Study on Volatile Organic Compounds of Tree Species and the Influence on Ozone and Secondary Organic Aerosol

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Abstract. Biogenic volatile organic compounds (BVOCs) which offer high reactivity are important precursors for the formation of ozone (O₃) and secondary organic aerosols (SOA), then leading to air pollution. In order to explore the potential correlation between BVOCs and O₃ and SOA, and to screen out better tree species for urban greening, in this paper, 32 tree species were selected to carry out related experiments. The results showed that: hydrocarbons, alcohols, and aldehydes were significantly correlated with SOA generation, and ketone, ester, hydrocarbons and alcohols also showed significant relationship with O₃. Analyzed by UPGMA cluster, Ailanthus altissima, Acer truncatum, Rhus typhina, Prunus cerasifera f. atropurpurea, Prunus persica f. Duplex and Cerasus serrulata var. lannesiana were found weak correlation with O₃ and SOA generation, while Salix matsudana, Populus tomentosa and Salix matsudana f. pendula were strongly related.

1. Introduction

The increase in the area of urban green space and the increase in plant diversity play a crucial role in optimizing the urban ecosystem [1]. Although plants can fix carbon, release oxygen and purify the air, the increase in their types and numbers may also affect the environment. The negative impact is mainly because plants can release plant-derived volatile organic compounds (BVOCs), which in turn affect air quality and human health [2]. The main components of BVOCs are isoprene and monoterpenes [3]. Isoprene is the compound that emits the largest number of plants, and its annual emissions are about half of the total emissions of BVOCs [4]. Studies have shown that under certain conditions, BVOCs can generate ozone (O₃) and secondary organic aerosols (SOA) through photochemical reactions, which in turn cause atmospheric pollution such as photochemical smog and haze. Therefore, BVOCs are the main sources of O₃, SOA and suspended particulate matter. Precursors [5]. From a global perspective, the total emission of BVOCs is nearly 10 times higher than that of anthropogenic volatile organic compounds (AVOCs) [6]. Wu et al. [7] used the MEGAN v2.1 model to estimate that Chinese total emissions of BVOCs in 2017 was 23.54 Tg, which is equivalent to twice the total emissions of China’s industrial VOCs (12.45 Tg) in 2018[8]. It shows that BVOCs has a large emission potential, and its impact on the atmospheric chemical process and regional environmental quality cannot be ignored.

The paper selects 32 common greening tree species in Beijing-Tianjin-Hebei, explores the characteristics of BVOCs emission composition of different tree species, estimates its potential for O₃ and SOA generation, and then explores the correlation between the composition of BVOCs and the potential for O₃ and SOA generation. The results of this study can provide basic data accumulation for related research on the characteristics of BVOCs and the impact on haze precursors in the Beijing-
Tianjin-Hebei region, optimize the composition of urban green space species, and provide scientific guidance for the selection and allocation of urban green space plants to accurately prevent air pollution.

2. Materials and Methods

2.1. Selection of greening tree species

With reference to the basic survey results of the Beijing-Tianjin-Hebei urban greening status and related documents, 32 common greening tree species were selected as the research objects (Table 1).

| Number | Name                        | Number | Name                        |
|--------|-----------------------------|--------|-----------------------------|
| Sp1    | Albizia julibrissin         | Sp17   | Acer mono                   |
| Sp2    | Sophora japonica           | Sp18   | Acer truncatum              |
| Sp3    | Sophora japonica f. pendula| Sp19   | Rhus typhina                |
| Sp4    | Sophora japonica 'Golden Stem' | Sp20 | Malus micromalus          |
| Sp5    | Robinia pseudoacacia       | Sp21   | Malus pumila                |
| Sp6    | Populus tomentosa          | Sp22   | Prunus cerasifera f. atropurpurea |
| Sp7    | Salix matsudana f. pendula| Sp23   | Prunus persica f. duplex    |
| Sp8    | Salix matsudana            | Sp24   | Prunus davidiana            |
| Sp9    | Pinus bungeana             | Sp25   | Cerasus serrulata var. lannesiana |
| Sp10   | Pinus tabulaeformis        | Sp26   | Broussonetia papyrifera     |
| Sp11   | Cedrus deodara             | Sp27   | Morus alba                  |
| Sp12   | Platycladus orientalis     | Sp28   | Ulmus pumila                |
| Sp13   | Juniperus chinensis        | Sp29   | Platanus × acerifolia       |
| Sp14   | Juniperus chinensis 'Kaizuka' | Sp30 | Ginkgo biloba               |
| Sp15   | Koelreuteria paniculata    | Sp31   | Toona sinensis              |
| Sp16   | Ailanthus altissima        | Sp32   | Fraxinus pennsylvanica      |

2.2. BVOCs composition analysis

In this experiment, the analysis and identification of BVOCs are mainly completed by the combination of thermal desorption and gas chromatography-mass spectrometry (TCT-GC/MS), and the instrument model is ATD350-Clarus 600 GC MS (PerkinElmer, USA). Use NIST 2008 Libraries to screen and confirm the chemical information represented by each peak in the data spectrum by computer search, compare the relative abundance, retention time and base peak three parameters, combine the retention index to obtain the molecular structure, and qualitatively determine the volatile components. The relative content of various volatiles is obtained by the area normalization method.

