Seasonal characteristics of biogenic and anthropogenic isoprene in tropical–subtropical urban environments

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HIGHLIGHTS

• Isoprene in urban environments at tropical–subtropical latitudes was studied.
• Seasonal and spatial differences in isoprene’s levels and sources were investigated.
• A temperature kick-start threshold of isoprene emissions was clearly demonstrated.
• Such a threshold may vary with vegetation types and temperature zones.

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ABSTRACT

Measurements of atmospheric isoprene and other selected volatile organic compounds (VOCs) were conducted in Taipei, a tropical–subtropical metropolis, to investigate diurnal variations, seasonal diversity and spatial differences in terms of the levels and sources of isoprene. Our study also investigated the responses of biogenic isoprene to both light flux and temperature in real urban settings that have a variety of plant species and traffic volumes. The robust ratio of isoprene/1,3-butadiene obtained from pure traffic emissions was used as a gauge to separate biogenic isoprene from traffic emissions. The four seasonal measurements at a typical urban site in the city showed that biogenic contributions overwhelmed their anthropogenic counterparts in summer and dominated the daytime isoprene levels in spring and autumn. Even in winter, biogenic sources still contributed a non-negligible fraction of approximately 44% to daytime isoprene. Furthermore, the concentration contour of isoprene extrapolated from the data at 38 sites throughout the city revealed that high levels of biogenic isoprene were generally a widespread phenomenon in summer in the tropical–subtropical city. A three-dimensional plot of the isoprene/1,3-butadiene ratio, ambient temperatures and radiation flux showed a temperature threshold of biogenic isoprene emissions, beyond which the biogenic contribution began to increase exponentially with enhanced ambient temperature. However, when the ambient temperature was below the threshold, there was no or negligible biogenic contribution to the ambient isoprene, regardless of the strength of the radiation flux. The temperature threshold (approximately 17–21 °C) of isoprene emissions in the tropical–subtropical city was much higher than the thresholds in cities and areas at temperate latitudes, indicating that the adaptation of vegetation to different temperature zones via isoprene emission may be characteristic.

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1. Introduction

Isoprene reacts actively with the hydroxyl radical (OH) and nitrate radical (NO3), leading to the production of diverse secondary oxidants, e.g., organic peroxy radicals (RO2), ozone (O3), and secondary organic aerosols (SOA), which potentially make a large impact on urban air quality, atmospheric oxidation capacity and even regional climates (Fuchs et al., 2013; Fuentes et al., 2000;
Isoprene has both biogenic and anthropogenic sources in urban areas (Borbon et al., 2001; McLaren et al., 1996; Hellen et al., 2012; Wang et al., 2013a). Vehicular exhaust is usually the dominant source of anthropogenic isoprene, whereas biogenic isoprene primarily comes from terrestrial plants (Borbon et al., 2001). Isoprene emission from biogenic sources is sensitive to a number of environmental parameters, especially temperature and light intensity (Guenther et al., 1993; Sanadze, 2004; Sharkey and Yeh, 2001; Pacifico et al., 2009). Numerous studies of enclosure measurements and above-canopy flux measurements have provided significant and essential information on the isoprene emission rates of many plant species in greenhouses with control conditions or in fields with relatively simple conditions (Guenther et al., 1993; Sanadze, 2004; Kuzma and Fall, 1993; Centritto et al., 2004; Fall et al., 1992; Monson et al., 1994). Because the magnitude of isoprene emissions varies geographically and mainly depends on the plant species and environmental conditions locally, additional studies for more different plant species in various environments are required. Cities in tropical and subtropical zones with high temperature and light flux provide conducive conditions for biogenic isoprene emissions. The high biogenic isoprene emission potentials in tropical and subtropical cities and its coherence with the hydroxyl radical (OH) diurnal pattern might produce a much larger loss of isoprene and more effective production of photochemical oxidants; such a situation would accentuate the potentially significant impact of biogenic isoprene on atmospheric photochemistry and urban air quality (Wang et al., 2013a; Lee and Wang, 2006; Fuchs et al., 2013).

