

Volatile organic compound emissions from urban trees in Shenyang, China

D.W. LI^{1,2}, Y. SHI^{1,*}, X.Y. HE¹, W. CHEN¹, and X. CHEN¹

¹Key Laboratory of Terrestrial Ecological Process, Institute of Applied Ecology, Chinese Academy of Sciences, P. O. Box 417, Shenyang 110016, People's Republic of China

²Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

(Received January 26, 2007; Accepted August 8, 2007)

ABSTRACT. Biogenic emissions of the volatile organic compounds isoprene and monoterpene (BVOCs) contribute to tropospheric ozone and secondary particle formation and have indirect effects on global climate change. However, little research has focused on BVOC emissions from urban trees. In this study, the monoterpene emissions of Chinese Pine (*Pinus tabulaeformis* Carr.) have been measured by GC/MS. The emission rates of α -pinene, β -pinene, camphene and limonene reached their maximum 78.55, 0.67, 0.82 and 0.31 $\mu\text{g g}^{-1} \text{dw h}^{-1}$ ($p < 0.05$), respectively, in August. For Δ^3 -carene, the highest emission rate, about 0.51 $\mu\text{g g}^{-1} \text{dw h}^{-1}$, was observed in June. The dominant monoterpene emitted was α -pinene. In August and September, this monoterpene accounted for more than 97% of the emissions. Correlation analyses revealed significant correlations among emission rates of α -pinene, β -pinene, camphene, and limonene ($p < 0.01$). This may imply that the biosynthesis of α -pinene, β -pinene, camphene, and limonene were controlled by some common metabolic routes.

Keywords: GC/MS; Isoprene; Monoterpenes; *Pinus tabulaeformis* Carr.

INTRODUCTION

In the troposphere, volatile organic compounds (VOCs) play an important role in a number of chemical processes including formation/decomposition of ozone and other oxidants as well as secondary formation of organic aerosols and organic acids (Padhy et al., 2005). Emission sources for these compounds are both anthropogenic and biogenic. Estimates of the global anthropogenic VOC emission range is between 56 and 98 Tg C yr⁻¹ (Holzke et al., 2006a). In comparison, it is reported that more than 1150 Tg C·yr⁻¹ of biogenic volatile organic compounds (BVOCs) has been released into the atmosphere (Simpson et al., 1999). The Center of Environment Science of Peking University has simulated the influence of BVOCs on ozone and considers that natural sources are more important than anthropogenic VOCs at present (Yang et al., 2001). Consequently, study of the emission rate and factors influencing BVOC emissions in different ecosystems is important if we are to gauge the effect they have on the environment.

Methods of sampling and analysis, as well as the source, distribution, and variations of VOCs have been studied (Li et al., 2005). Some reports on VOCs have focused on anthropogenic sources in the urban environment (Holzke et al., 2006a). Urban vegetation is often characterized by the presence of exotic species interspersed with natural

vegetation. The different management (e.g. pruning, fertilization) and the stressful conditions to which urban trees are subjected (including repeated exposure to soil and air pollution episodes and the acclimation problems of exotic species to environmental constraints) may affect BVOC emission rates (Centritto et al., 2005). Norwak et al. (2000) investigated the impact of urban trees in Washington, D.C., on ozone formation. They found that urban trees reduced ozone concentrations in cities, but overall ozone concentration in the wider model domain had increased. Thus it appears that urban tree canopies in some parts of the world may influence urban ozone chemistry in a significant way. In addition to their contribution to atmospheric chemistry, monoterpenes play important ecologic roles as defense compounds (Fischbach et al., 2000).

The aim of this paper is to study the emission rates, seasonal variations, patterns, and correlations of volatile organic compounds from urban Chinese Pine (*Pinus tabulaeformis* Carr.) trees in Shenyang, China.

MATERIALS AND METHODS

The measurements were performed on street trees in Shenyang (41°46'1.29" N, 123°26'27.51" E) in northeastern China. Chinese Pine (*Pinus tabulaeformis*) is a native dominant conifer species in Shenyang and the surrounding area. These studied trees were characterized by a canopy height of 5 m on average, tree age of 30 years, and good health conditions. Three trees were measured.

*Corresponding author: Email: shiyi@iae.ac.cn; Tel: +86-24-83970371; Fax: +86-24-83970436.

