

Seasonal Variations of Monoterpene Concentrations in a Pine Forest in Florida, USA

Jo-Chun Kim and Ki-Hyun Kim^{1),*}

Department of Environmental Engineering, Dongshin University, Naju, Korea 520-714

¹⁾*Department of Geoinformation Sciences, Sejong University, Seoul, Korea 143-747*

(Received 30 July 2002; accepted 5 September 2002)

Abstract

In order to study the distribution characteristics of natural volatile organic compounds (NVOCs), we investigated the seasonal variations of α - and β -pinene levels in a pine forest in Florida for a year. The mean concentrations of α - and β -pinene measured during the whole study period were computed to be 125 ± 86 (N = 65) and 86 ± 52 pptv (N = 56), respectively. According to our data grouping scheme, the seasonal means for both pinenes were observed to peak during fall with their max and min values in summer and winter, respectively. The overall results of our study suggest that terpenes are subject to highly strong temporal variability because of changes in their major source characteristics across seasons.

Key words : NVOCs, emission, temperature, monoterpene, season

1. INTRODUCTION

Volatile organic compounds (VOC(s)) are known to constitute one of the principal components in atmospheric chemistry (e.g., Zimmerman *et al.*, 1988). It is accepted that numerous types of VOC are emitted to the atmosphere from a variety of anthropogenic and natural sources (Kesselmeier *et al.*, 2000). The importance of anthropogenic VOC emitted from various industrial and/or transportation sources is well recognized (Mayer, 1999); they play the dominant role in the photochemical reactions in urban areas under the presence of various nitrogen oxides including peroxyacetyl nitrate (PAN). Similarly, the environmental cycle of the natural VOC (NVOC) is suspected to be tightly coupled

with that of ozone. Hence, these NVOCs can belong to the vital components of the tropospheric chemistry with their massive quantity of emissions. In addition, their presence in the earth's atmosphere can affect the global chemistry of greenhouse gases (CH₄), major pollutants (CO), secondary organic aerosols, etc. (e.g., Hoffman *et al.*, 1997).

Evidence collected from many of previous studies indicates that plants are the dominant source of NVOCs. A detailed speciation of those VOCs has shown that more than 400 types of NVOCs can be emitted by plants (e.g., Hewitt and Street, 1992). These NVOCs are found to consist of aldehydes, ketones, alcohols, alkanes, alkenes, isoprene, terpenes, and organic acids. It was estimated that the annual global flux of NVOCs could amount to 1150 Tg of C, exceeding that of anthropogenic counterparts. The total budget of NVOCs is found to be made up of isoprene (44%), mo-

* Corresponding author. E-mail : khkim@sejong.ac.kr

noterpenes (11%), reactive VOCs (22.5%), and others (22.5%) (Guenther *et al.*, 1995). However in a given locality, it is suggested that surrounding vegetation (i.e., local sources of NVOCs) can contribute substantially to their concentration levels (Arnts and Meeks, 1981). The fractional composition of ambient monoterpene levels from many coniferous forests around the world has carefully been examined (Harrison *et al.*, 2001; Kim, 2001; Biesenthal and Bottenheim, 1998; Ciccioli *et al.*, 1993; Feshenfeld *et al.*, 1992; Pio and Valente, 1988; Zimmermann *et al.*, 1988; Isidorov *et al.*, 1985). The results of those studies consistently indicate that the emissions of those NVOCs are dominated by two different monoterpene species, i.e., α - and β -pinene.

Although enormous studies were conducted previously to gain a better knowledge on the atmospheric chemistry of NVOCs, many unknowns still remain with respect to the extent of their contribution to total VOC budgets or their competitive relations with anthropogenic counterparts. Hence, there is a great demand to extend the database to better characterize the speciation and/or spatial-temporal distribution patterns of NVOCs. In an effort to better describe the environmental behavior of NVOCs, the seasonal distribution patterns of α - and β -pinene were investigated from a slash pine forest in northern Florida, USA during the period between 1994~1995.

2. EXPERIMENTAL

2.1 Sampling and analysis

The study site is located at the Austin Cary Forest, a two hectare cleared area surrounded by commercial slash pine plantations. This rural site is located approximately 15 kilometers NE of the downtown business district of Gainesville in the north central region of Florida, USA. Specific descriptions of the study site have been provided previously in our companion paper (Kim, 2001).

