Journal of Environmental Sciences Vol.17, No.1, pp.8—13, 2005

ISSN 1001—0742
CN11—2629/X

Article ID: 1001-0742(2005)01-0008-06 **CLC number**: X173; X511 **Document code**: A

Investigation of natural VOC emitted from tropical vegetations in China

WANG Zhi-hui[1], BAI Yu-hua[1,*], LIU Zhao-rong[1], WANG Xue-song[1], LI Qing-jun[2], L. F. Klinger[3]

(1. College of Environmental Sciences, Peking University, Beijing 100871, China. E-mail: yhbai@pku.edu.cn; 2. Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, Kunming 650223, China; 3. Institute of Noetic Sciences, 101 San Antonio Road, Petaluma, CA 94952, USA)

Abstract: Twenty-three kinds of typical plants in Xishuangbanna, the tropical area of southwestern China, were screened to estimate the emission rates of isoprene and monoterpenes by adopting bag-enclosure and curette sampling methods followed by a GC-FID analysis. It was found that the Ficus species were mainly emitting isoprene and most tropical vegetations were mainly releasing monoterpenes. The results also showed that the emissions of isoprene were affected by both temperature and PAR (Photosynthetic Active Radiation), while monoterpene emissions were mainly temperature-dependent.

Keywords: VOC; isoprene; monoterpenes; emission factor; Xishuangbanna

Introduction

Volatile organic compounds (VOCs) are emitted from the biosphere to the atmosphere (Guenther, 1995) and are involved in the photochemical formation of ozone in the troposphere (Fehsenfeld, 1992). Biogenic emission of VOCs is an important component of the earth system responsible for determining the composition of the atmosphere. Most living systems directly or indirectly exchange volatile chemical compounds with the atmosphere. Vegetation produces a wide variety of organic compounds, among which about 400 nonmethane hydrocarbons (NMHC) are more or less introduced into the troposphere (Graedel, 1979). Isoprene and monoterpenes are the most important compounds. Isoprene produced essentially by deciduous trees, while monoterpenes, produced principally by coniferous trees, are both of particular importance in atmospheric chemistry, due to the abundance of their emissions and to their high chemical reactivity. Indeed, due to the unsaturation of their structure, they are active reagents in tropospheric photochemistry.

Guenther *et al*. (Guenther, 1995) demonstrated that the biogenic emissions of VOC accounted for more than 90% global VOC emissions and forests were the main source of biogenic emission of 1150 Tg/a. This global model of hydrocarbon emissions from terrestrial ecosystem (Guenther, 1995) predicted isoprene emissions from tropical forests based upon an empirical understanding derived from studies of temperate zone plants and a single study that estimated isoprene emissions from a tropical moist forest outside of Manaus, Brazil (Zimmerman, 1988). These studies suggested that tropical regions are responsible for approximately 70% of the global emissions of isoprene, 350 Tg out of 500 Tg (Keller, 1999). Recent studies by Guenther *et al*. (Guenther, 1996) and Lerdau and Keller (Lerdau, 1997) extended the range of tropical ecosystems studied to include savannas and dry forest and found that the measured emission rates were similar to the ones estimated by the Guenther *et al*. (1995) model (Keller, 1999).

The most important changes are likely to be in tropical ecosystems for two reasons (Manuel, 2002). First, the high temperature and/or light conditions that are common to many tropical ecosystems, combined with the large number of VOC-emitting species, results in tropical forests contributing > 50% of total global VOC emissions. Second, these ecosystems are changing in both species composition and life form at a faster rate than any other ecosystem type (Manuel, 2002).

However, such reports in China especially in tropical area are limited. Annual woodland emissions are dominated by flux from the tropics which cover only 10.6% of the land surface but contribute 50% to the total annually emitted isoprene (Helas, 1997). It is very important to investigate the VOC emissions from tropical ecosystems, especially in the tropical area of China.

