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Analyzing Method on Biogenic Volatile Organic Compounds^①

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ABSTRACT

In order to analyze biogenic volatile organic compounds in the atmosphere, an automated gas chromatography is developed and employed at the laboratory of National Center for Atmospheric Research (NCAR) during January to July, 2000. A small refrigerator was used so as to remove water in the air sample from gas line, and get accurate concentrations of volatile organic compounds. At 5°C, good water removing efficiency can be obtained at controlled flow rate. Air samples were collected around the building of Mesa Lab. of NCAR and analyzed by this gas chromatography system. This paper reports this gas chromatography system and results of air samples. The experimental results show that this gas chromatography system has a good reproducibility and stability, and main interesting volatile organic compounds such as isoprene, monoterpenes have an evident diurnal variation.

Key words: Volatile organic compound, Gas chromatography, Isoprene, Terpene

1. Introduction

The chemical composition of the atmosphere is an important component of the global environment and observed trends in trace gas concentrations demonstrate that it is changing rapidly (Brasseur et al., 1998). Numerical atmospheric chemistry models have demonstrated that concentrations of ozone and other oxidants in the troposphere are sensitive to both biogenic and anthropogenic Volatile Organic Compounds (VOCs) concentrations (Chameides et al., 1988). The biogenic emission of isoprene plays an important role in atmospheric chemistry. Isoprene oxidation can influence the concentrations of OH and ozone, the production of CO, the formation of organic acids and the photochemical conversion of NO_y species, therefore, isoprene emission may indirectly impact climate (Guenther et al., 1999).

The model predicted that over 90% of the global annual nonmethane VOCs emission, to which isoprene contributes about half is produced by vegetation (Guenther et al., 1995). Guenther et al. (1995) estimated that the global total biogenic VOCs emission of about 1150×10^{12} grams (Tg) per year is more than seven times greater than the global total anthropogenic VOCs emission. Therefore, accurate estimates of both biogenic and anthropogenic VOCs emission rates are important components of the numerical studies that provide the basis of global change scenarios and regulatory emission control strategies

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(Guenther et al., 1994).

Some studies show that methanol, acetone, 2-methyl-3-butene-2-ol (MBO) to be the most abundant biogenic VOCs (Goldan et al., 1995; MacDonald and Fall, 1993a, Nemecek-Marshall et al., 1995; MacDonald and Fall, 1993b; Harley et al., 1998). Compared to methanol and acetone, MBO is more reactive and could lead to regional ozone production. MBO could also be a significant source of acetone in the troposphere due to its reaction with OH radical, and acetone photolysis may be a major source of HO_x radicals in the upper troposphere (Singh et al., 1995). There are more and more interesting work in biogenic emission of oxygenated volatile organic compounds (OVOCs) to the atmosphere, but it is unclear what the importance of those compounds is in the atmosphere, particularly with respect to tropospheric ozone production (Baker et al., 1999).

Due to the large diversion of chemical and plant species, the characteristics of biogenic VOCs sources are complex. The composition and quantities of more than 40000 VOCs found within plant cells vary greatly among the hundreds of thousands of plant species (Harborne, 1991). The investigations of foliar VOCs emissions have focused on dominant hydrocarbon compounds emitted, the hemiterpene (C₅) isoprene and several monoterpenes (C₁₀), and on the dominant trees of temperate forests (Guenther et al., 1994).

Chinese scientists have done some work in VOCs (Bai et al., 1995, Li et al., 1994, Shao et al., 1994, Xu et al., 1996, Bai et al., 1998), but lots of important work needs to be carried out and improved, such as analyzing technique and methods, and automated gas chromatography system for VOCs, systemic observation on VOCs emitted from different ecosystems. This paper reports an automated gas chromatography system, which is small and easy to be operated in field experiments.