In this work, the collection of NVOC samples was made using Tenax-TA sorbent for one to two times per day basis at intervals of several days or weeks. The collection of samples was generally made during the daytime (typically between noon to 6 PM) for the total duration of one to three hour periods (typically two hours). The analysis of NVOCs was then made by the GC system interfaced with an automated cryogenic focusing system (Tekmar, Model 5010-GT Automatic Desorber). The protocol for sampling and analysis was developed and used specifically for the measurements of monoterpene species. For the collection of NVOC from the ambient air and the slash pines, sampling tubes were prepared with pyrex glass tubes (od 1.27×18.1 cm long) filled with 900 mg of Tenax-TA. The collection of air samples was then made using a rechargeable personal air sampler (Model PAS-3000, Supelco) and a sampling adaptor (#14-1486-200, Tekmar) which consists of a sampling tube holder, O-rings for a sampling tube, and a metal (Ni) filter (Calogirou *et al.*, 1996). Once collected, samples were stored in a clean tube container (Tekmar) under a cool condition (< 4 °C). The recovery rates of all terpene hydrocarbons spiked in the field were found at 95 to 105% range within one to five days of storage. The precision of this NVOC measurement technique was generally determined below 10%. The detection limits for monoterpene species were found to be ~ 2 pptv at typical sampling volume of 20 L.

The analysis of NVOC was made by the two individual GC systems of GC-ITD and GC-FID that were produced by the same manufacturer (Perkin Elmer, GC-8420 and -8500). These systems were equipped with the same DB-5 capillary column and operated under the same analytical conditions. The similarity in the analytical systems made it possible to easily compare and interpret the mass spectrometric and flame ionization chromatograms acquired by both systems. More details on the sampling and analysis of the NVOC concentration and emission rates have been described previously (Kim, 2001).

3. RESULTS AND DISCUSSION

3.1 The overall picture of terpene measurements

In this study, the analysis of NVOCs was initially made to cover such species as: α -pinene, β -pinene, d-limonene, β -phellandrene and p-cymene. However, quantitative analysis of NVOCs was confined mostly to two pinenes for the problems associated with low concentrations of other species during most of time. (The depletion of species other than two pinenes may in some part be accounted for by their strong reactivities with two double bond structures.) The concentrations of NVOCs measured during this study are plotted as a function of time in Figure 1. The overall picture of NVOC distribution patterns in the study area can be deduced from a statistical summary of the measurement data (Table 1). First of all, two pinenes were generally found at their concentrations near 100 pptv range. (Although an unusually high level of total monoterpene (930 pptv) was observed near the end of August, 1994, this unusual value was excluded from the data analysis

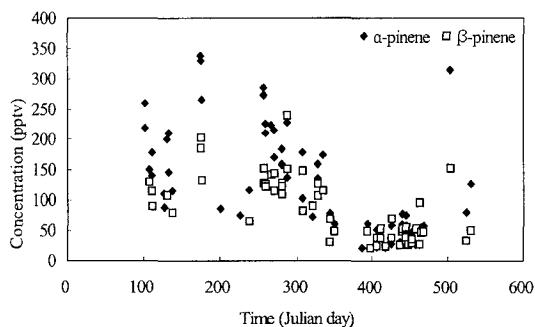


Fig. 1. Time series plot of α - (dark circle) and β -pinene (Empty box) over the whole study period.

to avoid distortion of the general tendency.) In addition, it also appears that there is a slight dominance of α - over β -pinene; the mean ratio of β/α was measured at 0.80 ± 0.26 with a moderate variability of $0.4 \sim 2$ ($N=55$).

It is reported in the literature that the concentrations of total monoterpene hydrocarbons fall in the wide range from as low as less than 10 to above a few tens of ppb (Laurila *et al.*, 1999; Janson, 1992). The low concentrations of terpene found from this study are hence comparable with those found in other coniferous forests (McClenny *et al.*, 1998; Johansson and Jason, 1993; Yokouchi and Ambe, 1988). In order to learn more about the general patterns of NVOC distributions, it may be worth comparing our results with those derived from other studies. It is suggested that the types and quantities of the surrounding vegetation are highly conducive to the determination of ambient biogenic hydrocarbon levels (Arnts and Meeks, 1981). According to their study, isoprene was the dominant hydrocarbon compound in a forest of oaks and hardwoods; these trees are known to be the principal emitters of isoprene. However, consideration of many other factors (e.g., temporal variability) is essential to explain the environmental behavior of NVOCs as described below.