Twenty-three kinds of emission rate data from typical tropical vegetation types in Xishuangbanna have been investigated by using a bag-enclosure sampling method followed by GC-FID analysis. And the results of this study will be the potential implications for modeling and for VOC controls in tropical area of southwest of China. The results will also make us better understand the role of biogenic VOC in regional tropospheric chemistry.

1 Experimental

1.1 Study site description

Study sites were located in the tropical Xishuangbanna Tropical Botanical Garden, Yunnan Province, China. The Xishuangbanna Tropical Botanical Garden, the Chinese Academy of Sciences (CAS) is situated in Xishuangbanna Dai Autonomous Prefecture, Yunnan Province, at 101°25′E, 21°41′N, and 570 m altitude, with annual mean temperature of 21.4℃, annual precipitation of 1556 mm and mean relative

Foundation item: The National Natural Science Foundation of China (No. 40075027; 40375038); * Corresponding author humidity of 83%. In the area of 900 hm^2, approximately 8000 species of tropical plants introduced from home and abroad are cultivated in nearly 30 living plant collections (gardens), such as Palm Garden, Ficus Garden and the Ex Situ Conservation Area for Rare and Endangered Plants. Still having large areas covered by tropical rainforest, the Garden is an ideal place for studying tropical biology and ecology.

1.2 Trace gas sampling method

In this study, an enclosure technique was used by means of a polyethene bag with a diameter of 43 cm and a length of 80 cm, placed around a living branch. In the laboratory, dry weight of the leaves enclosed were obtained by placing in a drying oven for 24 h at 80℃ and weighing on an analytical balance. The air samples accumulated in the bag were pumped into a canister after a fixed interval and taken back to the laboratory for analysis. During the period of sampling, temperature and irradiation were also measured.

1.3 Analysis procedure

The samples were determined using a Varian 3400 GC-FID with a capillary column and temperature programming (from 0℃ for 5 min to 200℃ at 3℃/min) after being preconcentrated at −50℃ in a trap of the GC. The compounds in biogenic emissions were identified by matching of retention times in the GC-FID analysis, and confirmed by retention time and mass spectrum matching in the GC/MS analysis, which was performed by US EPA (Bai, 1995). Quantification methods were based on GC-FID peak area with n-pentane as standard sample (10.5 ppm, ± 2%). Calibrations of the instruments were carried out frequently with n-pentane and a series of liquid standard terpene sample, including α-pinene, β-pinene, careen, α-terpinene, camphene, limonene, and ociene. The calibration curves for pentane and terpenes showed the adequate precision. Good linearity for chromatographic calibration was obtained by means of the least squares method, which showed the performance of this apparatus and the reliability of measurements results.

1.4 The measurement of emission rate

The emission rate of the plants were measured in this program and calculated by the following equation:

$$\text{Emission rate } (\mu gC/(g \cdot h)) = 40.9 \times (C_i \times M \times V)/(W \times t).$$

Where 40.9 is the conversion factor from ppm to $\mu g/m^3$; C_i is the concentration(ppmC) increment of i species emitted by plant in the sampling bag; M is the molecular weight of i species(M = 68 for isoprene); V is the gas volume in the sampling bag (m^3); W is the dry weight of the leaves enclosed; t is the sampling time(h).

2 Results and discussion

2.1 Speciation of VOC emissions

According to the emission rates measured in our present study and G93 algorithm (Guenther, 1993; Wang, 2003), the standard emission factors of different vegetation species we investigated can be determined. Isoprene emission rates (I) were plotted against $C_L \times C_T$. A lineal fit can be made cross the origin, and the slope of the straight line is the standard emission factors of isoprene (I_s; Wang, 2003). The monoterpene emission rates (M) were plotted against exp [$\beta(T-Ts)$]. A lineal fit can also be made cross the origin, and the slope of the straight line is the standard emission factors of monoterpenes (M_{Ts}; Wang, 2003). The results of the emission rates identified in this study are listed in Table 1, which were sampled by means of static sampling method. The emission rates in Table 2 are collected from previous study (Klinger, 2002) for comparison with our results.

