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Biogenic volatile organic compounds (BVOC) in ambient air over Hong Kong: analytical methodology and field measurement

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In this paper, an analytical method using a simple semi-manual cryo-trap technique coupled to gas chromatograph with flame ionisation detector (GC-FID) was developed for the determination of biogenic volatile organic compounds (BVOC) in ambient air. Five common BVOC species have been tested, including isoprene and 4 monoterpenes, i.e. α -pinene, β -pinene, 3-carene (Δ) and limonene. The detection limits were estimated to be about 20 ppt for isoprene and 10 ppt for monoterpenes, with sample injection volume of 50 μ L. Based on vegetation types, field measurement work was conducted over urban and rural sites of Hong Kong during summer and winter of 2007. Canister sampling technique was applied in the field measurement. Isoprene contents in rural ambient air were found to be in the range of 60–1560 ppt in winter and 260–3270 ppt in summer, respectively. However, in the measurement of monoterpenes, due to their extremely low concentration in the air samples, only β -pinene and limonene were detected by the developed analytical method.

Keywords: biogenic volatile organic compounds (BVOC); cryo-trap; GC-FID; ambient air; Hong Kong

1. Introduction

Photochemical smog which is a serious health hazard, especially in urban areas with hot and sunny climates is known to be greatly influenced by volatile organic compounds (VOCs). Vegetation emits large quantities of biogenic VOCs (BVOCs), and estimates for the United States have been reported at 30,860,000 tons of BVOC per year [1]. This is comparable to estimates of 21,090,000 tons of anthropogenic sources in 1990 [2]. Until recently, the impacts of BVOCs were not considered in ozone control strategies to limit emissions of either NO_x or VOC. Although the importance of BVOCs is now universally acknowledged, the full extent of their influence on atmospheric photochemical processes is still unknown. The BVOC project aims to obtain BVOCs data for more precise estimates of emission flux intensities and distribution through vegetation mapping, for the purpose of assessment of the relative importance of biogenic and anthropogenic VOC emissions

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and their respective roles in the formation of local and regional-scale photochemical smog in Hong Kong. This study is the first step of the whole project [3].

Ground-level ozone and particulate matter typically associated with photochemical smog are formed by the photooxidation of VOCs in the presence of nitrogen oxides (NO_x) [4]. VOCs play a crucial role in regional and global photochemistry, including organic aerosol formation. These processes greatly impact ozone formation, hydroxyl production and consumption, the abundance of some greenhouse and stratospheric ozone depleting gases, and production of secondary organic aerosols (SOAs) [5,6,7]. Several modelling studies have shown that inclusion of BVOCs is important to properly reproduce the photochemistry of the troposphere at a regional level, principally in areas having vegetation coverage and climatic conditions favouring BVOC emissions [8]. While there have been numerous air quality studies done in Hong Kong [9], full quantitative determination of BVOCs research has not yet been carried out [3]. Research done elsewhere, such as in the United States [10] and Europe [11,12], is limited and, moreover, is not applicable to Hong Kong because the ecological processes in a tropical climate are different. The establishment of a database of BVOC emissions for Hong Kong and the development of source profiles for BVOC emissions for source apportionment that is directly relevant to Hong Kong would be very useful to assist in better air quality management here.

Analytical methodology for VOC is commonly based on a pre-concentration technique coupling to a separation and detection system typically using gas chromatography–flame ionisation detector. Pre-concentration technique such as Tenax-Carbotrap adsorption tube, solid-phase micro extraction (SPME) [13,14] and cryo-trap technique are currently applied. In this paper, a simple semi-manual cryo-trap/thermo-desorption technique coupled to gas chromatograph with flame ionisation Detector (GC-FID) was developed for the determination of BVOCs.

