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Emission of Biogenic Volatile Organic Compounds from Trees along Streets and in Urban Parks in Tokyo, Japan

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ABSTRACT

Ozone concentration in Tokyo Metropolitan area is one of the most serious issues of the local air quality. Tropospheric ozone is formed by radical reaction including volatile organic compound (VOC) and nitrogen oxides (NO_x). Reduction of the emission of reactive VOC is a key to reducing ozone concentrations. VOC is emitted from anthropogenic sources and also from vegetation (biogenic VOC or BVOC). BVOC also forms ozone through NO_x and radical reactions. Especially, in urban area, the BVOC is emitted into the atmosphere with high NO_x concentration. Therefore, trees bordering streets and green spaces in urban area may contribute to tropospheric ozone. On the other hand, not all trees emit BVOC which will produce ozone locally. In this study, BVOC emissions have been investigated (terpenoids: isoprene, monoterpenes, sesquiterpenes) for 29 tree species. Eleven in the 29 species were tree species that did not emit BVOCs. Three in 12 cultivars for future planting (25 %) were found to emit no terpenoid BVOCs. Eight in 17 commonly planted trees (47%) were found to emit no terpenoid BVOC. Lower-emitting species have many advantages for urban planting. Therefore, further investigation is required to find the species which do not emit terpenoid BVOC. Emission of reactive BVOC should be added into guideline for the urban planting to prevent the creation of sources of ozone. It is desirable that species with no reactive BVOC emission are planted along urban streets and green areas in urban areas, such as Tokyo.

Key words: Biogenic volatile organic compound, Street lining trees, Urban vegetation, Oxidant formation, Photochemical reaction

1. INTRODUCTION

Biogenic volatile organic compounds (BVOCs) are known to have effects on regional air quality (Lee *et al*., 2010) and climate (Jiang *et al*., 2010). Not only forested area, but also urban areas have vegetation, such as tress along streets and green open spaces, to improve the urban environment and to provide relaxation for residents (Weber *et al*., 2014; Ishikawa and Fukushige, 2012). Regional modelling study suggests that biogenic emission in urban area is not very important on the ozone formation (Kiriyama *et al*., 2015), however, more detailed investigation for biogenic emission in urban area may change the modelling result. Some of these urban trees also release the BVOCs into the high nitrogen oxides (NO_x) urban atmosphere (Sakulyanontvittaya *et al*., 2008). Shon (2015) reports port area also contribute on the biogenic emission. Especially, Tokyo has a port area which emits significant amount of NO_x (Song *et al*., 2015).

Consequently, trees in urban area may contribute to tropospheric ozone (Chameides *et al*., 1988). In addition, some BVOCs are reactive and are increasingly emitted at higher temperatures, when the ozone formation and concentration also tends to be high (Nishimura *et al*., 2015). Therefore, the BVOC emission into the urban atmosphere should be investigated for its effect on air quality. Curtis *et al*. (2014) reported the BVOC emission from trees in urban area. Because emission of the BVOC highly depends on the species of tree, it is necessary to investigate the BVOC emission of each species. A guide which indicates the BVOC emission capacity of trees would, therefore, be useful. The guide could be used to select tree species along streets and/or green areas. Using the guideline, reactive VOC emission may be reduced.

Twenty nine tree species for the emission of isoprene, monoterpenes and sesquiterpenes (a group of reactive

BVOC referred to as terpenoids) have been investigated by a simple screening technique. Twelve species are cultivar trees in the TMAFRC for future planting. The remaining species (17) have been already planted on streets and green areas in Tokyo. The 17 species were selected from the 20 most dominant tree species in urban area in Tokyo and accounts 87.1% of the 20 dominant species by the number planted. In this study, we screened terpenoid BVOC emitting tree and non-terpenoid BVOC emitting tree by an enclosure sampling. The results could be considered in the guideline to select planting trees in urban area to prevent the creation of new reactive VOC sources.

2. EXPERIMENT

2.1 Sampling Sites

The leaf VOC emissions from selected trees were sampled at Tokyo Metropolitan Agriculture and Forestry Research Center (TMAFRC). The TMAFRC develops trees appropriate for use in urban plantings by propagating more suitable sub-species. There are around 370 of these cultivar trees in the TMAFRC. We selected 12 tree species which will be likely to be used in urban planting in near future. Another 17 trees (commonly used for urban plantings at present time) were sampled at Kiba Park (35°67′68″N 139°80′75″E) in Koto-Ku, Tokyo. Sampling at TMAFRC and Kiba Park were conducted on the end of August and from end of September to early October of 2014, respectively.

