, sesquiterpenes, other alkenes, and OVOCs were also detected from the 24 species evaluated, but the emission rates of sesquiterpenes, other alkenes and OVOCs were small.

A total of 14 monoterpene components were detected from 24 tree species. The common components were α-pinene, β-pinene, limonene, terpinene, myrcene, ocimene, camphene, 4-carene, and phellandrene. The emission rates of several terpenes (α-pinene, β-pinene, limonene, and terpinene) were relatively large. This research on the emission characteristics and emission rates of BVOCs in the vegetation of several forests can provide support for the study of emission inventories and emission models.

The OH reactivity of BVOCs emitted by tree species can represent the relative importance of tree species to atmospheric chemistry. The isoprene, α-pinene and β-pinene emission rates of part tree species are large and the reaction constant of isoprene, α-pinene and β-pinene with OH are also larger than other BVOCs. Hence, most of the OH reactivity of BVOCs emitted by tree species is mainly determined by

the isoprene, α-pinene and β-pinene emission rates of tree species. Therefore, in the case of greening and afforestation, trees with low isoprene, α-pinene and β-pinene emissions rates can be prioritized. For the Beijing area, taking into account the stock volume of tree species, *Pinus tabulaeformis*, *Platycladus orientalis* and *Robinia pseudoacacia* are plants that have a greater contribution to ozone and SOA generation, which deserves further attention and research.

Declaration of competing interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work. There is no professional or other personal interest of any nature or kind in any product, service or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled "Emission patterns of biogenic volatile organic compounds from dominant forest species in Beijing, China".

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