3.2 Comparison of temporal distribution patterns of terpenes

It is well known that the NVOCs can exhibit strong temporal variabilities over relatively short-term periods such as diurnally. Most of previous studies indicate the existence of consistency in the diurnal variability of NVOCs. By measuring NVOCs from a northern European boreal site, Hakola *et al.* (2000) reported that monoterpenes generally exhibit a minimum in the daytime and a maximum in the nighttime (with a rare ex-

Table 1. A statistical summary of NVOC concentrations and relevant environmental parameters determined during the whole study period of Apr. 1994 through June 1995. All concentrations are given in ppt unit.

	α -pinene	β -pinene	β/α	Temp. ($^{\circ}\text{C}$)	RH (%)
Mean \pm SD (Median)	125 \pm 86.3 (103)	86.3 \pm 51.7 (75.2)	0.80 \pm 0.26 (0.78)	26.2 \pm 5.14 (26.8)	50.2 \pm 17.6 (47.8)
Range (N)	21.7 ~ 338 (65)	21.5 ~ 240 (56)	0.40 ~ 2.0 (55)	12.2 ~ 38 (69)	23.1 ~ 100 (57)

Table 2. A statistical summary of NVOC concentrations and relevant environmental parameters for each of four seasons. All concentrations are given in ppt unit.

	α -pinene	β -pinene	β/α	Temp. ($^{\circ}$ C)	RH (%)
I. Spring					
Mean \pm SD (Median)	102 \pm 77.6 (60.3)	64.1 \pm 36.4 (51.3)	0.86 \pm 0.31 (0.80)	26.2 \pm 3.9 (26.7)	42.9 \pm 13.7 (41.5)
Range (N)	26.7 ~ 314 (29)	26.6 ~ 153 (22)	0.49 ~ 1.90 (22)	13.5 ~ 31.1 (30)	23.1 ~ 80 (29)
II. Summer					
Mean \pm SD (Median)	177 \pm 114 (122)	112 \pm 73 (99)	0.51 \pm 0.09 (0.53)	33 \pm 3.2 (33)	50.3 \pm 3 (50.2)
Range (N)	75 ~ 338 (8)	33.7 ~ 203 (6)	0.40 ~ 0.62 (6)	29 ~ 38 (8)	46.8 ~ 54 (4)
III. Fall					
Mean \pm SD (Median)	183 \pm 55 (176)	131 \pm 34 (127)	0.75 \pm 0.20 (0.69)	27.9 \pm 2.5 (28.2)	66.8 \pm 14.7 (65)
Range (N)	73 ~ 285 (18)	83 ~ 240 (18)	0.47 ~ 1.24 (18)	23 ~ 32.3 (18)	46 ~ 100 (13)
IV. Winter					
Mean \pm SD (Median)	44.5 \pm 19.7 (47.6)	40.0 \pm 15.2 (38.4)	0.93 \pm 0.14 (0.88)	19.7 \pm 4.2 (21.7)	49.6 \pm 20.6 (43)
Range (N)	21.7 ~ 78.6 (10)	21.5 ~ 69.1 (10)	0.75 ~ 1.13 (9)	12.2 ~ 25.7 (13)	25 ~ 90 (11)

ception of certain compound like sabinene). In fact, Riba *et al.* (1987) measured the total concentrations of atmospheric terpene from a pine forest area in France. They reported that the concentrations measured during September were less than 500 pptv in the daytime and went up to 2,000~4,000 ppt at night. By contrast, there also appears an opposing result in which daytime enhancement is seen consistently from a forest environment (Buffer and Wegmann, 1991). However, evidence is abundant enough to support the relative enhancement of nighttime monoterpene levels from many regions around the globe including far east Asia (Yokouchi *et al.*, 1988) and Russia (Isidorov *et al.*, 1985). This relative enhancement in monoterpene concentration is believed to come mainly from nighttime reductions in (or absence of) reactive chemical species (e.g., OH and O₃). It may also be possible to infer that those unusually high concentrations of terpene might have been favored by enhanced atmospheric stability during nighttime periods with the formation of atmospheric inversion as can be seen frequently from temporal patterns of other trace components like mercury (e.g., Kim and Kim, 2001).

