Comparison of Aromatic and Natural VOC Concentrations in the Ambient Air

Jo-Chun Kim[1], Ki-joon Kim, Young Sunwoo, Jin-Suk Han[2]

[1]Department of Environmental Engineering, Konkuk University, Seoul, 143-701, Korea
[2]Department of Atmospheric Chemistry, National Institute of Environmental Research, Incheon, 404-170, Korea

The ambient concentrations of benzene, toluene, and α-/β-pinene were measured from July, 2002 to August, 2002 at the Gumsung mountain site in Jeonnam province. The mean concentration of benzene for this study was 62.6 ± 43.9pptv (Min. 20.4 ~ Max. 151.2 pptv), and that of toluene was 619.8 ± 330.2pptv (264.8~1,386pptv). It was observed that the concentrations of α -pinene and β -pinene were 169.0 ± 97.7pptv (72.9~396.1pptv) and 34.9 ± 27.9pptv (7.5 ~95.9 pptv), respectively. The ambient concentrations of aromatic and natural VOCs were found at the pptv level. In this study, the toluene/benzene ratios were 13.9 ± 11.2, but they were a little higher than those found in the domestic study and approximately 5 times greater than the values in the foreign study. The β -/ α -pinene ratios ranged between 0.05 and 0.55, and this range was found to be similar in the foreign study.

Key words : NVOC, Ambient concentration, Benzene, Toluene, α -pinene.

1. Introduction

Numerous types of volatile organic compounds (VOCs) are emitted to the atmosphere from a variety of anthropogenic and natural sources[1)]. The major anthropogenic VOCs in urban areas are emitted from various industrial and/or transportation sources[2)]. VOCs emitted into the atmosphere contribute to the formation of photochemical oxidation and deterioration of ambient air quality. Several kinds of VOCs are harmful to human health as carcinogenic and toxic substances.

Recently, there has been increased interest in the potential environmental effects of global climatic change on the biogenic VOC emissions from trees, and in their impact on air quality and ozone formation[3~4)].

The fractional composition of ambient monoterpene levels from many forests around the world has been carefully examined. However, the study results about domestic ambient concentrations of monoterpene have seldom been reported.

In order to compare the characteristics of ambient VOC distribution between anthropogenic and biogenic VOCs, the concentration ratios of toluene/benzene (T/B), β -/α -pinene (β /α), and α -pinene/toluene (α /T) were investigated. Our results were compared with the previous ones presenting the ambient levels of aromatic and biogenic VOCs.

Corresponding Author ; Jo-Chun Kim, Department of Environmental Engineering, Konkuk University, Seoul 143-701, Korea
Phone : +82-2-450-4009
E-mail : jckim@konkuk.ac.kr

2. Experimental Methods

2.1 Sampling site and period

The sampling site of this study is located in Mt. Gumsung in Jeollanamdo province and is about 20km away from Gwangju city. The site is full of coniferous and deciduous trees and is not affected directly by VOC emission sources. An ambient air sample from *Cryptomeria japonica* forest was obtained in Jangsung. The sampling study was conducted from 12 July to 28 August, 2002, and was carried out during daytime from 09:20 to 17:20. The range of the mean temperature during the sampling period was 20.7~36.0℃, and the mean temperature was 27.8℃.

2.2 Sampling and analysis

The adsorbent traps were used for ambient VOC sampling at the field site. The tubes were prepared by filling a 0.45cm o.d.× 17.7cm long pyrex glass tube with Tenax TA (60/80 mesh, Supelco, USA) and Carbotrap (20/40mesh, Supelco, USA). An extensive performance test was carried out in a laboratory at the sampling conditions in order to see the precision and accuracy of performance of the sample traps for the chemicals of concern, so that 94.7%(± 4.5%, n=5) of recovery was obtained. Adsorbent trap sampling was carried out at a location above 1.5m from the ground, and the sampling flow rate and duration were 100ml/min and 4~9 hours, respectively.