2. Experimental

2.1 Apparatus and chemicals

A simple semi-manual cryo-trap/thermo-desorption technique coupling to gas chromatograph with flame ionisation detector (GC-FID) was developed for the BVOC determination. A gas chromatography (Shimazu 15A) using capillary column HP PONA $50\text{ m} \times 0.2\text{ mm} \times 0.5\text{ }\mu\text{m}$ was currently used in the laboratory. Figure 1 shows the schematic of the currently-used system. Air sample is first pre-concentrated by being frozen in the cryo-trap at around -186°C (cooling by cryogen of liquid argon). The sample gas is then loaded by using a pressure-canister or glass syringe injection into the trap-coil after the trap is cooled by liquid argon. Then the trap is heated up to $90\sim 100^\circ\text{C}$ using boiling water, so-called thermo-desorption, meanwhile the VOC components will be vaporised from the trap and injected directly into the GC capillary column by the carrier gas of helium. The gas chromatography is used to separate the different VOC components showing different retention time in the chromatograms. After passing through the GC capillary column, VOC analytes will be detected by the FID at the end of the GC column. The system is then baked-out by heating for cleaning after a measurement run and ready for the next analysis process.

For the purpose of test and evaluation of the analytical system in this work, the US EPA Photochemical Assessment and Monitoring System (PAMS) standard air sample was

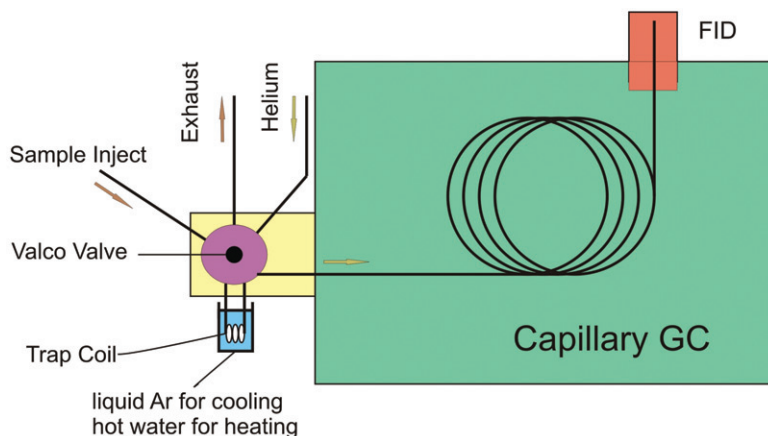


Figure 1. Schematic of the cryo-trap/thermo-desorption/GC-FID system.

applied as the standard for retention time and quantification comparison, which was purchased from Spectra Gases, NJ, USA. The EPA PAMS requires monitoring for approximately fifty (57) volatile and semi-volatile organic chemicals in many metropolitan areas. These chemicals are considered to be photochemical smog precursors and sources of ozone depletion, including the most representative BVOC emission species, i.e. isoprene. Four monoterpenes were also applied as the standard samples for typical BVOC species, i.e. α -pinene, β -pinene, 3-carene (Δ) and limonene. One μL of pure monoterpene liquid was firstly injected into a 6-L canister with zero air. After vaporisation, this 'standard' air sample was then diluted into a desired concentration using zero air in the laboratory. However, the concentrations of monoterpenes were not fully calibrated and the measurement results of monoterpenes are continuing to be developed.

2.2 Field work and sampling

Sampling and measurement of BVOC emissions should consider temporal and environmental variations in BVOC levels, since BVOCs emissions can be affected by the temperature, light, photosynthetically active radiation (PAR) and CO_2 concentration [15], all of which may vary diurnally and seasonally. For example, a Mediterranean oak (*Quercus ilex*) showed an increase in acetaldehyde and acetone emissions but only in the autumn [11], and Rosenstiel *et al.* [16] reported significantly decreased emissions of isoprene from the Common Cottonwood (*Populus deltoids*) grown under elevated CO_2 . Therefore, as well as studies of specific species, seasonal and annual variations in temperature, light and humidity levels and their relationship to BVOC emissions are needed for more reliable air quality modelling. In our work, two sampling campaigns were conducted in winter and summer of 2007 for the aim of seasonal variation, with all the related parameters recorded at the same time.

Air samples were collected from the spots of individual plants at selected sites in Hong Kong. These sites were selected by airborne investigation, to give representative communities which can be identified using remote sensing. Sampling locations were shown in Figure 2. The detailed sampling spots with different typical vegetation types in rural and urban sites are listed in Table 1. Tree species near the sites were also stated in the table.