In assessing the importance and influence of biogenic isoprene on atmospheric chemistry in urban areas, an in-depth understanding of the temporal variation and spatial characteristics of biogenic and anthropogenic isoprene is essential. The knowledge of diurnal and seasonal characteristics forms the perspectives of isoprene levels and source types are pivotal to the understanding of the potentials of both biogenic and anthropogenic isoprene producing secondary pollutants in different periods. Furthermore, air sampling at a large number of sites spreading over a city is helpful to the understanding of the spatial characteristics in the overall distribution and the differences in biogenic and anthropogenic isoprene. These types of studies could also supplement and/or modify isoprene’s inventory in urban areas, which is of importance for regional photochemical modeling. Nevertheless, there are infrequent reports of field investigations (observations) on the temporal and spatial characteristics of isoprene in urban settings, especially in tropical and subtropical cities. It is likely that the environmental conditions and plant species in urban areas are more complicated, and isoprene emissions in urban areas are not only contributed by biogenic emissions but also by anthropogenic emissions. Because of the potentially significant influence of isoprene on atmospheric chemistry, this study aims to provide a clearer understanding of the seasonal variation and spatial characteristics of both biogenic and anthropogenic isoprene in a tropical–subtropical metropolis and to relate isoprene emissions to the surrounding meteorological and environmental conditions.

2. Methods

2.1. Site description and sampling periods

The study was conducted in Taipei (25°00′N/121°53′E, 20 m a.s.l.), the capital of Taiwan, which is located in a tropical–subtropical zone. The city is a typical metropolis with a population greater than six million; there are four million registered vehicles, and traffic emissions account for the main source of anthropogenic pollutants in the city (Wang et al., 2002). Similar to many global urban areas, ground-level ozone and fine particulate matter continues to be an air pollution issue in Taipei (Taiwan EPA, 2012). The high temperatures and strong solar intensity in hot seasons and heavy traffic all year render Taipei an ideal location to assess the importance of biogenic and anthropogenic isoprene for the air quality and atmospheric chemistry. Fig. 1 shows a map of the sampling sites and surrounding environments. Mountainous areas are in darker green, and highly populated and urbanized areas (the eastern part is the business quarter and western part is the traditional residential areas mixed with some small factories) are in gray. Two types of sampling were conducted for the study: 1. Ambient air was collected at an urban site over four seasons to obtain the diurnal and seasonal characteristics of isoprene, 2. Two batches of air samples were collected at 38 sites throughout metropolitan Taipei to obtain the spatial distribution of isoprene and investigate the spatial differences between biogenic and anthropogenic isoprene.

The four season sampling was conducted at National Taiwan University (NTU), which is in the southeast region of the city and surrounded by shops, busy streets, business buildings and residential apartments (Fig. 1). The site is a typical urban site within Taipei, and the plant species within a 3 km × 3 km area from the site consist of nearly tropical to subtropical broad-leaved trees, including Liquidambar formosana, Ficus microcarpa, Ficus benjamina, Melaleuca leucadendra, Koelreuteria henryi and Cinnamomum camphora, which are common species in the city. These species can be classified by the classification system for the normalized isoprene emission rates (Guenther et al., 1994). Liquidambar formosana was found to be a high isoprene emitter; Melaleuca leucadendra and Ficus benjamina are moderate isoprene emitters; Ficus microcarpa and Cinnamomum camphora are low-to-negligible isoprene emitters (Sun and Leu, 2004; Tsai et al., 2009; Tambunan et al., 2006). The sampling inlet was installed on the roof of a 5-story building (~25 m above ground) at NTU. The sampling was conducted over four seasons: spring (16–29 April 2013), summer (4–11 July and 15–22 August 2011), autumn (15–29 October 2012) and winter (11–24 December 2012). The data of summer and autumn have been employed in our previous study to point out the significance of biogenic isoprene in hot seasons in tropical–subtropical urban settings (Wang et al., 2013a), whereas this study further strengthens the seasonal diversity and geographical differences in terms of the levels and sources of isoprene. During the sampling periods, a one-hour integrated air sample was collected in a canister every two hours to obtain time-series data on isoprene, 105 additional volatile organic compounds (VOCs) and methane (CH4). Meteorological data such as wind speed, wind direction, ambient temperature, humidity were collected with a compact weather station (WXT520, Vaisala, Finland), and photosynthetically active radiation (PAR) was measured with a quantum sensor (LI-190SA, Licor Inc., Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lincoln, Lin...
Nebraska, USA). The one-hour integrated air samples (648 samples) and meteorological data were integrated for the study.