Table 1 The standard emissious rates of isoprene and monoterpenes from vegetation species in Xishuangbanna(μgC/(g·h); static sampling)

Genus spicies	N plots	Isoprene	Monoterpene
Pometia tomentosa	9	2.5 ± 1.1	3.9 ± 1.5
Chukrasia tabularis var. *velutina*	9	0.9 ± 0.1	5.9 ± 1.4
Ficus hispida	9	12.1 ± 2.3	2.5 ± 0.7
Paramichelia baillonii	9	0.1 ± 0.1	2.1 ± 0.7
Annona muricata	3	0.16 ± 0.03	1.7 ± 0.3
livistona sp.	3	0.2 ± 0.1	0.7 ± 0.1
Duabanga grandiflora	9	0.8 ± 0.3	3.1 ± 0.7
Macaranga denticulata	3	0.7 ± 0.3	0.4 ± 0.1
Ficus altissima	6	3.8 ± 2.4	1.0 ± 0.2
Parashorea chinensis	9	0.7 ± 0.2	3.3 ± 1.1
Vatica shishuangbannaensis	9	1.4 ± 0.6	0.9 ± 0.1
Mayodendron igneum	6	1.9 ± 0.3	3.9 ± 1.4
Citrus maxima	3	0	1.4 ± 0.1
Phoenix roebelenii	3	19.6 ± 5.4	1.8 ± 0.2
Horsfieldia pandurifolia	3	3.3 ± 1.4	3.3 ± 1.2
Bambusa vulgaris	3	2.7 ± 0.6	11.9 ± 0.7
Terminalia myriocarpa	6	0	1.0 ± 0.2
Lagerstroemia tomentosa	3	6.2 ± 2.3	9.1 ± 1.9
Ficus benjemina	3	9.4	0
Ficus religiosa	3	25	0
Ficus tinctoria var. *gibbosa*	3	127	0
Ficus virens var. *sublanceolata*	3	27	0
Hevea brassiliensis(61)	9	2.6 ± 0.8	15.6 ± 6.3
Hevea brassiliensis(71)	6	0.3 ± 0.1	6.6 ± 2.3
Hevea brassiliensis(81)	6	0.5 ± 0.1	9.6 ± 2.0
Hevea brassiliensis(91)	9	0.9 ± 0.4	6.5 ± 1.0

Fig.1 to Fig.4 show some of results of the regression method for isoprene and monoterpene emissions. Fig.1 and Fig.2 give the standard isoprene emission factors of *Pometia tomentosa* and *Mayodendron igneum*, respectively. Fig.3 and Fig.4 give the standard monoterpene emission factors of *Mayodendron igneum* and *Paramichelia baillonii* respectively.

Table 1 and Table 2 show the relation between the emission factors and the genus. *Ficus* is a genus including a large number of species with different isoprene emission rates. Of these species of *Ficus*, the isoprene emission factors of *Ficus tinctoria* var. *gibbosa* and *Ficus auriculata* are higher than 100 μgC/(g·h). However, the emission rate of *Ficus cyrtophylla* is only 0.06 μgC/(g·h). In regard to other tropical vegetation, most of them are low isoprene emitters. *Citrus maxima* and *Terminalia myriocarpa* do not emit isoprene. The isoprene emission factors of *Chukrasia tabularis* var. *velutina*, *Paramichelia baillonii*, *Annona muricata*, *livistona* sp., *Duabanga grandiflora*, *Macaranga denticulate*, *Hevea brassiliensis* and *Parashorea chinensis* are below 1 μgC/(g·h). The remaining species are also low isoprene emitters.