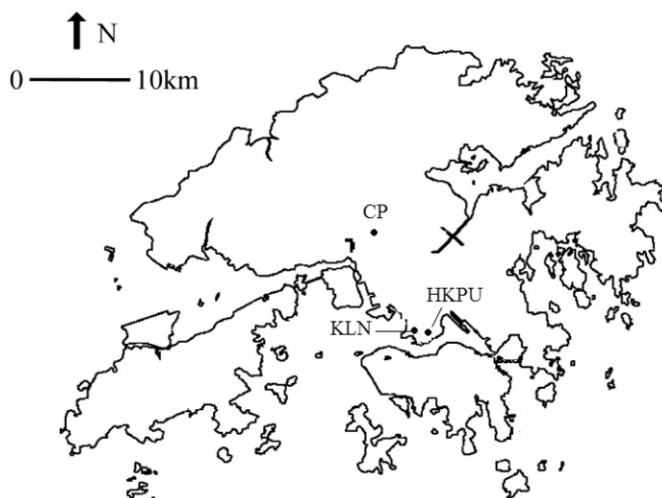


Figure 2. Sampling locations in Hong Kong.

Table 1. Sampling spots for BVOC measurement over Hong Kong.

Rural sites (in Sing Mun Country Park, CP)	Urban sites (Elevation: 5–10 m)	
1. Lowland Forest (E. 413 m)	Kowloon Park (KLN Park)	1. Shrubland
2. Montane Forest (E. 507 m)		2. Trees/Forest
3. Meleleuca Quinquinervia (E. 243 m)	HKPU site	3. Grassland
4. Shrubland (E. 437 m)		4. Public Square
5. Grassland (E. 518 m)		1. Flower Podium
All locations and their elevations were measured by GPS.		2. Grassland
		3. Roadside

Notes: Sample numbers: 46 for rural sites and 21 for urban sites in the winter period; 54 for rural sites and 35 for urban sites in the summer period.

Two parallel samples were taken at the same time for each sampling spot or location. Totally, more than 150 air samples were collected during the winter and summer sampling period. The air samples were collected in evacuated 2-L electro-polished stainless steel canisters with a fixed interval. Integrated air samples over the desired time period were collected directly using a flow regulator. Air samples were taken at different times during the day since it is believed that air masses mix very well and BVOCs emissions are strongly dependent on solar radiation. The samples were taken every one to two hours in mornings and afternoons with different solar radiation conditions. The canisters were shipped to the HKPU for chemical analysis using gas chromatography (GC) by the developed analytical system in the air laboratory.

3. Results and discussion

3.1 Analytical method development

In order to enhance GC separation, the operation parameters were optimised as follows. Separation resolution for VOC species by GC is significantly dependent on the GC oven