Seventy two air samples were collected at 38 sites throughout metropolitan Taipei (Fig. 1) in two different periods, which had contrasting meteorological conditions. One sampling was conducted at noon (11:30–12:30) in summer (31 July 2013) because high levels of biogenic isoprene are expected in conditions of high temperature and light flux. The other sampling was carried out at dawn (5:00–6:00) in winter (14 February 2012) in conditions of lower temperature and light flux, which was used as a contrast to the summertime data. During the summer collection period, the weather was hot (32–35 °C), the relative humidity ranged from 42% to 58%, and there was mild to moderate wind (~2 m/s), which are the typical weather conditions in Taipei in summer. For the wintertime sampling period, the temperature varied from 18 °C to 21 °C, relative humidity ranged from 79% to 91%, and there were mild breezes (<1 m/s). The air samples were collected in the urbanized areas (urban and suburban areas) of the city. All samples were collected in open fields to avoid the over-influence of nearby sources.

2.2. Sampling method and sample analysis

All of the air samples were collected in 2-L electropolished stainless-steel canisters. The canisters were humidified and evacuated to <0.05 mmHg prior to sampling, and the cleaning procedures for the canisters accorded to the U.S. EPA compendium method TO-15 (1997). The filled samples were returned to the laboratory for analysis within two weeks. The canister sample was first analyzed by an automated GC–MS/FID (450-GC and 240-MS, Varian, Walnut Creek, CA) system to simultaneously analyze C1–C11 VOCs, and it was then transferred to a CRDS (G2401, Picarro Inc., Santa Clara, CA, US) for CH4 measurement. Further information on the flask-CRDS method can be found in Wang et al. (2013b).

The automated GC–MS/FID for VOC analysis is an upgrade of the one described in the reference (Wang et al., 2012). In brief, the air sample collected in the canister was drawn through a cryo-trap packed with fine glass beads and cooled with liquid nitrogen (controlled at ~170 °C) at 40 mL/min for three minutes to yield an aliquot of 120 mL. Subsequently, desorption was performed by flash heating the trap to 100 °C, and a stream of ultra-high purity helium (99.9999%) was then used to back-flush the analytes from the trap onto the columns. Internal standards were blended with each sample aliquot to verify the stability of the MS and back-correct the drift in the instrumental stability. Two standard gas mixtures of 65 C2–C11 NMHCs (Scott Marrin Inc., USA) and 55 C1–C10 VOCs (Linde SPECTRA Environmental Gases, USA) were used for the concentration calibration and quality control purposes. Based on the seven repeated analyses of the standard gas mixtures, the repeatability of most of the target species was 0.5–2% and the limits of detection for most of the species were 3–30 pptv. Of the 106 measured VOCs, 66 non-methane hydrocarbons (NMHCs), including isoprene and three categories of alkanes, alkenes and aromatics that have higher reactivity or abundance in urban atmospheres, were selected for discussion in the study and the details of 66 NMHCs were described in Wang et al. (2012).

2.3. Biogenic and anthropogenic contributions to urban isoprene

Several studies reported 1,3-butadiene as a suitable exhaust tracer for the estimate of anthropogenic isoprene because of its high correlation with isoprene in on-road vehicular emissions and close chemical properties with isoprene (Reimann et al., 2000; Borbon et al., 2001; Wang et al., 2013a). The tracer method that employs the ratio of isoprene to 1,3-butadiene is quite robust in urban areas where vehicular exhaust is the single-most dominant source of anthropogenic isoprene and 1,3-butadiene; however, the approach is not applicable in environments where anthropogenic isoprene and 1,3-butadiene can be partially contributed by non-traffic sources, such as industrial emissions and wood combustion (Borbon et al., 2001; Knighton et al., 2012; Hellen et al., 2012; Karl et al., 2003). In urban areas where vehicular exhaust dominates the sources of anthropogenic isoprene and 1,3-butadiene, the concentration ratio of isoprene to 1,3-butadiene obtained from pure traffic emissions (e.g., on-road vehicular emissions) can be used as a gauge to estimate the traffic contributions to ambient isoprene, and then separate biogenic isoprene from traffic emissions.