2. Instrumental system

The Gas Chromatography (GC) system can be divided into the following parts: 1) Dilution system: 2 Tylan Mass Flow Meters are used to control the flow rates of standard gas and zero air respectively, a vacuum pump is connected at the end of gas line to drive the air flow. The dilution system is housed in a sealed box with constant temperature, and it can dilute the standard gas to desired concentration based on dilution ratio. Then the diluted standard gas is collected accurately in the sample loop. The collecting flow rate and volume are determined by the third Tylan mass flow meter. 2) Mixing system: standard gas, zero air and air sample are mixed well in a mixing cylinder with a certain volume. 3) The water removing system: before air sample going into the column of gas chromatography, the water must be removed, because the water or water vapor can influence the accuracy of VOCs concentration. In order to obtain low temperature, making a certain length of gas line pass a small refrigerator, the temperature of refrigerator is set and controlled by computer, thermocouple, heater, and temperature controlling circuit. By controlling of gas flow rate and temperature, better water removing efficiency can be obtained. The experiment was carried out at the Mesa Lab. of National Center for Atmospheric Research (NCAR), the results at different temperature show that the best water removing efficiency was obtained at the temperature of 5°C. The standard gases of VOCs, including isoprene, mixed with water vapor of 100% relative humidity, passed this system, then were separated by the analytical column of gas chromatography, and their concentrations kept constant. 4) Injection system: it consists of cartridge, valves (one 4-port valve, two 6-port valves), sample loop, relays, controlling circuit, mass flow meters and pump. After the injecting program was set and stored in the computer, the injecting work is

controlled and operated by computer automatically. The purpose of this system is to collect a certain volume of air sample in the sample loops, so as to make it be detected easily by flame ionization detector (FID). The specific steps are as follows: A. absorption: A certain volume air sample went through the first 4-port valve to the cartridge vacuumed by a pump at the end of gas line, and was trapped in the cartridge packed with absorbents of carbo-sive and carbotrap that absorb light and heavy hydrocarbons. B. Desorption: heating the cartridge to 275°C, keeping it for a period. Heater, thermocouple, controlling part of temperature and computer, carried out this function. In the meantime of desorption, through the turns of another two 6-port valves, the air sample was transferred and then cryofocused into the sample loop immersed in liquid nitrogen dewar. C. Rapid heating the sample loop to 100°C in 15 seconds, keeping it for a period. In the meantime, through the turns of 6-port valve, the air sample can be carried into analytical column of GC by carrier gas and be separated by the column. 5) Analyzing and recording system: the retention time and peak area of compounds separated by the analytical column are stored in integrator and computer.

The analytical column is DB-624 capillary column, 60 m × 0.250 mm I.D., gas chromatography is GC-8A model, flame ionization detector gas chromatography. The temperature program for analytical column is: keep 40°C for 2 minutes, then increase temperature to 180°C in 10 minutes and keep it for 8 minutes. The carrier gas flow rate of Helium is 1 mL / minute, transfer and backflush flow rate of Helium is 10 mL / minute, and makeup gas flow rate of Helium is 20 mL / minute. The flow rate of hydrogen and air is 50 and 500 mL / minute, respectively.

The whole analyzing time for one run is about 1 hour including the collection of air sample. In order to get better analyzing result of VOCs, the gas line after mixing system and before analytical column of GC was heated by heating line.

The identification and quantification for all compounds separated from analytical column were determined by retention time, retention index and peak area of standard gas. Most standard gases in our experiments made by the Lab. of NCAR, some are Scott speciality gases.

When air sample went into analytical column, the computer controlled the turns of all the valves, and made helium back flush the whole gas line including the system of removing water at a certain flow rate. Figure 1 shows the whole structure of this system.

Firstly, taking the experiment of removing water as an example for the performance of this GC system. The result for removing water is given briefly. The VOCs standard gas was diluted by zero air controlled by a certain dilution ratio through two mass flow meters, then passed mixing system, the system of removing water, injecting system, gas chromatography,

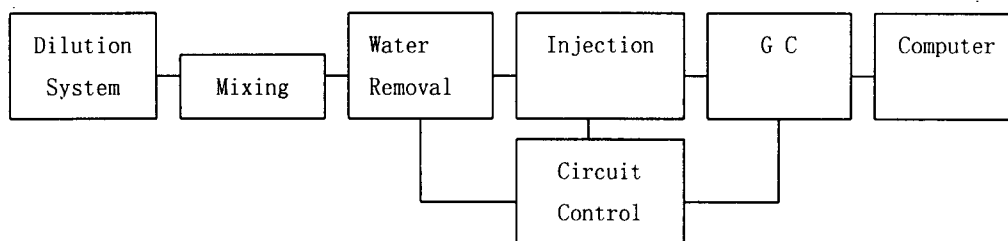


Fig. 1. The whole structure of GC system.