Table 2 The standard emissions rates of isoprene and monoterpenes from vegetation species in Xishuangbanna(μgC/(g·h); dynamic sampling)

Species	Isoprene	Monoterpenes
Ficus altissima	70	0.1
Ficus auriculata	139	0.32
Ficus callosa	84.7	0.03
Ficus cyrtophylla	0.06	0.25
Ficus elastica	14	0.1
Ficus fistulosa	54.3	0.01
Ficus hirta	70	0.1
Ficus hispida	29.9	0.04
Ficus langkokensis	29.7	0.00
Ficus microcarpa	1.41	0.68
Ficus racemosa	10.4	1.50
Ficus superba	70	0.1
Hevea brasielsis	0.17	20.4
Macaranga dendiofolia	0.04	0.07
Pometia tomentosa	0.20	3.89
Terminalia myriocarpa	0.02	0.18

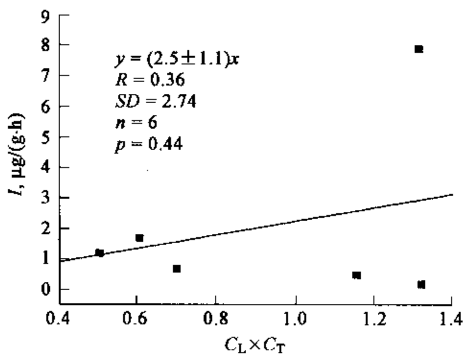

Fig. 1 Isoprene emissions from *Pometia tomentosa* plotted against $C_L \times C_T$

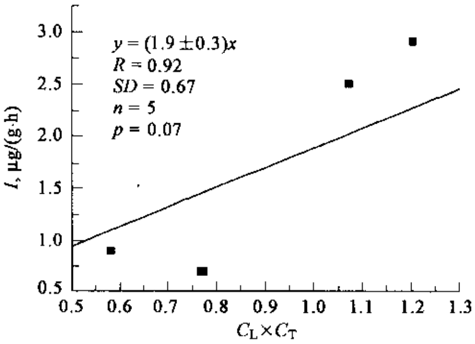

Fig. 2 Isoprene emissions from *Mayodendron igneum* plotted against $C_L \times C_T$

The most important monoterpene emitter is *Hevea brassiliensis*, which has a monoterpene emission rate of more than 10 μg C/(g·h), followed by *Bambusa vulgaris*. Most species of the Ficus have been proved to be no monoterpene emitters or low monoterpene emitting species. *Macaranga denticulata*, *livistona* sp. and *Vatica shishuangbannaensis* are three low monoterpene emitters, which have monoterpene emission factor lower than 1.0 μgC/(g·h). Most of the other vegetations are high monoterpene emitters.

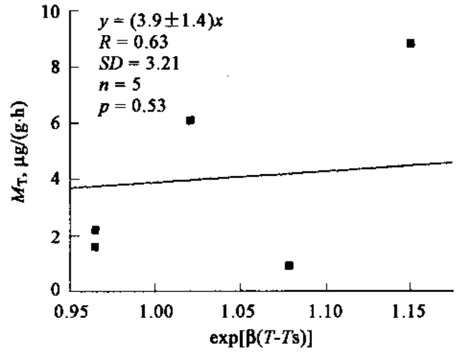

Fig. 3 Moneterpenes emissions from *Mayodendron igneum* plotted against exp[β(T-Ts)]

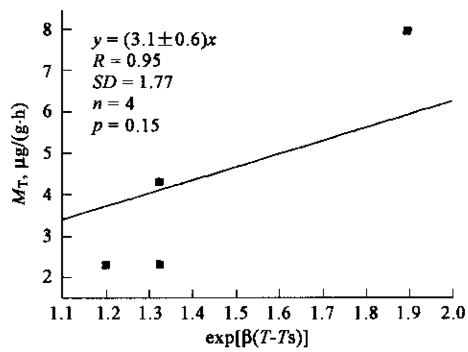

Fig. 4 Moneterpenes emissions from *Paramichelia baillonii* plotted against exp[β(T-Ts)]

2.2 Influence of environmental parameters on VOC emissions

Monson *et al*. (Monson, 1995) reported that the principal environmental variables that interact with basal isoprene emission rate to produce the instantaneous emission rate are temperature and light intensity(photo flux density). And temperature, humidity and diffusion resistance interact with pool size to determine the instantaneous monoterpene emission rate(Monson, 1995). In our present study, we only discuss the factors of temperature and light intensity that affect the instantaneous isoprene and monoterpene emission rates.