The measurements in 2006 were performed once every month around the 20th on a clear day in the months from May to September. On each date, six replicate samples were collected between 8:00 and 10:00 am.

Transparent plastic bags were used to cover well-lighted branches or clumps of foliage, and the base of each bag was carefully closed. Background BVOC emissions of empty plastic bags were checked and found negligible. Care was taken to avoid BVOC release due to rough handling, for damaged or crushed foliage usually increases BVOC emissions remarkably (Karlik et al., 2002).

The samples were collected from inside of the bags on adsorbent tubes filled with Tenax-TA using a constant-flow type pump. The flow rates were 100 ml/min, and the sampling time was 10 min.

After emission sampling, the leaves enclosed in the bags were removed from the trees, and placed in a drying oven at 60°C for 48 h. The dry weights were used for normalization of BVOC emission rates to unit leaf mass.

Ambient air temperature and illuminance were recorded inside and outside the branch enclosure while emission samples were taken during sampling. Temperature was measured with a digital thermometer (TES-1364, Taiwan). Illuminance was measured with a digital luminometer (TES-1330A, Taiwan).

The sampling tubes were thermally desorbed by an Aero trap desorber (Tekmar 6000, Dohrmann, USA) at a temperature of 225°C for 20 min, and the desorbed BVOCs were carried by ultra-pure helium gas (99.9999 %) to a charcoal trap cooled with liquid nitrogen to -165°C. The trap was then thermally desorbed at 240°C for 4 min and BVOCs were transferred to the CryoFocus Module (CM) at -150°C. Finally, the CM was heated rapidly to 225°C for sample injection to GC/MSD (HP 5890 with HP 5972 mass selective detector, Hewlett-Packard, Palo Alto, USA) for detection.

GC-MS analysis of the samples was performed on a Hewlett Packard 5890 gas chromatograph (carrier gas: He at 1 ml/min; splitless injection temperature 240°C) with the PONA (50 m × 0.2 mm × 0.5 μm) column temperature programmed from 0°C for 1 min, followed by a rise of 10°C/min until 100°C for 1 min, which was then increased to 150°C at a rate of 5°C/min, and at last increased to 280°C by 12°C/min, connected to a 5972 quadrupole-type

mass selective detector with a transfer line temperature of 220°C, a source temperature of 180°C, a multiplier voltage of 2.24 Kv, and a scan range of 40-250 amu. The lowest limit was 7^{-12} ~ 40^{-12} V/V, the recovery was 88-111%, with an average of $100.8 \pm 5.6\%$; and the bias error of precision was 2-14%, with an average of 6.6%. The blank values were measured and subtracted.

The mass spectrometer with an electron impact ionization source was operated on a selective-ion monitoring mode. Monitoring ions of *m/z* 67 were used for quantification of isoprene and *m/z* 93 and 136 for monoterpenes. A standard VOC mixture (TO-14) containing 37 hydrocarbon species of 100 ppbv was analyzed once a day for calibration before the atmospheric samples were processed.

All data were subjected to one-way analysis of variance (ANOVA) and correlation analysis in the SPSS statistical package.

RESULTS

Seasonal variations in emission rates

The emission rates of α -pinene, β -pinene, camphene, and limonene reached their maximum 78.55 (df=4 and 25, $F=2.949$, $p<0.05$), 0.67 (df=4 and 25, $F=2.165$, $p<0.05$), 0.82 (df=4 and 25, $F=3.738$, $p<0.05$), and $0.31 \mu\text{g g}^{-1}\text{dw h}^{-1}$ (df=4 and 25, $F=5.167$, $p<0.05$), respectively, in August (Figure 1). However, for Δ^3 -carene, the highest emission rate, about $0.51 \mu\text{g g}^{-1}\text{dw h}^{-1}$ (df=4 and 25, $F=2.269$, $p<0.05$), was observed in June. Moreover, our study shows that the isoprene emission rate ranged from 0.01 to $0.39 \mu\text{g g}^{-1}\text{dw h}^{-1}$ (from May to July), and this result approximated that of Chinese pine in Beijing (Li et al., 1994).