at finally, the concentration of VOCs can be obtained from integrator and computer. There are two conditions in the zero air line: 1) connected a bubbler with pure water, which can produce 100% relative humidity water vapor, 2) removed bubbler from zero air line. In the same condition of injecting volume, the temperature of small refrigerator changed between -15°C and 25°C , the concentrations of VOCs between with water and without water changed. But, at 5°C , the relative deviation between these two conditions is the smallest. One experimental result at 5°C on April 5, 2000 is given here: taking isoprene as a sample, the peak areas of standard gas without water for 4 runs are 216158, 224317, 213099, 215729, respectively, the average value is 217326; the peak areas of standard gas with water for 2 runs are 217103, 214660. The relative deviation of peak areas between these 2 runs and the average of 4 standard runs without water are 0.10% and 1.23%, respectively. At the same day, the peak areas of standard gas with water at 0°C for another 2 runs are 178397 and 174257, the relative deviation of peak areas between these 2 runs and the average of 4 runs are 17.9% and 19.8%, respectively. The similar results of other VOCs standard gases were also obtained, the difference is that there is a larger relative deviation for other VOCs compared to isoprene. For example, at 5° , the experimental results of standard gases for acetaldehyde, methanol, acetone, methylethylketone (MEK), α -pinene with water and without water displayed that the relative deviation is less than $\pm 10\%$ for most of them, but less than $\pm 15\%$ for acetaldehyde and methanol.

Based on the results of peak areas of isoprene and other VOCs standard gases at different temperature and different conditions (with water and without water), the reproducibility and performance for this GC system are stable and reliable.

A lot of experiments were made for different kinds of VOCs standards and different plants cultivated in the Mesa Lab. of NCAR, good results were also obtained. Two experiment results are reported bellow. First, VOCs standard gases ① are acetaldehyde, methanol, isoprene, acetone, 2-methyl-3-butene-2-ol (MBO), α -pinene, their concentrations are 5.3 ppm (mixing ratio, 10^{-6}), the dilution rate for standard gases is $1/60$. Table 1 shows the analyzing results for three runs, including retention time (RT), peak area (PA), peak area average for three runs (PA avg.), relative biases (δ) for three runs.

Table 1. The analyzing results of VOCs standard gases ① by GC system

	Runs	acetaldehyde	methanol	isoprene	acetone	MBO	α -pinene
RT (minutes)	1	3.557	3.750	4.770	5.140	7.417	13.017
	2	3.550	3.740	4.757	5.120	7.397	13.013
	3	3.567	3.750	4.777	5.140	7.420	13.027
PA	1	33021	27384	242212	91861	216995	487881
	2	28989	25414	233322	90267	214897	483773
	3	30579	25977	234969	90992	215392	481873
PA avg.		30863	26258	236834	91040	215761	484509
$\delta(\%)$	1	6.9	4.3	2.3	0.9	0.6	0.7
	2	-6.1	-3.2	-1.5	-0.8	-0.4	-0.2
	3	-0.9	-1.1	-0.8	-0.1	-0.2	-0.6

It can be seen that retention time and peak area have good reproducibility and stability. The relative biases of peak area for different components are very small, less than 3%, apart from acetaldehyde and methanol.

Second, VOCs standard gases ② are *n*-butane (3 ppm), isoprene (3 ppm), methanol (10 ppm), acetaldehyde (10 ppm), acetone (10 ppm), ethanol (5 ppm), 1-butanol (5 ppm), methylethylketone (MEK) (5 ppm), methacrolein (MACR) (5 ppm), butanal (4 ppm), the dilution rate for standard gases ② is also 1 / 60. Table 2 shows the analyzing results for three runs.

Table 2. The analyzing results of VOCs standard gases ② by GC system

		<i>n</i> -butane	acetaldehyde	methanol	ethanol	isoprene	acetone	MACR	butanal	MEK	1-butanol
RT	1	3.367	3.57	3.767	4.68	4.800	5.183	6.417	6.90	7.147	8.65
	2	3.360	3.56	3.757	4.66	4.777	5.167	6.403	6.89	7.147	8.68
	3	3.356	3.55	3.757	4.66	4.777	5.160	6.390	6.86	7.120	8.62
PA	1	118302	79971	47429	32250	150981	149893	100565	75818	95934	88339
	2	120680	80703	47718	28769	147702	145715	105709	76009	91333	85275
	3	116939	80967	47710	32415	151129	156249	111174	81732	101605	90054
PA avg.		118640	80547	47619	31145	149937	150619	105816	77853	96291	87889
δ (%)	1	-0.3	-0.7	-0.4	3.6	0.7	-0.5	-4.9	-2.6	-0.4	0.5
	2	1.7	0.2	0.2	-7.6	-1.5	-3.3	-0.1	-2.4	-5.2	-3.0
	3	-1.4	0.5	0.2	4.1	0.8	3.7	5.1	4.9	5.6	2.5