As most of our measurements were made intensively during daytime periods (e.g., noon~6 PM), the concentration data obtained during our study periods are unlikely useful enough to examine the diurnal variability.

However, as measurements were conducted at similar time schedule for an extended period of time, the results may be plausible enough to describe distribution patterns over monthly or seasonal scale. Results summarized in Table 2 indicate that there are large variabilities in the computed seasonal mean values. The results of this study clearly show that the highest and lowest seasonal mean values for the two pinenes occur consistently at fall and winter season, respectively. According to our study, seasonal distribution patterns of NVOCs are characterized by the dramatically reduced concentrations during winter season. It is also interesting to find out that the highest seasonal mean for terpenes occur during fall rather than summer. Results of recent studies generally indicate that the relative abundances of the terpenoid compounds can vary significantly across seasons. For example on the basis of the field study from a Finnish boreal forest, Hakola *et al.* (2000) reported that α -pinene can comprise more than 70% of terpenoid during May but that isoprene can grow to make up the half of the total terpenoid during July. The existence of such strong temporal variabilities in relative terpenoid composition is in fact in line with directly quantified emission rates under various field conditions (e.g., Boissard *et al.*, 2001). However, the causes of relatively reduced concentrations for summer-term in this study may in part be sought from

limited measurements during that season because of frequent rain events. In fact if concentration differences in two terpenes between summer and fall are checked by t-test, the level of difference is not statistically significant.

4. CONCLUSIONS

In this study, the environmental behavior of NVOCs was investigated by measuring the concentrations of both α - and β -pinene and the relevant environmental parameters from a slash pine forest in Florida, USA. According to our analysis, there were large variabilities in the computed seasonal mean values of two pinenes. It was also seen that both pinenes exhibited consistently the highest and lowest seasonal mean values at fall and winter season, respectively. These results are compatible with the previous findings that the relative abundances of the terpenoid compounds can vary significantly across the seasons. On the basis of our study, it is concluded that the presence of strong temporal variability in two terpenes concentration levels appears to be the distinctive characteristics of NVOC distributions.

ACKNOWLEDGEMENTS

This project was sponsored by the Alabama Regional Center, National Institute for Global Environmental Change (NIGEC). We wish to acknowledge Dr. Eric R. Allen, Daniel Stetzer, Alfredo Armendariz of the UF Environmental Engineering Sciences Department for their assistance during this work.

REFERENCES

- Arnts, R.R. and S.A. Meeks (1981) Biogenic hydrocarbon contribution to the ambient air of selected areas. *Atmospheric Environment*, 15, 1643–1651.
- Biesenthal, T.A. and J.W. Bottenheim (1998) The chemistry of biogenic hydrocarbons a rural site in eastern Canada. *Journal of Geophysical Research* 103, 25487–25498.
- Boissard, C., X.L. Cao, C.Y. Juan, C.N. Hewitt and M. Gallagher (2001) Seasonal variations in VOC emission rates from gorse (*Ulex europaeus*). *Atmospheric Environment* 35, 917–927.
- Bufler, U. and K. Wegmann (1991) Diurnal variation of monoterpene concentrations in open-top chambers and in the Welzheim forest air, FRG. *Atmospheric Environment* 25, 251–256.
- Calogirou, A., B.R. Larson, C. Brüssel, M. Duane, and D. Kotzias (1996) Decomposition of terpenes by ozone during sampling on Tenax. *Anal. Chem.* 68, 1499–1506.
- Ciccioli, P., B. Enzo, F. Massimiliano, C. Angelo, and B. Alessandro (1993) Ubiquitous occurrence of semi-volatile carbonyl compounds in tropospheric samples and their possible sources. *Atmospheric Environment* 35, 917–927.
- Fehsenfeld, F., J. Calvert, R. Fall, P. Goldan, B.A. Guenther *et al.* (1992) Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry. *Global Biogeochemical Cycles* 6, 389–430.
- Guenther, A.B., C.N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W.A. Mackay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, and P.R. Zimmerman (1995) A global model of natural volatile organic compound emissions. *Journal of Geophysical Research* 100 (D5), 8873–8892.
- Hakola, H., T. Laurila, J. Rinne, and K. Puhto (2000) The ambient concentrations of biogenic hydrocarbons at a northern European, boreal site. *Atmospheric Environment* 34, 4971–4982.
- Harrison, D., M.C. Hunter, A.C. Lewis, P.W. Seakins, B. Bonsang, V. Gros, M. Kanakidou, M. Touaty, I. Kavouras, N. Mihalopoulos, E. Stephanou, C. Alves, T. Nunes, and C. Pio (2001) Ambient isoprene and monoterpene concentrations in a Greek fir (*Abies Borisii-regis*) forest. Reconciliation with emissions measurements and effects on measured OH concentrations. *Atmospheric Environment*, 35, 4699–4711.
- Hewitt, C.N. and R.A. Street (1992) A qualitative assessment