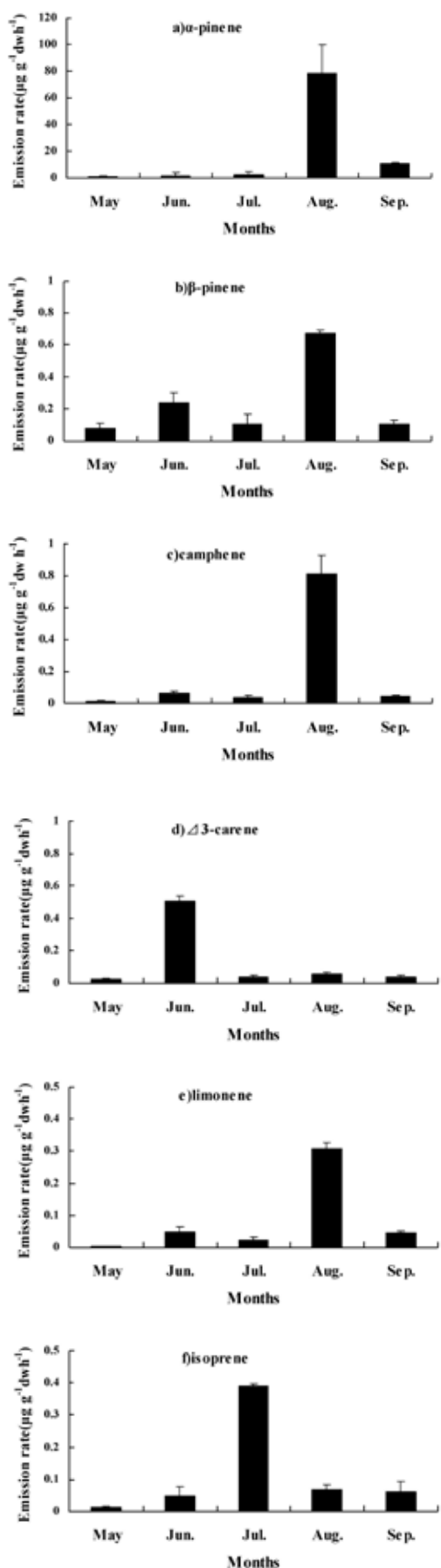
Table 1. The relative abundance (%) of the terpenoid compounds.

	May	June	July	Aug.	Sep.
Camphene	1.30	2.67	1.42	1.01	0.41
Δ^3 -carene	1.88	21.14	1.51	0.07	0.37
β -pinene	6.49	9.96	3.83	0.84	0.94
Isoprene	0.94	2.02	14.50	0.08	0.56
α -pinene	89.21	62.25	77.89	97.61	97.31
Limonene	0.18	1.96	0.85	0.38	0.42

Table 2. Correlation coefficient (r) among the emission rates of six terpenoid compounds.

	α -Pinene	β -Pinene	Δ^3 -Carene	Camphene	Limonene	Isoprene
α -Pinene	1	0.952**	0.434	0.997**	0.992**	0.496
β -Pinene		1	0.675	0.961**	0.981**	0.635
Δ^3 -Carene			1	0.471	0.542	0.522
Camphene				1	0.994**	0.507
Limonene					1	0.557
Isoprene						1

**Is significant at $p < 0.01$ in ANOVA analysis.



BVOC emission pattern

Due to their different sources, the relative abundance of the monoterpenes and isoprenes vary throughout the growing season. Table 1 showed that α -pinene was the most abundant compound throughout the season, the other important terpenoid compounds being β -pinene, $\Delta 3$ -carene, limonene, camphene, and isoprene. In August and September, more than 97% of the compounds were α -pinene. However, in June, $\Delta 3$ -carene accounted for 21% of the total terpenoid, and in July isoprene accounted for near 15% of the total. The other monoterpenes were emitted in lesser quantities.

Correlation analysis

Correlation analyses of terpenoid compounds (Table 2) showed that there were significant correlations of α -pinene with β -pinene, camphene, and limonene, and of β -pinene with camphene and limonene ($p < 0.01$), respectively.