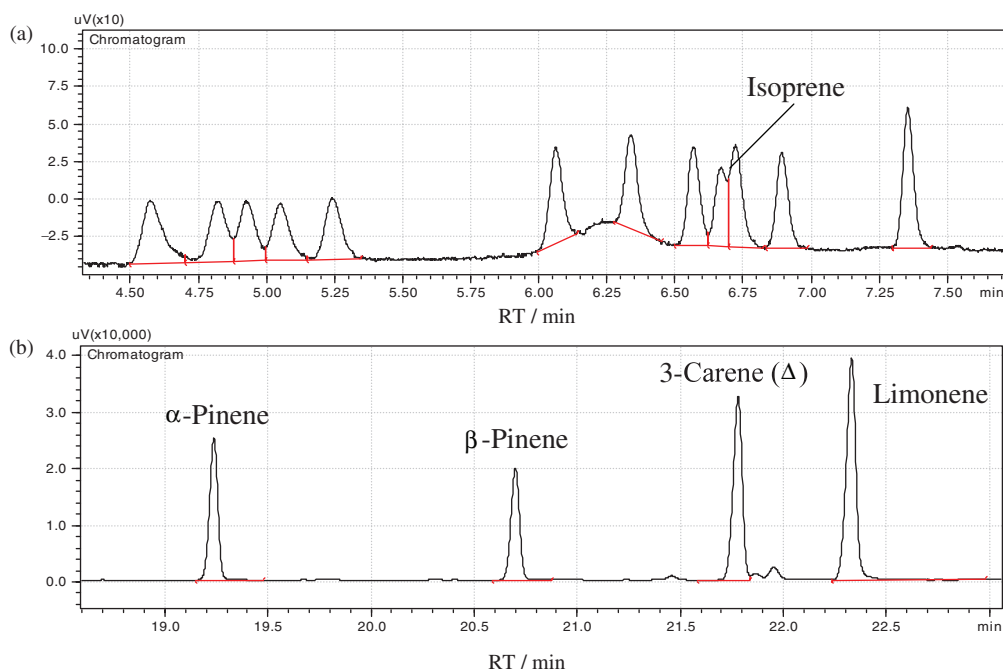


Figure 3. Separations of some VOC species by the gas chromatograph system. (a) Chromatogram of a PAMS standard air sample (1.75 ppb, 25 mL injected), only C4 and C5 hydrocarbons shown in the plot. (b) Chromatogram of a monoterpene standard air sample (4 species, ca. 125 ppb, 50 mL injected).

temperature programming. The optimised oven temperature programs are shown as follows: (a) For VOC analysis: initiate at -60°C hold 3 min, $15^{\circ}\text{C}/\text{min}$ to 40°C , $4^{\circ}\text{C}/\text{min}$ to 150°C , 150°C hold 5 min for final; (b) For BVOC analysis: initiate at 5°C hold 1 min, $10^{\circ}\text{C}/\text{min}$ to 80°C , $5^{\circ}\text{C}/\text{min}$ to 150°C , 150°C hold 10.5 min for final. The pressure of carrier gas helium was set to 200 psi, with the temperature of injection at 100°C and detector at 200°C . All parameters of GC and cryo-trap were optimised by experimental tests.

Difficulties in the separation and detection of VOC analysis are mainly from the low molecular weight VOC species, due to their relatively low boiling points. Small molecules of C_2 and C_3 are easily 'lost' in thermo-desorption, although they are frozen and focused in the cryo-trap. Fortunately, BVOC species are normally considered as C_5 hydrocarbons and bigger molecules. The BVOC analysis using the system described is satisfactory for the requirements of this work.

As can be seen in Figure 3, separations of the target VOCs species in the GC chromatograph, i.e. isoprene and monoterpenes in C_5 and C_{10} species, are satisfying enough for the qualitative and quantitative analysis. Isoprene can be distinguished from the standard and real air sample although it is overlapped with another C_5 hydrocarbon in the complicated mixture of VOC standard sample in this case, while the 4 monoterpenes are clearly separated at high resolutions. To make sure that isoprene can be qualified clearly in the GC separation, a commercial preconcentrator (Nutech[®]) coupling to a GC-MS system was employed in the methodology. Figure 4 shows a typical