2.2.1 Isoprene emissions

Isoprene emissions are affected by both temperature and light intensity.

Fig. 5 and Fig. 6 show the isoprene emission rate increases with the higher temperature and stronger light intensity for *Hevea brassiliensis*. Fig. 7 and Fig. 8 show isoprene emission rate increases with the higher temperature and stronger light intensity for *Lagerstroemia tomentosa*. Actually, most of the results showed the isoprene emission rates increase when temperature and light intensity increase.

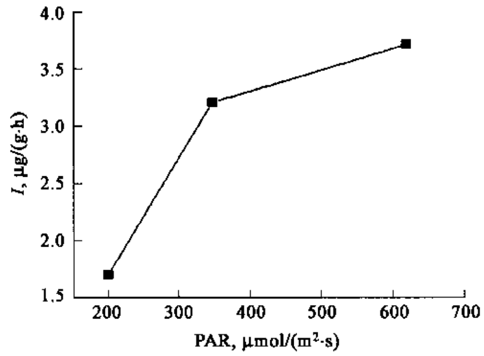

Fig.5 Isoprene emission rate PAR dependency for *Hevea brassiliensis*

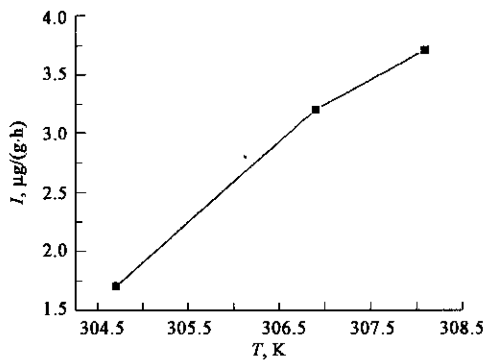

Fig.6 Isoprene emission rate temperature dependency for *Hevea brassiliensis*

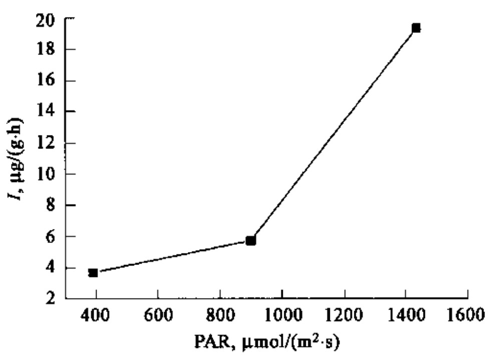

Fig. 7 Isoprene emission rate PAR dependency for *Lagerstroemia tomentosa*

2.2.2 Monoterpene emissions

Fig.9 to Fig.12 show the monoterpene emission rate is dependent by temperature for four vegetation species: *Hevea brassiliensis*, *Paramichelia baillonii*, *livistona* sp. and *Bambusa vulgaris*. When temperature increases, the monoterpene emission rate increases.

2.3 Seasonal variation of the emission rate of *Hevea brasiliensis* (H.B.K) Muell.-Arg

Due to the largely increased *Hevea brasiliensis* in Xishuangbanna, the man-made vegetation distributions in this area have been changed much. The VOC emissions of *Hevea brasiliensis* were investigated in this study in three different seasons. The results obtained in this investigation are listed

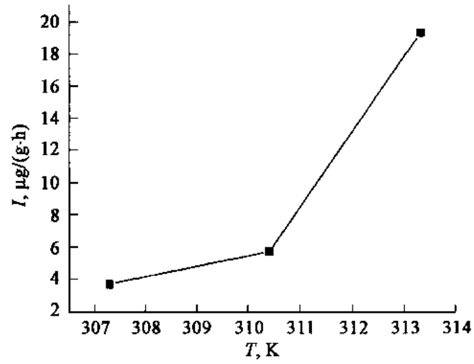

Fig.8 Isoprene emission rate temperature dependency for *Lagerstroemia tomentosa*