2.2 Sampling Procedure and Analysis of BVOC

The emission of the BVOC was investigated using a closed branch enclosure. The enclosure is made by placing the end of branch in an approximately 5 L FEP bag. After approximately 5 minutes of installing the bag, one liter of air from the bag was pulled through an adsorbent tube which traps BVOCs at flow rate of 200 mL min^{-1}. Samplings were conducted for three branches of each species. There are two types of adsorbent tubes. One is for a thermal desorption technique (for the analysis of C_5-C_{15} hydrocarbons), filled with a 200 mg of Tenax TA and 100 mg of Carbotrap B (Sigma-Aldrich, St. Louis, MO, U.S.A.). The tube was analyzed in the laboratory employing an automated thermal desorption system (Turbo matrix 650, Perkin Elmer, Waltham, MA, U.S.A.) gas chromatography mass spectrometer (GC-MS; 7890GC and 5975C MSD, Agilent, Santa Clara, CA, U.S.A.). GC program is described in Matsunaga *et al.*, 2011. Ionization was done by electron impact (70 eV). MS analysis was conducted by scan mode. The second absorbent tube is for a liquid extraction technique which is used for the analysis of hydrocarbons and oxygenated hydrocarbons larger than C_{15}. It is filled with approximately 60 mg of HaeySep Q (RESTEK, Bellefonte, PA, U.S.A.). The liquid extraction is conducted at the site. The adsorbed BVOCs were extracted by approximately 1 mL of hexane (hexane for pesticide residue and polychlorinated biphenyl analysis, which is 5000 times concentrated and tested), (Wako, Osaka, Japan) and replaced into a 1.5 mL glass vial with a PTFE lined cap. The extract was concentrated by a gentle nitrogen flow to approximately 20 μL in the laboratory (Matsunaga *et al.*, 2009; Matsunaga *et al.*, 2008). One μL of the concentrated extract was injected into a GC-MS (7890GC and 5975C MSD). The MS analysis was performed on scan mode. Approximately 10-20% of analyte is lost during the concentration process.

Although this sampling and analytical procedure cannot determine the BVOC emission rate, it can distinguish whether there is BVOC emission. Identification of isoprene and monoterpenes was made by comparing the retention time of the GC and their mass spectrum with an authentic standard. Because we did not have authentic standard for sesquiterpenes at that time, sesquiterpenes were identified based on NIST mass spectrum library. Some monoterpenes (e.g., ocimene) were also identified by the NIST library due to same reason.

3. RESULTS AND DISCUSSION

3.1 BVOC Emission

Table 1 shows presence of the BVOC emission from leaf of investigated trees. BVOCs were categorized to be four types, isoprene, monoterpenes (MNT), sesquiterpenes (SQT) and others. We classified intensity of the emission 3 levels, "±" indicates that emission is more than the detection limit, however, the emission is relatively low. On the other hand, an indicator "+" means that the BVOC emission was obviously high compares to "±" case. The symbol "−" indicates below the detection limit. *Acer buergerianum*, *Camellia japonica* and *Livistona chinensis* were not planted in the park, therefore, BVOC emission of these species were not measured. Although Calfapietra *et al.*, 2013 and other study report that *Ginkgo biloba* emits VOC, no emission was detected in this study. This may be caused by that the sampling was conducted close to falling season.

BVOC emitting tree may be a source of reactive VOC and contribute to the formation of ozone. Therefore, trees which emit no reactive BVOC are more desirable to plant, especially in urban areas where NO_x concentration is high. In this study, a BVOC emitter was more frequently in the cultivar trees than commonly planted trees. No BVOC emission, except for wax, was detected

Table 1. Emissions of bleed improved trees and commonly planted trees in Tokyo at present time.