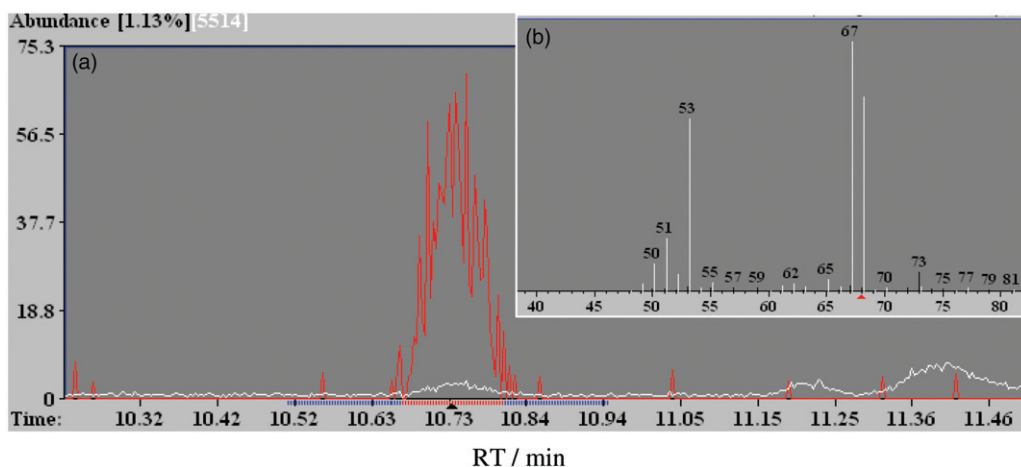


Figure 4. Gas chromatograph of an ambient air sample using Nutech[®]-GC-MS system. (a) Chromatograph of an ambient air sample (near the peak of isoprene/10.73 min). (b) The extract mass spectrum of the peak at 10.73 min in picture (a).

chromatograph of an ambient air sample, and the peak at 10.73 min was identified as isoprene by extracting the mass spectrum. As can be seen, isoprene existed alone within 1-min range, showing that the ambient air sample in this work was simpler than the mixing standard air sample. Therefore it is proved that isoprene can be easily separated and determined using the developed method.

The detection limits were estimated to be about 20 ppt (10 s) for isoprene and 10 ppt (10 s) for monoterpenes respectively, with sample injection volume of 50 mL into the cryo-trap system, and the linear range up to 5 ppb by volume in the real sample measurements. However, the concentrations of target species in the air sample vary in a wide range from about 10 to 10^4 ppt. In this case, several calibration curves of different ranges were necessary to guarantee analytical quality, although the theoretical response of FID is stable enough for such a wide content range. A typical calibration curve of isoprene contents in the range of 0–5000 ppt is shown in Figure 5, indicating a very satisfying linearity ($R^2=0.9991$).

3.2 Determination of isoprene

3.2.1 Winter isoprene contents

Air samples were collected during winter time (January–February) of 2007. About 70 measurement results were acquired from rural and urban sites during this sampling period. Five types of typical vegetation of a country park at the north of Kowloon downtown (i.e. Lowland Forest, Montane Forest, Meleleuca Q., Shrubland and Grassland) and 6 types (Shrubland, Grassland, Mixed Vegetation at Roadside, Trees/Small Forest, Flowerland and Public Square) in two downtown areas were selected as the sampling spots as shown in Table 1. Owing to relatively low biogenic emission levels in winter time, only isoprene data were obtained in the field work during winter.

Isoprene contents of the rural and urban sampling sites are shown in Figure 6. Average isoprene contents in the ambient air samples of rural and urban sites were 411 ppt and

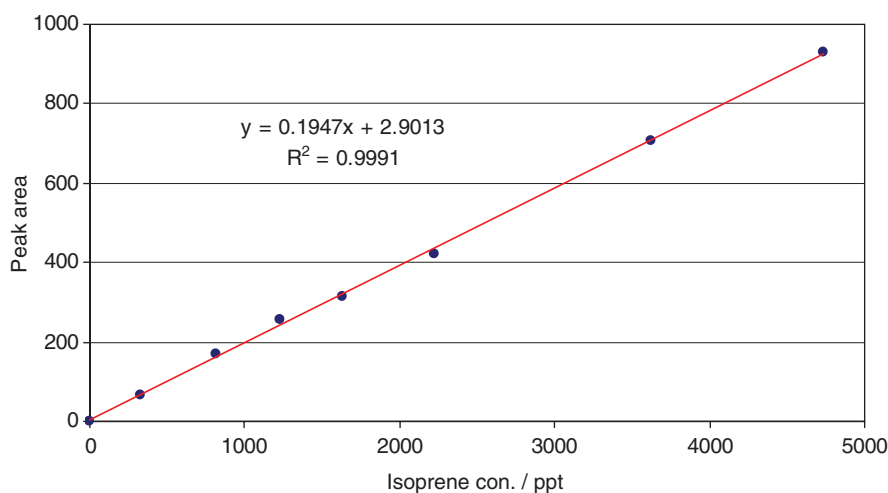


Figure 5. A calibration curve of isoprene contents in the range of 0–5000 pptv.