DISCUSSION

Seasonal variations in emission rates

The rates of monoterpenes and isoprene emission from Chinese Pine showed evident seasonal variations, which were similar to the seasonal dynamics of emission rates of monoterpenes from Scots pine previously observed in Sweden (Janson et al., 1999). Hakola et al. (1998) reported the seasonal variation of emissions from tea-leaved willow (*Salix phylicifolia*), aspen (*Populus tremula*), and silver birch (*Betula pendula*). The emissions of willow and aspen reached the highest values in May and then decreased. The emission rates in Birch were highest in August and lowest in June and September. A similar observation was made on ambient air above a boreal coniferous forest in Finland (Hakola et al., 2003). However, Kim et al. (2005) reported that the emission rates from *Pinus koraiensis* were not significantly different in the spring and summer. The isoprene and monoterpene emissions are mainly correlated to the air temperature and solar radiation (Simon et al., 2005). Because of the higher temperature (31°C) and strong incident solar radiation in August in Shenyang (>20000 lx), the emission rates of monoterpenes were higher than those of other months. Moreover, previous studies observed an emission reduction in summer and fall that was correlated to the lower activity of some terpene synthases (Lehning et al., 1999). This indicates that the emissions are not only dependent on exogenous but also on endogenous parameters such as the developmental state of the investigated branches (Holzke et al., 2006a). This may explain the results reported here concerning seasonal changes in isoprene and monoterpene emission rates.

Figure 1. Emission rates of isoprene and monoterpene from pine (*Pinus tabulaeformis* Carr.). Data shown are the means and standard deviation of six replicates ($\mu\text{g g}^{-1}\text{dw h}^{-1}$).

BVOC emission pattern

A number of *Pinus nigra* populations have been reported to emit primarily monoterpenes (Bojovic et al., 2005). The pattern of volatiles reported here is similar to that found in other studies, where α -pinene was also found to be the main constituent of pine needle volatiles (Bai et al., 1994; Wang et al., 2003). Gao et al. (2005) quantified monoterpene species emitted from the pine needles by GC-MS and found that the composition ratios for monoterpenes differed significantly among tree species like *P. tabulaeformis*, *P. bungeana*, *S. chinensis*, and *S. japonica*, over the observation period. Our results are also in agreement with observations by Holzke et al. (2006b) on Scots pine in field studies. Janson and De Serves (2001) reported that α -pinene and Δ^3 -carene were the most abundant compounds in the emissions of *P. sylvestris*. These results are different from VOC flux measurements carried out above a boreal coniferous forest in June 1996. The most abundant compounds found above this canopy were isoprene and α -pinene (Hakola et al., 2003). Staudt et al. (2000) revealed large seasonal changes in both the quantity and quality of the monoterpene emissions from *Pinus pinea*, and significant monoterpene emissions had been reported from *Salix phylicifolia* and *Populus tremula* soon after bud-break and prior to the beginning of the isoprene emissions (Hakola et al., 1998).

Correlation analysis

Plants have an enormous capacity to synthesize huge amounts of diverse isoprenoids, particularly via the combination of the isoprenoid biosynthetic route and other secondary metabolic pathways. Zeng and Hu (1992) indicated that the synthesis of monoterpenes was controlled by different genes, so the correlations were not always significant among various monoterpenes. However, the good correlations in our work suggested that the synthesis of α -pinene, β -pinene, camphene and limonene were controlled by some common gene. The positive correlation ($r=0.95$) found between α -pinene and β -pinene was in agreement with the result reported by Hiltunen and Laakso (1995). It has been shown with *Pinus contorta* that α -pinene can actually be produced by several enzymes (Savage et al., 1995). If in a group of tree species, several enzymes were to produce the same constituent, one would probably find complex correlations for α -pinene, β -pinene, camphene, and limonene. The strong correlation of α -pinene and camphene was not specific for *Pinus tabulaeformis* Carr., as this has also been found in Norway spruce (Sjodin et al., 2000). The significant correlation between α -pinene and camphene might imply a common precursor to camphene and α -pinene. Such a precursor has been suggested by Wise and Croteau (1999) although Hiltunen and Laakso (1995) found no significant relationship between α -pinene and camphene emissions. More complex relations were found among monoterpene species since the correlation coefficients among pine species showed great variation (Fäldt et al., 2001).

To sum up, the dominant monoterpene emitted was α -pinene, and its emission rates reached a maximum of $78.55 \mu\text{g g}^{-1} \text{dw h}^{-1}$ ($p<0.05$) in August. BVOC can enhance O_3 and other oxidant levels, especially in locations rich in nitrogen oxides. VOC is held in air for several hours, but the influence on urban ozone chemistry should not be neglected.

Acknowledgments. This research was financially supported by the National Natural Science Foundation of China (Key Program 90411019). The authors wish to express their appreciation to Prof. Dali Tao, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang, China, for his helpful suggestions and constructive review of this manuscript.