Scientific name	Number*	Isoprene	MNT	SQT	Other	Note
Cultivar trees						
Ilex pedunculosa ‘Harashima’		−	−	−	+	Wax
Acer palmatum ‘Tsukasa Silhouette’		−	+	−	+	α-Pinene, wax
Lagerstroemia fauriei ‘Tuscarora’		−	−	−	+	Wax
Chionanthus virginicus		−	−	−	+	Wax
Magnolia × *kewensis* ‘Wada’s Memory’		−	±	−	−	Ocimene like
Liriodendron tulipifera ‘Fastigiatum’		−	±	±	−	Limonene, α-farnesene
Styrax japonica ‘kotoensis’		−	±	±	−	Limonene, α-farnesene
Cornus capitata ‘Mountain Moon’		−	+	−	+	Many, wax
Ilex integra ‘Ougon’		−	+	+	−	Ocimene like, β-caryophyllene
Prunus Youkou		−	±	−	−	Limonene, ocimene like
Rhodoleia ‘henryi’		−	+	−	−	Ocimene like
Metasequoia glyptostroboides		−	+	±	−	α-Pinene, others, β-caryophyllene
Commonly planted trees						
Ginkgo biloba	61977	−	−	−	−	
Cornus florida	61054	±	±	±	−	Could not identify (MNT, SQT)
Prunus spp.	44176	−	−	−	−	
Acer buergerianum	37216					Not planted in the park
Platanus spp.	31244	+	−	−	−	
Zelkova serrata	30800	−	−	−	−	
Cinnamomum camphora	19738	−	+	−	−	Ocimene like, others
Lithocarpus edulis	17149	−	±	−	−	Could not identify (MNT)
Morella rubra	13795	−	+	−	−	Could not identify (MNT)
Styphnolobium japonicum	12713	±	±	−	−	Could not identify (MNT)
Magnolia kobus	11598	−	−	−	−	
Liriodendron tulipifera	10220	−	−	−	−	
Lagerstroemia indica	8916	±	±	−	−	Could not identify (MNT)
Liquidambar styraciflua	8706	+	+	±	−	α-Pinene, limonene
Camellia japonica	7789					Not planted in the park
Quercus myrsinifolia	7147	−	+	−	−	α-Pinene, others
Aesculus turbinata	6422	−	−	−	−	
Livistona chinensis	5526					Not planted in the park
Firmiana simplex	5413	−	−	−	−	
Ulmus parvifolia	4939	−	−	−	−	

*: Number of the trees planted in Tokyo as street lining trees at the present time.
MNT: monoterpenes
SQT: sesquiterpenes
+: Obvious emission was detected.
±: Low emission higher than blank level was detected.
−: Below detection limit.

from cultivars *Ilex pedunculosa* ‘Harashima’, *Lagerstroemia fauriei* ‘Tuscarora’ and *Chionanthus virginicus* and the commonly planted trees, *Ginkgo biloba*, *Prunus* spp., *Zelkova serrata*, *Magnolia kobus*, *Liriodendron tulipifera*, *Aesculus turbinate*, *Firmiana simplex* and *Ulmus parvifolia*, respectively. Three of 12 (25%) cultivars emitted no BVOC (isoprene, monoterpenes or sesquiterpenes), while 8 in 17 (47%) commonly planted species emitted no BVOCs. There seemed that there are no specific patterns for the emission in genus or other factor among both cultivars and commonly planted species.

Table 1 includes wax, which is mixture of heavy alkanes ($>C_{16}$). Wax is not very reactive compared to terpenoids. Including wax emission, all of the investigated cultivar trees emitted some volatiles. It might be interesting that cultivars may tend to emit more BVOCs than commonly planted species. For example, *Liriodendron tulipifera* ‘Fastigiatum’ is a cultivar species of *Liriodendron tulipifera* and emits some monoterpene and sesquiterpene while *Liriodendron tulipifera* does not emit any BVOCs. Cultivars may make some trees more suitable to plant along streets and parks (e.g., easy to maintain, shape, etc.). However, this has resulted in the selection of tree species with higher BVOC emissions.

3.2 Guideline for Planting Trees

To reduce formation of tropospheric ozone in urban area, emission of reactive VOC including BVOC should be reduced. On the other hand, there are many criteria to select urban planting trees (e.g., fire prevention, shape, etc.). Therefore, cultivation is important to create more suitable tree selections for urban planting. We propose that the emission of BVOC should also be added into the guideline of the planting trees. We investigated only 12 cultivars in 370 species in this study. More investigation will find cultivars which do not emit BVOC. Subsequently, it is desirable that the guideline will be updated to consider the BVOC emission, and that cultivar species without reactive BVOC emission should be used for planting in Tokyo.

4. CONCLUSION

Twenty nine tree species have been investigated for their BVOC emissions from the leaf. Twelve of the 29 species were cultivar trees for urban planting. The rests of 17 species were already commonly planted in Tokyo. Three in 12 cultivar species were found not to emit BVOCs (25%) while 8 in 17 commonly planted species (47%) did not emit BVOCs. Because the cultivar species have many advantage compare to commonly planted species (e.g., easy to maintain, not enhance branches, etc.) and are commonly chosen for planting instead of the traditionally planted species, further investigation is required to find cultivar species which do not emit BVOCs to prevent the creation of new sources of reactive VOC in urban area in Tokyo.

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