It can also be seen that retention time and peak area of most components display a good stability and reproducibility. Although those two VOCs standard gases were analyzed on different days, the retention time is more stable, for example, isoprene and acetone. So, this GC system is qualified for measuring VOCs in the future.

3. Collecting and analyzing air sample

In order to test the performance of this GC system and know the variety regularity and concentration for those plants around the Mesa Lab. of NCAR, the air sample was collected and analyzed. The results of this experiment are reported here.

The Mesa Lab. of NCAR is located on the top of Table Mesa, Boulder, various kinds of plants and grass grow on the top and at the bottom of this mountain. The sampling site 1 was selected in pine's area on the top of Table Mesa, the sampling site 2 was selected on the top of building of Mesa Lab.. Sampling tools are cartridge and 500 mL syringe, 2 liters air sample was collected into cartridge by using a syringe at a controlled flow rate. The samples were analyzed by the GC system in the Lab. of NCAR, otherwise, it must be kept in the refrigerator.

The concentrations of 29 VOCs from C₂ to C₁₁ (carbon atom number) were obtained. The concentrations and their daily variation of main interesting VOCs are investigated. The main VOCs in which we are interested are acetaldehyde, methanol, ethanol, isoprene, acetone, methacrolein (MACR), methylethylketone (MEK), 2-methyl-3-buten-ol (MBO), butanol, α -pinene, β -pinene, limonene, camphene, γ -terpene, myrcene.

Isoprene and monoterpenes including α -pinene, β -pinene, Limonene, Camphene, γ -terpene, Myrcene are important hydrocarbons emitted from plants. Apart from the monoterpenes, other VOCs such as MBO, MEK, MACR listed above also have important influences on tropospheric ozone and OH radical. So, we also show analyzing results of those VOCs in this paper.

Figures 2 and 3 show the diurnal variations of main VOCs at site 1 on June 19 and site 2 on June 29, respectively.