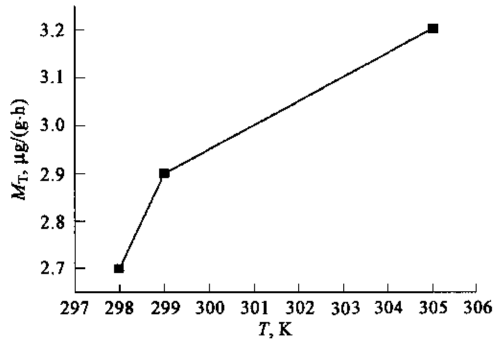

Fig.9 Monoterpene emission rate temperature dependency for *Hevea brassiliensis*

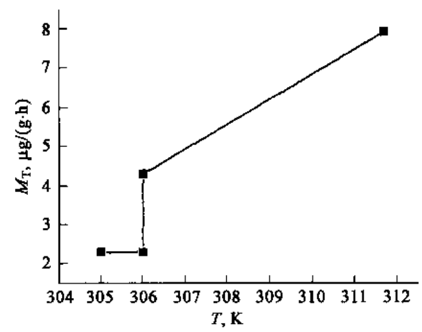

Fig.10 Monoterpene emission rate temperature dependency for *Paramichelia baillonii*

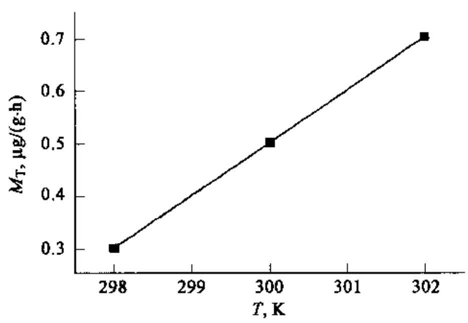

Fig. 11 Monoterpene emission rate temperature dependency for *livistona* sp.

in Table 3. Although the emission factors of *Hevea*

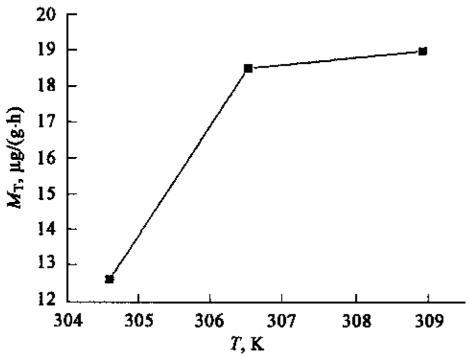

Fig. 12 Monoterpene emission rate temperature dependency for *Bambusa vulgaris*

brasiliensis having different ages are different, the trends of the emission factor in different seasons can be found. In August, the emissions of monoterpene are the highest, and then in May, and in January the emissions are the lowest.

Table 3 The emission rates of isoprene and monoterpenes from *Hevea brasiliensis*

Date	Age/a	N /Plots	Ef., μgC/(g·h)	
			Isoprene	Monoterpenes
2001 - 08	40	1*	0.5	14.8
	30	1*	0.2	9.9
	20	1*	0.3	46.2
	10	1*	0.3	6.7
2002 - 01	40	3	1.0 ± 0.4	2.6 ± 1.6
	30	6	0.3 ± 0.2	1.9 ± 0.8
	20	6	0.5 ± 0.1	2.1 ± 0.6
	10	3	0	8.7 ± 0.5
2002 - 05	40	3	2.7 ± 0.2	26 ± 7.2
	30	3	0.3 ± 0.2	9.1 ± 4.8
	20	3	0.4 ± 0.3	15 ± 3.4
	10	3	1.3 ± 0.6	4.6 ± 1.0

Note: * Dynamic sampling method followed by GC-MS analysis

2.4 Comparison of the static sampling method and dynamic sampling method

Some species were investigated by dynamic sampling method(Table 2) using a CID CI-300. The results of the static sampling method and dynamic sampling method can be compared(Table 4).