LITERATURE CITED

- Bai, Y.H., J.L. Li, and B.X. Zhang. 1994. The qualitative determination of hydrocarbon emitted from woods and vegetations over Beijing area. *Res. Environ. Sci.* **7(2)**: 49-54.
- Bojovic, S., M. Jurc, D. Drazic, P. Pavlovic, M. Mitrovic, L. Djurdjevic, R.S. Dodd, Z. Afzal-Rafii, and M. Barbero. 2005. Origin identification of *Pinus nigra* populations in southwestern Europe using terpene composition variations. *Trees-Struct. Func.* **19**: 531-538.
- Centritto, M., S.R. Liu, and F. Loreto. 2005. Biogenic emission of volatile organic compounds by urban forests. *Chin. Fore. Sci. Tech.* **4**: 20-26.
- Fäldt, J., K. Sjödin, M. Persson, I. Valterová, and A.-K. Borg-Karlson. 2001. Correlations between selected monoterpene hydrocarbons in the xylem of six *Pinus* (*Pinaceae*) species. *Chemoecol.* **11**: 97-106.
- Fischbach, R.J., I. Zimmer, R. Steinbrecher, A. Pfichner, and J.P. Schnitzler. 2000. Monoterpene synthase activities in leaves of *Picea abies* (L.) Karst. and *Quercus ilex* L. *Phytochemistry* **54**: 257-265.
- Gao, Y., Y.J. Jin, H.D. Li, and H.J. Chen. 2005. Volatile Organic Compounds and their Roles in Bacteriostasis in Five Conifer Species. *J. Integrat. Plant Biol.* **47**: 499-507.
- Hakola, H., J. Rinne, and T. Laurila. 1998. The hydrocarbon emission rates of tea-leaved willow (*Salix phylicifolia*), silver Birch (*Betula pendula*) and European aspen (*Populus tremula*). *Atmos. Environ.* **32(10)**: 1825-1833.
- Hakola, H., V. Tarvainen, T. Laurila, V. Hiltunen, H. Hellen, and P. Keronen. 2003. Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmos. Environ.* **37(12)**: 1623-1634.
- Hiltunen, R. and I. Laakso. 1995. Gas chromatographic analysis and biogenic relationships of monoterpene enantiomers in Scots pine and juniper needle oils. *Flavour Fragr J.* **10**: 203-210.
- Holzke, C., T. Hoffmann, L. Jaeger, R. Koppmann, and W. Zimmer. 2006a. Diurnal and seasonal variation of monoterpene and sesquiterpene emissions from Scots pine (*Pinus sylves-*