2.3. Calculation method of O3 generation potential

The reaction to produce O3 in the atmosphere depends on the concentration of BVOCs in the atmosphere, the specific oxidation mechanism, the rate of oxidation, the concentration of NOx and the influence of other substances [4]. Due to the complex types of BVOCs involved, only isoprene and monoterpenes, which account for a large proportion of the BVOCs components, were selected to calculate the ozone generation potential.

The maximum incremental reaction activity of VOCs was used to quantify their ozone generation potential. The calculation formula is:

\[
OFP_i = VOC_i \cdot MIR_i
\]

Where: \( OFP_i \) is the maximum value of O3 produced by a certain VOC species \( i \), g/a; \( VOC_i \) is the
environmental concentration or release amount of the $i$-th VOC species, g/a; $MIR_i$ is the maximum incremental response of the $i$-th VOC species activity, g/g. In the calculation, the latest research results of Cater $^{[9]}$ on MIR are used. The value of isoprene is 10.61g/g, and the value of monoterpene is 4.04g/g.

2.4. Calculation method of SOA generation potential
BVOCs are important precursors for the formation of SOA, and SOA is also one of the important indicators for evaluating air quality. The aerosol generation coefficient is used to quantify the influence of VOCs on the potential of SOA generation. The smoke box experiment of Grosjean $^{[10]}$ assumes that the SOA photochemical reaction only occurs during the daytime from 8:00 to 17:00, while VOCs only react with OH to generate SOA. The calculation formula is:

$$SOA_i = VOC_{i0} \cdot FAC_i$$

Where: $SOA_i$ is the amount of SOA produced by a certain VOC species $i$, g/a; $VOC_{i0}$ is the initial emission amount of the $i$-th VOC species emitted by the emission source, g/a; assuming that all VOCs released by plants come from $VOC_{i0}$; $FAC_i$ is the first SOA generation coefficient of $i$ species of VOC, according to the research data of Grosjean $^{[10]}$ on FAC, is 2% for isoprene and 30% for monoterpene.

3. Results and Discussion

3.1. Analysis on the potential of O$_3$ and SOA
Robinia pseudoacacia and Broussonetia papyrifera have a greater impact on O$_3$ production potential, with values of 2603.722 g/(plant·a) and 6625.726 g/(plant·a), which are much higher than other tree species. The tree species that have a greater impact on the potential of SOA generation are Salix matsudana f. pendula, Sophora japonica, Salix matsudana and Pinus tabulaeformis, with values of 99.297 g/(plant·a), 89.471 g/(plant·a), 66.831 g/(plant·a) and 51.234 g/(plant·a).

Analysis of the tree species family found that Fabaceae and Salicaceae species have higher potential for O$_3$ and SOA generation than other families. Relatively speaking, the potential of SOA generation is one to two orders of magnitude lower than that of O$_3$ in terms of value, indicating that the BVOCs emitted by greening tree species have relatively weak potential for SOA generation.

Fig.1 Correlation matrix of O$_3$, SOA and five compounds in BVOCs. (Scatterplots of each pair of numeric variable are drawn on the left part of the figure. Pearson correlation is displayed on the right. Variable distribution is available on the diagonal. ***, $P<0.001$; **, $0.001<P<0.01$; *, $0.01<P<0.05$)
3.2. Research on the relationship between BVOCs and O$_3$, SOA generation potential
From the results in Fig.1, the correlation coefficient between O$_3$ generation potential and alcohols is 0.767 ($P<0.001$), the correlation coefficients with ketones and esters are 0.667 ($P<0.001$) and 0.633 ($P<0.001$), and the correlation coefficient with aldehydes release is only 0.382 (0.01<$P<0.05$). SOA generation potential is significantly correlated with hydrocarbons, alcohols and aldehydes ($P<0.001$). The correlation coefficient between SOA and hydrocarbons is 0.793, and the correlation coefficient with alcohols was 0.680, and there was no significant correlation with ketones ($P>0.05$).

3.3. Cluster analysis of greening tree species based on released components
In order to understand the clustering characteristics of different tree species, select the release components that have a significant impact on O$_3$ and SOA, and cluster the tree species through the UPGMA method to select tree species with less negative environmental impact. Based on the results of the above correlation analysis, the selections for SOA are hydrocarbon, alcohol, and aldehyde, and the selections for O$_3$ are ketone, ester, hydrocarbon and alcohol.

From the results in Fig.2, the greening tree species with strong potential to generate O$_3$ and SOA are *Salix matsudana*, *Populus tomentosa* and *Salix matsudana f. pendula*, while *Ailanthus altissima*, *Acer truncatum*, *Rhus typhina*, *Prunus cerasifera f. atropurpurea*, *Prunus persica f. Duplex* and *Cerasus serrulata var. lannesiana* have weak potentials for O$_3$ and SOA generation.

4. Conclusion
O$_3$ generation potential is significantly related to the release of hydrocarbons, esters, alcohols, and ketones, and SOA generation potential is significantly related to the release of hydrocarbons, alcohols, aldehydes and esters. According to the results of UPGMA cluster analysis, it is recommended that *Ailanthus altissima*, *Acer truncatum*, *Rhus typhina*, *Prunus cerasifera f. atropurpurea*, *Prunus persica f. Duplex* and *Cerasus serrulata var. lannesiana* should be used in urban greening, and the planting scale of *Salix matsudana*, *Populus tomentosa* and *Salix matsudana f. pendula* should be reduced.

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