211 ppt by volume, respectively. It is obvious that the isoprene mixing ratio in rural ambient air is much higher than that of urban areas—with more vegetation, more biogenic emissions, showing higher isoprene contents. As can be seen in Figure 6a, isoprene mixing ratios of 5 types of vegetation areas are in the order of: Montane Forest > Lowland Forest \approx Meleleuca Q. > Shrubland > Grassland. These isoprene mixing ratios depend not only on the plants species of the vegetation, but also on the air mixing conditions and other meteorological parameters such as solar radiation, humidity, wind speed and direction, etc. In the urban sampling sites, isoprene contents can be listed in the order of Trees > Roadside > Flower/Shrubland > Grassland, as shown in Figure 6b.

Isoprene emission rates of individual plant species were studied by many previous investigations [17–21]. Grassland is commonly considered as non-BVOC emission vegetation. However, the isoprene mixing ratio at grassland sampling sites in this work was found to be non-zero, most likely because isoprene was transported from other isoprene-emitting vegetation areas, despite its relatively short chemical life-time of less than 3 hours during daytime [22]. Isoprene mixing ratios measured in this work are not aimed at determining emission rate, but the ambient air contents of BVOC. Therefore, these data are not compared to those emission rates of individual plant species in other previous works. Although the exact vegetation species/plant species were not distinguished in the isoprene measurement during the field campaign, this data set will be applied to the BVOC mapping based on vegetation over Hong Kong in future work.

3.2.2 Summer isoprene contents

Summer isoprene contents were determined during summer time of 2007 (June–July), at the same sampling sites as winter field work. Fifty-five samples from rural sites and 35 samples from urban sites were measured. The average isoprene mixing ratio was 1028 ± 25 ppt at rural sites and 1333 ± 21 ppt at urban sites respectively, which are 2–4 times higher than those of winter time. Table 2 shows the isoprene mixing ratios of this work and the field work at Hong Kong urban sites in 2003 conducted by another research