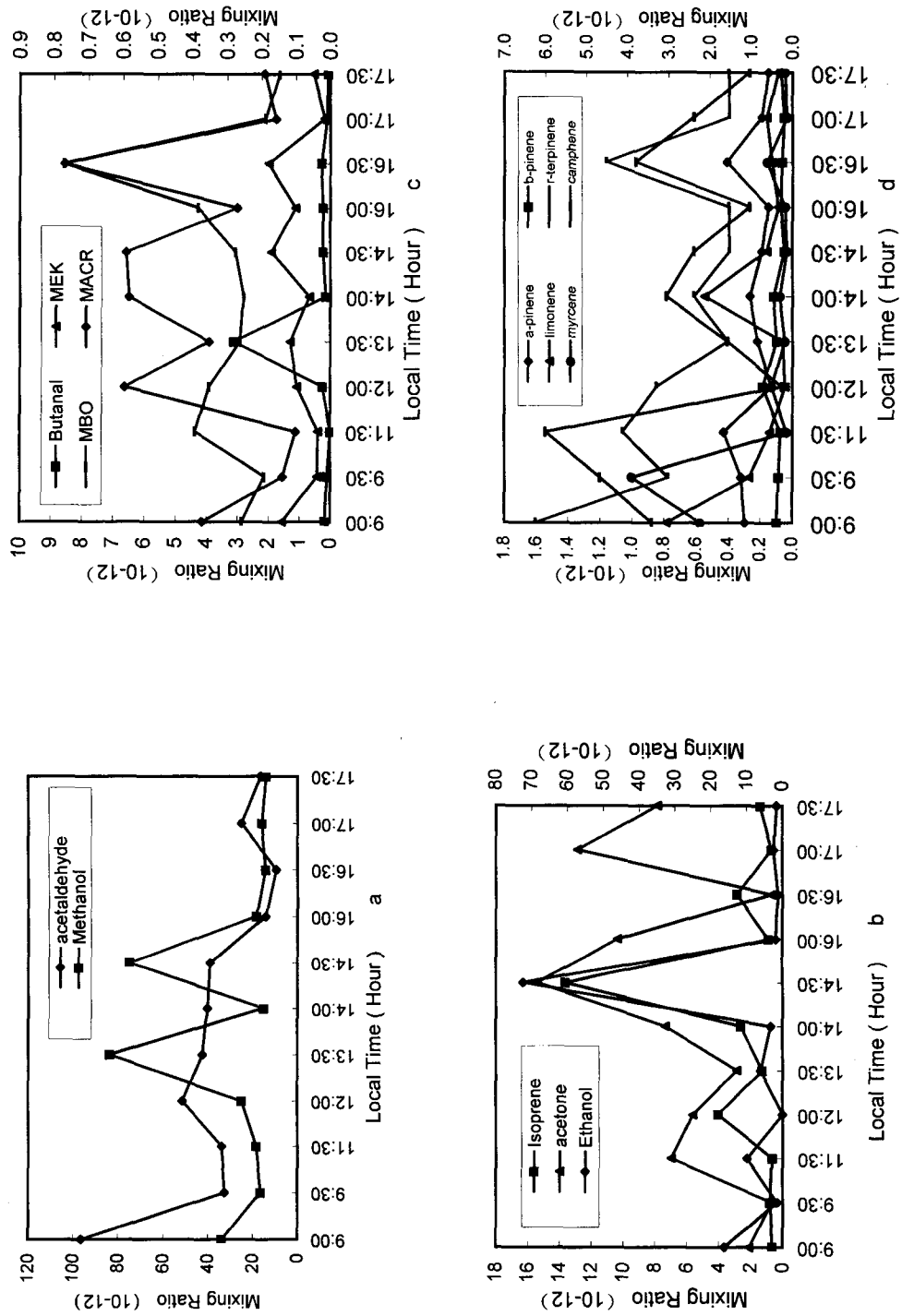


Fig. 2. Diurnal variation of volatile organic compounds.