The samples collected in the field were stored in a refrigerator until they were analyzed. The samples collected on cleaned sample traps were desorbed using the commercial automated thermal desorber (Aerotrap 6000, Tekmar, Cincinnati, OH), and GC/MSD (HP Model 6890/5973) was used for qualitative analysis. Aerotrap 6000 and GC/FID (HP Model 5890 Series II) system were used for quantitative analysis. Two HP-624 columns (60m× 0.53mm× 3 ㎛, 60m× 0.32mm× 1.8 ㎛) were used for two separate GCs. Sensitivities (below detection limit, 3 std. dev.) for GC/FID analyses were less than 0.39 ng for all the compounds concerned, and the overall precision (RSD) was estimated as 6.7 % during the analyses.

3. Results and Discussion

In this study, the characteristics of representative aromatic and natural VOC compounds ambient benzene, toluene, α –pinene, and β -pinene concentrations were investigated. The distribution of the ambient VOC concentration is seen in Table 1. The mean concentration of benzene was 62.6 ± 43.9pptv, and that of toluene was 619.8 ± 330.2pptv. The ambient concentrations of both benzene and toluene were found at the pptv levels. It is expected that the rural VOC concentration is different from those of urban areas.

The ambient concentrations of benzene and toluene in this study were compared with those of other cities (Table 3). Comparison between the ambient concentrations obtained from this rural city and other urban cities is difficult to do directly due to the several different factors such as sampling site, sampling periods, and ambient temperature. Compared with the ambient concentrations from other cities, those of benzene and toluene were relatively low. These suggest the distribution of VOC concentrations in the forest area is quite different from that of the urban area. A measurement study in a forest located in Hyytiala of Central Finland was very similar to this study. Their concentration of benzene was very close to our data of 87 (± 54) pptv, but the concentration of toluene showed a large difference with 55 (± 66) pptv.

The ambient VOC concentrations from *Cryptomeria japonica* are seen in Table 2. It was found that the concentrations of benzene and toluene in the rural areas were much lower than those found in the general urban area.

Table 1. A statistical summary of concentrations of aromatic and natural VOCs (Unit: pptv, n=13)

	Benzene	Toluene	α -pinene	β -pinene
Mean	62.6	619.8	169.0	34.9
S.D.	43.9	330.2	97.7	27.9
RSD (%)	70.2	53.3	57.8	80.1
Min	20.4	264.8	72.9	7.5
Max	151.2	1,386.2	396.1	95.9
Median	44.8	509.5	154.0	19.7

Table 2. Ambient concentrations of VOCs in the forest of *Cryptomeria japonica* (Unit: pptv)

	Benzene	Toluene	α -Pinene	β -Pinene
Site A	54.1	165.0	93.5	51.7
Site B	58.4	178.0	100.8	55.7
Site C	81.1	396.9	138.5	57.2
Site D	70.4	358.2	121.0	48.9

As a summary of our study, the α -pinene and β -pinene were measured at 169.0 ± 97.7 pptv and 34.9 ± 27.9 pptv, respectively. The mean concentration of α -pinene at the forest site in Finland was 104 ± 54 pptv (n=53), and that of β -pinene was reported as 25 ± 21 pptv (n=53). These results were similar to our study results. The concentration pattern of α -pinene was 177± 114 pptv in the slash pine forest (northern Florida, USA)[12], and that of β -pinene was 112± 73 pptv. Compared with their results, the α -pinene data was similar to ours, but the

β -pinene data was about 3 times higher than our values.

Table 3. Ambient VOC concentrations at various cities (Unit: ppbv)

	Benzene	Toluene	T/B ratio
Our study, 2002	0.06 (± 0.04)	0.62 (± 0.33)	13.9
Gwangju, 1999 [5]	0.35 (0.06~0.82)	2.72 (0.05~7.05)	7.8
Kwanghwamun, Seoul 1998[6]	1.1	10.6	9.6
Cheongyrang, Seoul 1998[7]	0.75	5.8	7.7
Taegu, 1999[8]	1.63 (± 0.71)	13.0 (± 12.8)	8.0
Hamburg, Osaka[9]	3.2	8.2	2.6
London[10]	1.1	2.2	2.0
Hyytiala Forest, Finland 2000-2002[11]	0.087 (± 0.054)	0.055 (± 0.066)	0.6

The comparison ratio of a specified substance, based on benzene, is used as a way for evaluating the degree which emission sources are the major influencing factor[6]. Toluene and benzene are emitted mainly from vehicles in a normal urban area. Toluene, especially, is a major solvent-related source, but benzene is not. The T/B ratio was observed to be as high as 13.9 ± 11.2. It can be inferred that the ambient air in this study might be affected by emission sources other than vehicles[8].