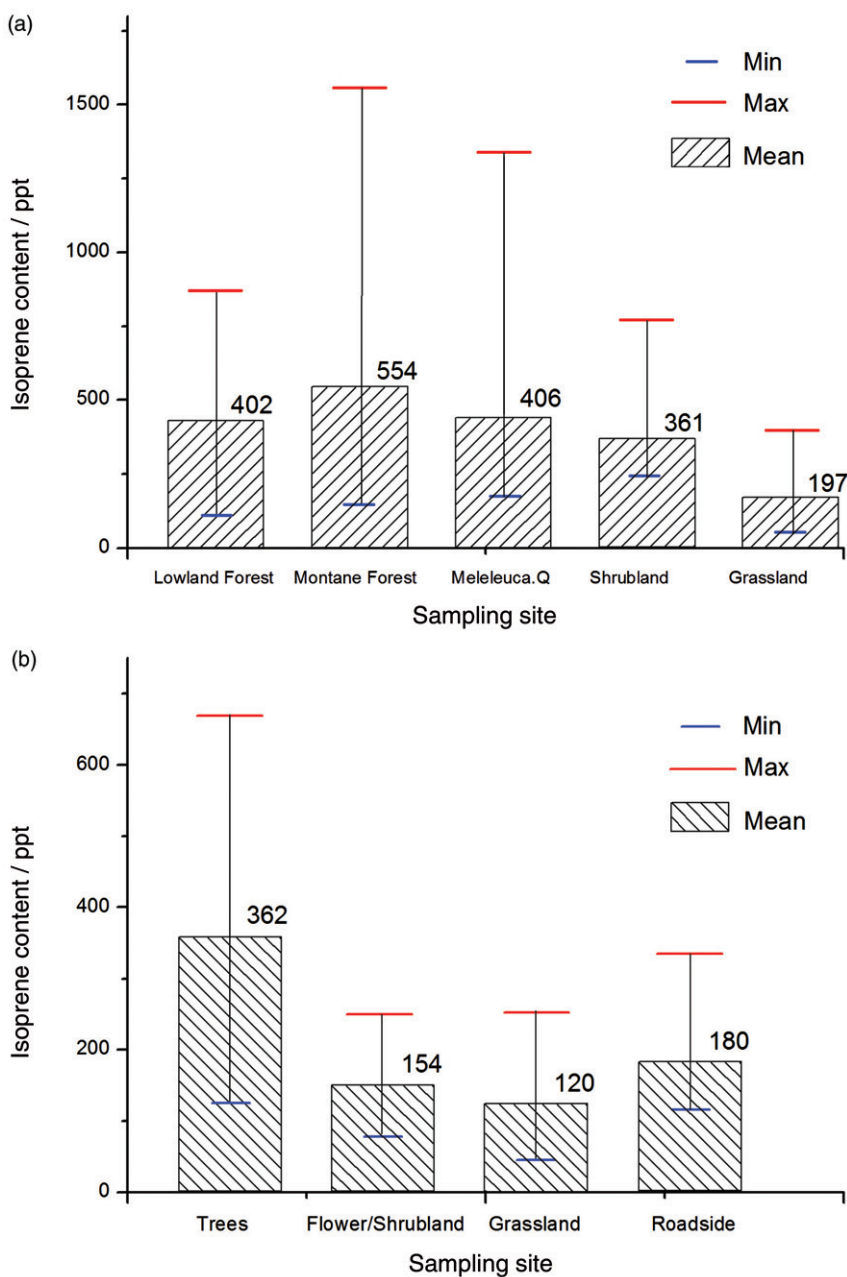


Figure 6. Winter isoprene contents in ambient air of Hong Kong: (a) rural sampling sites, (b) urban sampling sites.

group from Hong Kong and USA [23]. It is clear to conclude that isoprene contents are higher in summer than those in winter time, which is obviously due to the greater biogenic emission rates during summer time. Also, isoprene contents in rural sites are found at higher levels than those of urban sites. Differences of isoprene contents between sampling

Table 2. Isoprene contents in ambient air over Hong Kong.

Seasons/sites	Campaign in 2007				Campaign in 2003*	
	Winter		Summer		Winter	Summer
	Rural	Urban	Rural	Urban		
Sample numbers	46	21	54	35	108	65
Minimum/ppt	60.1 ± 5.1	55.0 ± 3.8	260 ± 9.7	not detected	11.0	17.0
Maximum/ppt	1559 ± 35	671 ± 12	3270 ± 53	3576 ± 46	2353	1633
Median/ppt	284 ± 11	143 ± 8.5	950 ± 32	1166 ± 37	93.0	404
Average/ppt	411	211	1028	1333	161	452

Note: *Sampling sites located at roadsides and tunnels over Hong Kong urban area.

sites were similar to those of winter field work, i.e. Montane Forest > Lowland Forest ≈ Meleleuca Q. > Shrubland > Grassland in rural areas, and Trees > Roadside > Flower/Shrubland > Grassland in urban areas.

It is interesting to find that the isoprene contents in urban sites in summer 2007 were as high as 1300 ppt by volume. There are certain plant species that are strong isoprene emitters in urban areas, especially during the daytime in summer. For instance, *Casuarina equisetifolia* is one of the top 10 isoprene emitters [18,24], which is quite common in south China and is distributed throughout Hong Kong. Moreover, isoprene emission from vehicles in urban sites has been recently documented [25,26], as well as the local tunnel study on vehicular emission of VOCs [27]. In future work, identifying this local isoprene source will require more accurate mapping of BVOC emissions based on vegetation, a detailed distribution of plant species throughout Hong Kong, and emission rates of individual species, which together are critically important for calibration and modelling calculations.

It is generally believed that biogenic isoprene emission is significantly dependent on the solar radiation, especially during summer. To determine the relation between isoprene emission and solar radiation, a diurnal variation test of isoprene contents was measured at an urban sampling site—HKPU roadside with trees, monitoring time of 8:00 ~ 20:00 as the daytime period. Weather conditions during the experiment day were carefully selected as sunny, clear with low wind. The diurnal variation of isoprene contents with the direct intensity of the sunlight measured at the same time is shown in Figure 7. As can be seen, the isoprene contents varied strongly with the solar radiation in the plot. In the morning, almost no isoprene was detected although solar radiation was starting to increase. With increasing intensity of solar light till midday, isoprene contents increased to its peak-high value at noon. In the afternoon, isoprene contents were found to decrease with the decreasing solar radiation, until out of the detection limit after sunset at 20:00. Although only a limited 2-day data set was obtained, it is obvious that the biogenic isoprene emission is significantly influenced by the sunlight intensity, as reported by the previous work [28,29].