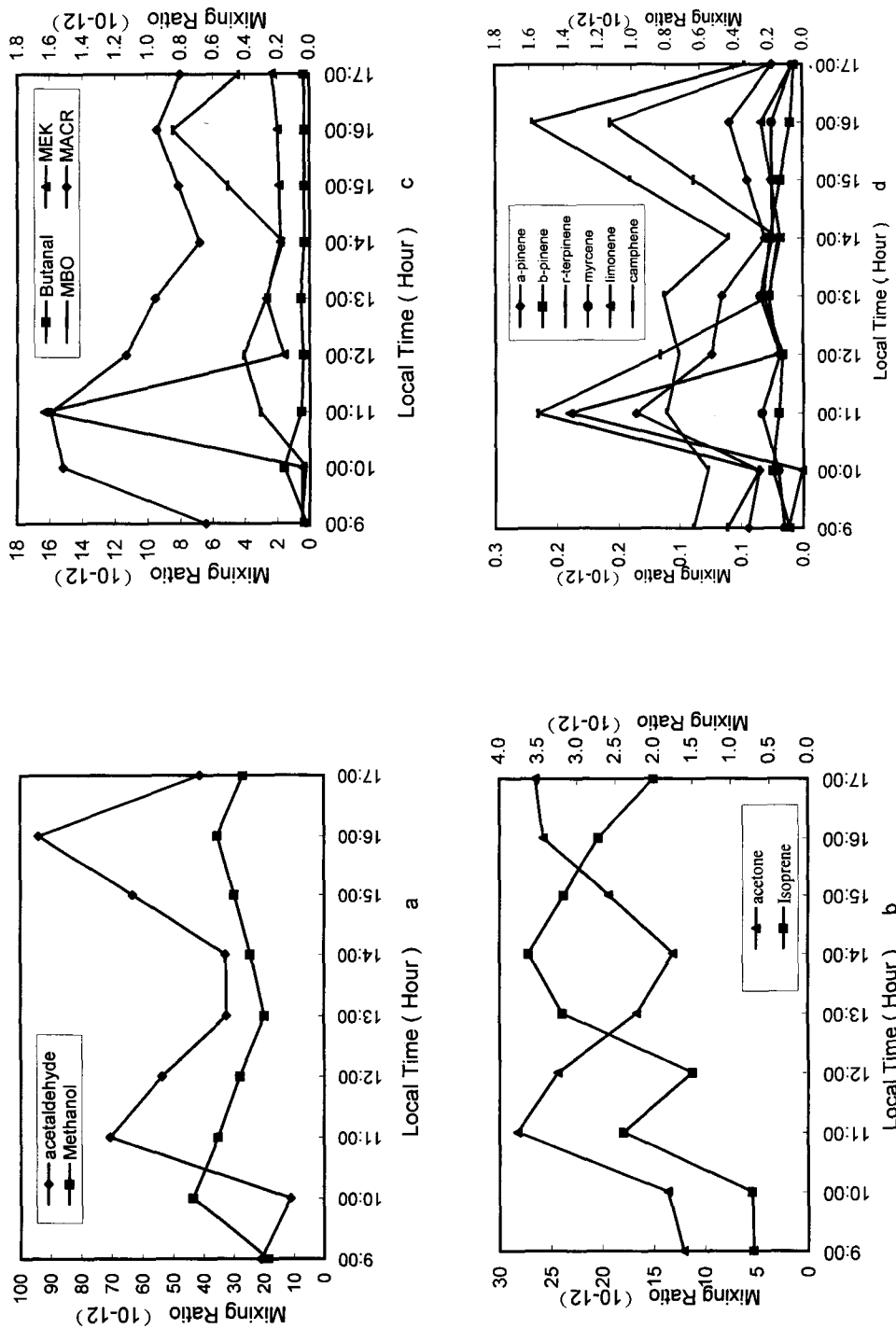


Fig. 3. Diurnal variation of volatile organic compounds.

It can be seen from Figs. 2 and 3 that most VOCs display evident diurnal variation. Figure 2 gives the result of air sample on site 1. June 19 was a cloudy and windy day, and the wind direction was not stable. Most VOCs show a maximum around noon at about 11:30–12:00, 14:00–14:30 and mid-afternoon at 16:30, monoterpenes show the similar variation regularity. Isoprene displays a maximum at 14:30, MBO and acetone give the same phase variation before noon and opposite phase variation after noon in general.

June 29 was a clear, breeze day, cloudiness was less than 3 for the whole day, and the wind direction was not stable. Most VOCs show a maximum at 11:00 or 16:30. Monoterpenes also show the similar variation regularity, which means the characteristics of their emission, physical and chemical process in the troposphere are similar. Isoprene displays a maximum at 14:00, similar to that of June 19. This phenomenon indicates that isoprene has high correlation with air temperature (Bai et al., 1995; Jobson et al., 1994; Bai et al., 1998). MBO and acetone show the same phase variation, their correlation coefficient is 0.71.

Under clear and cloudy conditions, diurnal variations of MBO and acetone display evident difference, because there is a large difference of solar actinic radiation. In fact, the regularity of photochemical reactions in the clear sky condition is more representative. The most important thing is that the concentrations and emission rate of VOCs are related to the photosynthetically active radiation, temperature and other parameters, so, more detailed experiment is needed.

4. Conclusions

The study on VOCs should be focused on the synthetic researches: 1) To accurately measure the emission rate for typical plants which have great quantity, and the concentrations of VOCs in the atmosphere; to study and determine the key controlling factors in VOCs emission processes; 2) To study physical, chemical and photochemical characteristics of VOCs in the laboratory; 3) To develop regional and global model including new findings of VOCs in laboratory and field experiments. Only in this way, the roles that VOCs play in the processes of atmospheric physics, atmospheric chemistry and atmospheric photochemistry can be determined and simulated accurately.

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植物挥发性有机物的分析方法

白建辉 王明星 胡非

摘 要

为了分析植物排放到大气中的挥发性有机物,在2000年1–6月期间,与美国国家大气研究中心(NCAR)的科学家共同发展和研究了一套自动的气相色谱系统和分析方法。该系统引入一个小型冰箱以除去空气样品进样时的水分,得到了对挥发性有机物样品进行分析时比较好的准确度。在5℃以及稳定的进样速率的条件下,可以得到比较好的除水效果。对NCAR附近的大气进行了采样,并利用此系统做了分析。本文简单介绍此自动系统以及样品分析结果。实验结果表明,此套系统具有良好的重复性和稳定性,主要的挥发性有机物的成分如异戊二烯和单萜烯等具有明显的日变化。

关键词: 挥发性有机物,气相色谱仪,异戊二烯,萜烯