The comparison of Table 4 presents the emission factors of the same species by different sampling methods (static sampling method and dynamic sampling method). The results proved that the emission factors identified by this study and Dr. Klinger are very similar(Klinger, 2002).

3 Conclusions

Twenty-three kinds of emission rate data of the typical tropical vegetation types of Xishuangbanna have been identified for emission factors of isoprene and monoterpenes in this study. *Ficus* is a genus including a large number of species with different isoprene emission rates. And most species of *Ficus* are not emitting monterpenes . Most of the

Table 4 Comparison of the results of static sampling method and dynamic sampling method

Species	Dynamic sampling, μgC/(g·h)		Static sampling, μgC/(g·h)	
	Isoprene	Monoterpene	Isoprene	Monoterpene
Hevea brasielsis (61)	0.17	20.4	2.6 ± 0.8	15.6 ± 6.3
Ficus altissima	70	0.1	3.8 ± 2.4	1.0 ± 0.2
Ficus hispida	29.9	0.04	12.1	2.5
Macaranga dendiofolia	0.04	0.07	0	0.1
Pometia tomentosa	0.20	3.89	0	2.3
Terminalia myriocarpa	0.02	0.18	< 0.1	0.4

remaining tropical vegetations are also low isoprene emitters. The isoprene emission factors of *Chukrasia tabularis* var. *velutina*, *Paramichelia baillonii*, *Annona muricata*, *livistona* sp., *Duabanga grandiflora*, *Macaranga denticulate*, *Hevea brassiliensis* and *Parashorea chinensis* are below 1 μgC/(g·h). Most of the other vegetations are high monoterpene emitters. The emissions of monoterpene from *Hevea brassiliensis* have a seasonal variation. The results proved that the emission factors identified by static sampling method and dynamic sampling method are very similar. The results will be of great help for us to understand the biogenic VOC emission patterns in tropical area of China.

Acknowledgements: The authors wish to thank the staff of the Xishuangbanna Tropical Botanical Garden, and some scientists of NCAR, who arranged and greatly facilitated this research collaboration. For field, technical, and logistical assistance we especially thank Deng Xiaobao, Wang Yongfeng, Zhao Chongjiang and Wang Hong.

References:

Bai Y H, Li J L, Zhang B X *et al*., 1994. The quanlitative of determination of hydrocarbon emitted from woods and vegetations over Beijing area[J]. Journal of Environmental Sciences Research, 7(2): 48—54.

Bai Y H, Li J L, Liang B S *et al*., 1995. IUPAC[J]. Pure and Applied Chemistry, 67: 1415—1419.

Benjamin M T, Winer A M, 1998. Estimating the ozone-forming potential of urban trees and shrubs[J]. Atmospheric Environment, 32: 53—68.

Fehsenfeld F *et al*., 1992. Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry [J]. Global Biogeochem Cycles, 6: 389—430.

Graedel T E, 1979. Chemical compounds in the atmosphere[M]. New York: Academic Press.

Guenther A, Zimmerman P, Harley P *et al*., 1993. Isoprene and monoterpene emission rate variability: Model evaluation and sensitivity analysis[J]. Journal of Geophysical Research, 98: 12609—12617.

Guenther A, Zimmerman P, Wildermuth M, 1994. Natural volatile organic compound emission rate estimates for U.S woodland and landscapes[J]. Atmospheric Environment, 28: 1197—1210.

Guenther A, Hewitt C N, Erickson D *et al*., 1995. A global model of natural volatile organic compound emissions[J]. Journal of Geophysical Research, 100: 8873—8892.