The β /α ratio was investigated as 0.23 ± 0.19 in this study, and the ratio from the study in Finland was similar to the results in this study as 0.24. For instance, β /α ratio from the slash pine forest in Northern Florida was about 2 times higher than the results of this study as 0.51 ± 0.09[12]. The α /T ratios indicating the ratio of representative aromatic and natural VOC were 0.31 ± 0.16.

4. Conclusions

The ambient concentrations of benzene, toluene, α- and β-pinene were measured at the Gumsung mountain site in Jeonnam province. The mean concentration of benzene of this study was 62.6 ± 43.9 pptv, and that of toluene was 619.8 ± 330.2pptv. It was observed that the concentrations of α -pinene and β -pinene were 169.0 ± 97.7 pptv and 34.9 ± 27.9 pptv, respectively. The ambient concentrations of aromatic and natural VOCs were found at the pptv level. In this study, the toluene/benzene ratios were 13.9 ± 11.2. However, although they were a little higher than those found in other domestic studies, they were approximately 5 times greater than the values in the foreign studies. The β /α ratios ranged between 0.05 and 0.55, and was found to be similar compared to the foreign studies.

References

1) Kesselmeier, J., U. Kuhn, A. Wolf, M.O. Andreae, P. Ciccioli, E. Brancaleoni, M. Frattoni, A. Guenther, J. Greenberg, P.C. Vasconcellos, T. 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.
2) Mayer, H., 1999, Air pollution in cities, Atmospheric Environment, 33, 4029-4037.
3) Guenther A., C.N. Hewitt, D. Erickson, R. Fall and C. Beron, 1995, A global model of natural volatile organic compound emissions. J. Geophys. Res. 98, 12609-12617.
4) Coeur C., V. Jacob and P. Foster, 1999, Aerosol formation from the gas-phase reaction of hydroxyl radical with the natural hydrocarbon bornyl acetate, Atmospheric Environment, 33, 1615-1620.
5) Lee, Y.J., D.Y. Shin, H.S. Lee, B.W. Kang and J.S. Han, 2001, Atmospheric concentrations of volatile organic compounds (VOC) of day/night periods during the summer season in Kwangju, J. Korean Society for Atmospheric Environment, 17(2), 169-177.
6) Na, K.S, Y.P. Kim and K.C. Moon, 2003, Diurnal characteristics of volatile organic compounds in the Seoul atmosphere, Atmospheric Environment, 37, 733-742.
7) Na, K.S. and Y.P. Kim, 2001, Seasonal characteristics of ambient volatile organic compounds in Seoul, Korea, Atmospheric Environment, 35, 2603-2614.
8) Kim, M.H., S.G. Park and S.O. Baek, 2002,

Characteristics of atmospheric concentrations of volatile organic compounds at a heavy-traffic site in a large urban area, J. Korean Society for Atmospheric Environment, 18(2), 113-126.
9) Derwent, R.G., T.J. Davies, M. Delaney, G.J. Dollard, R.A. Field, P. Dumitrean, P.D. Nason, B.M.R. Jones and S.A. Pepler, 2000, Analysis and interpretation of the continuous hourly monitoring data for 26 C2-C8 hydrocarbons at 12 United Kingdom sites during 1996, Atmospheric Environment, 34, 297-312.
10) Moschonas, N. and S. Glavas, 1996, C3-C6 Hydrocarbons in the atmosphere of Athens, Greece, Atmospheric Environment, 30, 2769-2772.
11) Hakola, H., V. Tarvainen, T. Laurila, V. Hiltunen, H. Hellen and P. Keronen, 2003, Seasonal variation of VOC concentrations above a boreal coniferous forest, Atmospheric Environment, 37, 1623-1634.
12) Kim, J.C and K.H. Kim, 2002, Sesonal variations of monoterpene concentrations in a pine forest in Florida, USA, J. Korean Society for Atmospheric Environment, 18(E3), 175-180.