3.3 Determination of monoterpenes

Due to their extremely low mixing ratios in the ambient air, the measurement of monoterpenes in this work was a challenge. Only β -pinene and limonene were detected as

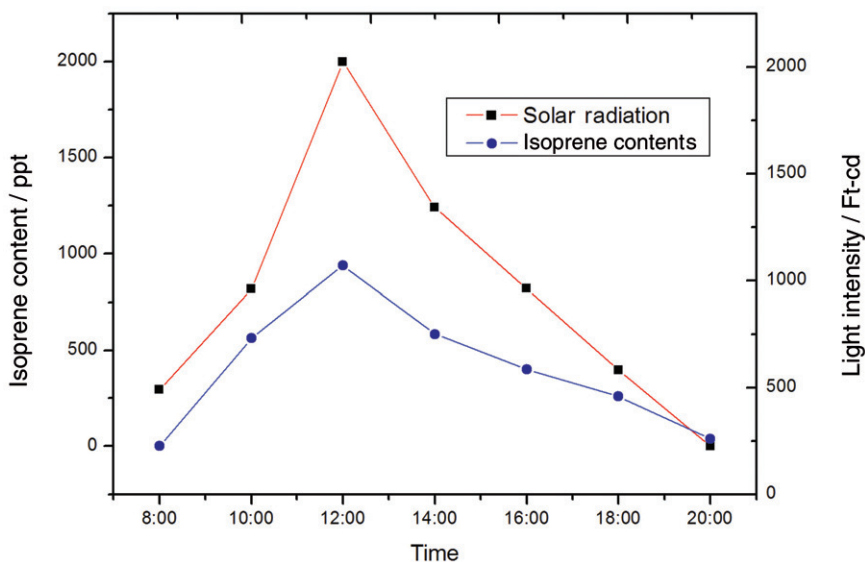


Figure 7. Diurnal variation of isoprene contents with solar radiation at an urban sampling site.

monoterpene BVOC species in 87 air samples of summer field work. Mixing ratios of β -pinene were up to 632 ppt with an average of 238 ± 17 ppt at urban sites, compared to 99–851 ppt with an average of 349 ± 26 ppt at rural sites. Limonene contents were in the range of 55–388 ppt with an average of 195 ppt at urban sites, compared to 128–326 ppt with an average of 200 ± 9 ppt at rural sites. Another typical biogenic monoterpene, α -pinene, was not detected by the developed analytical methodology, although this has been double checked. The method has to be improved in this case. This data set of monoterpenes is very limited, which should be completed in the next field work before being applied to the further calculation and mapping in the project. However, the isoprene data set can be satisfyingly applied to the mapping of BVOC emission since isoprene is commonly considered as the most representative biogenic emission species. This small monoterpene data set can be used as references in the mapping work.

4. Conclusions

The analytical method for the determination of isoprene, using a semi-manual cryo-trap technique coupling to GC-FID, has been developed successfully, and the method to determine monoterpenes is continuing to be developed. The detection limits were estimated to be about 20 ppt for isoprene and 10 ppt for monoterpenes respectively, with sample injection volume of 50 mL. Based on vegetation types, field measurement work was conducted over urban and rural sites of Hong Kong during the winter and summer of 2007. Canister sampling technique was applied in the field measurement. Isoprene contents in rural ambient air were found to be in the range of 60–1560 ppt in winter and 260–3270 ppt in summer, respectively. More than 150 isoprene contents in ambient air were obtained to fill the data gap of BVOC in Hong Kong. However, in the measurement of monoterpene, due to their extremely low concentration in the air samples, only β -pinene

and limonene were detected by the developed analytical method. The data set will be applied to the mapping of biogenic emission of VOC based on vegetation types over Hong Kong in future work.

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