Guenther A, Greenberg J, Harley P *et al*., 1996. Leaf, branch, stand and landscape scale measurements of volatile organic compound fluxes from U.S. woodlands[J]. Tree Physiology, 16: 17—24.

Harley P, Guenther A, Zimmerman P, 1997. Environmental controls over isoprene emission in deciduous oak canopies[J]. Tree Physiol, 17: 705—714.

Helas G, Slanina S, Steinbrecher R, 1997. Biogenic volatile organic compounds in the atmosphere[M]. Amsterdam: SPB Academic Publishing.

Helmig D, Klinger L, Guenther A *et al.*, 1999. Biogenic volatile organic compound emissions, I. Identifications from three continental sites in the U.S.[J]. Chemosphere, 38: 2163—2187.

Keller M, Lerdau M, 1999. Isoprene emission from tropical forest canopy leaves [J]. Global Biogeochemical Cycles, 13(1): 19—29.

Klinger L F, Li Q J, Guenther A B *et al.*, 2002. Assessment of volatile organic compound emissions from ecosystems of China[J]. Journal of Geophysical Research, 107(D21): 4603—4624.

König G, Brunda M, Puxbanm H *et al.*, 1995. Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected mid-European agriculture and natural plant species[J]. Atmospheric Environment, 29: 861—874.

Lerdau M, Keller M, 1997. Controls on isoprene emission from trees in a subtropical dry forest[J]. Plant Cell Environ, 20: 569—578.

Li J L, Bai Y H, Hu J X *et al.*, 1994. Diurnal variation in the concentration of terpenes and it's emission rate measurements from oil pine[J]. Chinese Environmental Sciences, 14(3): 165—169.

Manuel Lerdau, Lawrence Slobodkin, 2002. Trace gas emissions and species-dependent ecosysytem services[J]. Trends in Ecology & Evolution, 17(7): 309—312.

Monson R K, Lerdau M T, Sharkey T D *et al.*, 1995. Biological aspects of constructing volatile organic compound emission inventories[J]. Atmospheric Environment, 29: 2989—3002.

Simpson D, Winiwarter W, Börjesson G *et al.*, 1999. Inventorying emissions from nature in Europe[J]. Journal of Geophysical Research, 104: 8113—8152.

Wang Z H, Zhang S Y, Lu S H *et al.*, 2003. Screenings of 23 plant species in Beijing for volatile organic compound emissions[J]. Environmental Sciences, 24(2): 7—12.

Zimmerman P, Greenberg, Westberg C, 1988. Measurement of atmospheric hydrocarbons and biogenic emission fluxes in the Amazon boundary layer[J]. J Geophys Res, 93: 1407—1416.

(Received for review February 23, 2004. Accepted April 30, 2004)

Introduction to author's research group

The research group is in the Department of Environmental Sciences of Peking University. In recent years it involves air pollution and atmospheric chemistry, as well as laboratory and field studies. Many kinds of fundings have been granted, including National Sciences Funding and UNDP etc. Below are some specific programs:

Biogenic volatile organic compounds emissions

Emission factors of more than 50 kinds of vegetations in China and influence of environmental parameters on VOC emissions have been investigated. Based on these results and the bioorganic VOC emission algorithm of A. Guenther, the BVOC emission inventory for different areas in China can be presented.

Indoor pollution and indoor air quality

Field and laboratory studies on indoor pollution have been conducted in the campus of Peking University and the satellite base of Chinese Ministry of Aviation in Shanxi. In present, the group is participating in a UNDP project "the evaluation and controlling strategies on indoor air pollution in Guiyang".

Air quality modeling

Using air quality modeling, the quantity of the primary pollutants including SO_2, PM_{10} and NOx, as well as the secondary pollutants including ozone and acid rain etc. was investigated by the group.

Developing the displaying system of pollutant sources and concentrations

Combined with GIS and some database, the field measurements and simulation results of wind field, distribution of pollutants and variations of pollutant concentrations vs. time in an appointed area can be displayed.