- of the emission of non-methane hydrocarbon compounds from the biosphere to the atmosphere in the UK: present knowledge and uncertainties. *Atmospheric Environment*, 26, 3069-3077.
- Hoffmann, T., J.R. Odum, F. Bowman, D. Collins, D. Klockow, R.C. Flagan, and J.H. Seinfeld (1997) Formation of organic aerosols from the oxygenation of biogenic hydrocarbons. *Journal of Atmospheric Chemistry*, 26, 189-222.
- Isidorov, V.A., I.G. Zenkevich, and B.V. Ioffe (1985) Volatile Organic Compounds in the Atmosphere of Forests. *Atmospheric Environment*, 19, 1-8.
- Janson, R. (1992) Monoterpene concentrations in and above a forest of Scots pine. *Journal of Atmospheric Chemistry*, 14, 385-394.
- Johansson, C. and R.W. Janson (1993) Diurnal Cycle of Ozone and Monoterpenes in a Coniferous Forest: Importance of Atmospheric Stability, Surface Exchange, and Chemistry. *J. Geophys. Res.*, 98, 5121-5133.
- Kesselmeier, J., U. Kuhn, A. Wolf, M.O. Andreae, P. Ciccioli, E. Brancaleoni, M. Frattoni, A. Guenther, J. Greenberg, P. De Castro Vasconcellos, T. de Oliva, T. Tavares, and P. Artaxo (2000) Atmospheric volatile organic compounds (VOC) at a remote tropical forest site in central Amazonia. *Atmospheric Environment*, 34, 4063-4072.
- Kim, J.C. (2001) Factors controlling natural VOC emissions in a southeastern US pine forest. *Atmospheric Environment*, 35, 3279-3292.
- Kim, K.-H. and M.Y. Kim (2001) The temporal distribution characteristics of total gaseous mercury at an urban monitoring site in Seoul during 1999 to 2000. *Atmospheric Environment*, 35(25), 4253-4263.
- Laurila, T., H. Hakol, and V. Lindfors (1999) Biogenic VOCs in continental northern Europe-Concentrations and photochemistry. *Physics and Chemistry of Earth (B)* 24, 689-693.
- Mayer, H. (1999) Air pollution in cities. *Atmospheric Environment* 33, 4029-4037.
- McClenny, W.A., J.D. Pleil, G.F. Evans, K.D. Oliver, R.K. Monson, and R. Fall (1989) Isoprene Emission from Aspen Leaves. *Plant Physiol.*, 90, 267-274.
- Pio, C.A. and A.A. Valente (1998) Atmospheric fluxes and concentrations of monoterpenes in Resin-Tapped pine forests. *Atmospheric Environment*, 32, 683-691.
- Riba, M.L., J.P. Tathy, N. Tsiropoulos, B. Monsarrat and L. Torres (1987) Diurnal Variation in the Concentration of Alpha and Beta Pinene in the Landes. Forest (France). *Atmospheric Environment* 21, 191.
- Yokouchi, Y. and Y. Ambe (1988) Diurnal Variations of Atmospheric Isoprene and Monoterpene Hydrocarbons in an Agricultural Area in Summertime. *J. Geophys. Res.*, 99, 16609.
- Zimmerman, P.R., J.P. Greenberg, and C.E. Westberg (1988) Measurements of Atmospheric Hydrocarbons and Biogenic Emission Fluxes in the Amazon Boundary Layer. *J. Geophys. Res.*, 93, 1407-1416.