- tris* L.). *Atmos. Environ.* **40**: 3174-3185.
- Holzke, C., T. Dindorf, J. Kesselmeier, U. Kuhn, and R. Koppmann. 2006b. Terpene emissions from European beech (*Fagus sylvatica* L.): Pattern and emission behaviour within two vegetation periods. *J. Atmos. Chem.* **55**: 81-102.
- Janson, R.W., C. De Serves, and R. Romero. 1999. Emission of isoprene and carbonyl compounds from a boreal forest and wetland in Sweden. *Agric. For. Meteorol.* **98-99**: 671-681.
- Janson, R. and C. De Serves. 2001. Acetone and monoterpene emissions. from the boreal forest in northern Europe. *Atmos. Environ.* **35**: 4629-4637.
- Karlik, J.F., A.H. McKay, J.M. Welch, and A.M. Winer. 2002. A survey of California plant species with a portable VOC analyzer for biogenic emission inventory development. *Atmos. Environ.* **36**: 5221-5230.
- Kim, J.C., K.J. Kim, D.S. Kim, and J.S. Han. 2005. Seasonal variations of monoterpene emissions from coniferous trees of different ages in Korea. *Chemosphere* **59**: 1685-96.
- Lehning, A., I. Zimmer, R. Steinbrecher, N. Brüggemann, and J.P. Schnitzler. 1999. Isoprene synthase activity and its relation to isoprene emission in *Quercus robur* L. leaves. *Plant Cell Environ.* **22**: 495-504.
- Li, J.L., Y.H. Bai, and J.X. Hu. 1994. Diurnal variation in the concentration of terpenes and its emission rate measurements from Chinese pine. *Chin Environ Sci.* **14(3)**: 165-169.
- Li, D.W., Y. Shi, and X.Y. He. 2005. Research advances in the effects of elevated atmospheric carbon dioxide and ozone on biogenic VOCs emission. *Chin J. Appl. Ecol.* **16(12)**: 2454-2458.
- Norwak, D.J., K.L. Civerolo, S.T. Rao, G. Sistla, C.J. Luley, and D.E. Crane. 2000. A modeling study of the impact of urban trees on ozone. *Atmos. Environ.* **34**: 1601-1613.
- Padhy, P.K. and C.K. Varshney. 2005. Emission of volatile organic compounds (VOC) from tropical plant species in India. *Chemosphere* **59(11)**: 1643-1653.
- Savage, T.J., H. Ichii, S.D. Hume, D.B. Little, and R. Croteau. 1995. Monoterpene synthases from gymnosperms and angiosperms: stereospecificity and inactivation by cysteinyl- and arginyl-directed modifying reagents. *Arch Biochem Biophys.* **320**: 257-265.
- Simon, V., L. Dumergues, P. Bouchou, L. Torres, and A. Lopez. 2005. Isoprene emission rates and fluxes measured above a Mediterranean oak (*Quercus pubescens*) forest. *Atmos. Res.* **74**: 49-63.
- Simpson, D., W. Winiwarter, and G. Borjesson. 1999. Inventorying emissions from nature in Europe. *J. Geoph Res.* **104**: 8113-8152.
- Sjödin, K., M. Persson, J. Faldt, I. Ekberg, and A.K. Borg-Karlson. 2000. Occurrence and correlations of monoterpene hydrocarbon enantiomers in *Pinus sylvestris* and *Picea abies*. *J. Chem. Ecol.* **26**: 1701-1720.
- Staudt, M., N. Bertin, B. Frenzel, and G. Seufert. 2000. Seasonal variations in amount and composition of monoterpenes emitted by young *Pinus pinea* trees - implications for emission modeling. *J. Atmos. Chem.* **35**: 77-99.
- Wang, Z.H., Y.H. Bai, and S.Y. Zhang. 2003. A biogenic volatile organic compounds emission inventory for Beijing. *Atmos. Environ.* **37**: 3771-3782.
- Wise, M.L. and R. Croteau. 1999. Monoterpene biosynthesis [C]. In J. Fäldt, K. Sjödin, M. Persson, I. Valterová, and A.-K. Borg-Karlson. 2001. Correlations between selected monoterpene hydrocarbons in the xylem of six *Pinus* (*Pinaceae*) species. *Chemoecol.* **11**: 97-106.
- Yang, D.Q., Y.H. Bai, J.L. Li, N.M. Pan, K.H. Yu, L. Tang, L.X. Peng, and H. Su. 2001. A study on hydrocarbon compounds emitted from natural forest sources in Pearl River Delta. *Guangzhou Environ. Sci.* **16(3)**: 34-38.
- Zeng, Y.H. and X.J. Hu. 1992. Geographic variation in components of monoterpene and sesquiterpene in *Pinus armandi*. *Sci. Silvae Sin.* **28**: 161-166.

中國瀋陽市樹木揮發性有機物釋放規律研究

李德文 史 奕 何興元 陳 瑋 陳 欣

中國科學院瀋陽應用生態研究所 陸地生態過程重點實驗室

植物所釋放的異戊二烯和單萜具有很高的化學活性，可影響低層大氣的化學組成，促進光化學污染的形成，對溫室效應和全球變化具有潛在的影響。城市樹木對人體健康及城市環境均具有重要影響，目前對其揮發性有機物釋放規律的研究較少。本文採用GC/MS方法對瀋陽市主要綠化樹種油松的異戊二烯及單萜的排放速率進行測定，結果表明： α -pinene, β -pinene, camphene 及 limonene 排放速率在8月達到最大值，分別為 78.55, 0.67, 0.82 和 0.31 $\mu\text{g g}^{-1}\text{dw h}^{-1}$ ($p<0.05$)，而 Δ 3-carene 在 6 月份即達到最大值 0.51 $\mu\text{g g}^{-1}\text{dw h}^{-1}$ ； α -pinene 為油松揮發性有機物的主要成份；相關性分析表明 α -pinene, β -pinene, camphene 及 limonene 間的排放速率呈顯著相關 ($p<0.01$)，並推測這幾種物質具有相同的生物合成途徑。

關鍵詞：GC/MS；異戊二烯；單萜；油松。