Fig. 1. Sampling locations with the geographic terrain. Flask sampling sites are indicated by numbers, and the site with four season sampling is indicated by the green box. Mountainous areas are in darker green, and the gray areas are the densely populated, urbanized areas. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
2.4. Response of biogenic isoprene to temperature and radiation flux in urban environments

Many studies of enclosure measurements in greenhouses with control conditions or in fields with relative simple environmental conditions have reported that biogenic isoprene emissions depend primarily on different species of plants, temperature and light (Guenther et al., 1993; Sanadze, 2004; Sharkey and Yeh, 2001). In urban areas, the environmental conditions and plant species are more complicated, and urban isoprene is not only from biogenic emissions but from anthropogenic emissions as well. To investigate the response of biogenic isoprene to environmental conditions in urban areas, biogenic contribution should be first separated from the anthropogenic counterpart. As mentioned above, the isoprene/1,3-butadiene ratio can indicate the magnitude of biogenic contribution to ambient isoprene, and this study would try to exploit the isoprene/1,3-butadiene ratio to assess the relationship between biogenic contribution, temperature and light flux in the tropical–subtropical city. Additional advantage of using the ratio is that since isoprene and 1,3-butadiene would be subjected to the identical meteorological modulations during sampling, therefore 1,3-butadiene can be used as a reference species to correct for the dilution effect on isoprene.

3. Results and discussion

3.1. Seasonal and diurnal characteristics of isoprene, 1,3-butadiene, NMHCs and meteorological parameters

The diurnal and seasonal variations in the mixing ratios of the total NMHCs (66 species including isoprene), isoprene, 1,3-butadiene, temperature, PAR and wind speed at the urban site (NTU) are shown in Fig. 2. The total NMHCs for four seasons showed similar patterns but different levels. The pattern with two humps during rush hour traffic (6:00–8:00 and 18:00–21:00) was similar to the pattern of typical traffic emissions, which implies that most of NMHCs were emitted from traffic sources. Lower NMHC values during midday were attributed to the relatively few emissions of anthropogenic NMHCs and a dilution effect caused primarily by the rising boundary layer around noon, which was especially apparent in summer and autumn. Comparing the data for the four seasons, the level of the total NMHCs in autumn was lower than that of other three seasons, particularly after noontime. The phenomenon may be mainly attributed to the higher wind speed (Fig. 2f) and deeper boundary layer in autumn, which are conditions favorable to the dilution of gaseous species.

Isoprene revealed different levels in the four seasons as shown in Fig. 2b. The daytime average concentrations of isoprene were 0.28, 1.26, 0.37 and 0.17 ppbv in spring, summer, autumn, and winter, respectively. The isoprene level in summer in the city was comparable to the levels in other subtropical metropolises (Park et al., 2011; Wiedinmyer et al., 2001; So and Wang, 2004); however, it was much higher than the levels seen in several temperate cities (von Schneidemesser et al., 2011; Borbon et al., 2001; Hellen et al., 2012; Legreid et al., 2007). The observed isoprene levels varied significantly with latitudes indicate that isoprene may play a more important role in the summertime photochemistry in tropical–subtropical cities than in temperate cities.

Except winter, the measured isoprene levels showed simple patterns in the other three seasons, with the daily maximum isoprene occurring at approximately noon. After that, the isoprene levels decreased gradually to the minimum level before dawn. Higher isoprene concentrations occurring at noon than in the other periods of the day were usually associated with biogenic sources. In Fig. 2d and e, the temperature and sunlight intensity show regular diurnal patterns of maximum temperatures during the midday hours and minimum temperatures at night. The isoprene profiles with a noon maximum value in the three seasons (spring, summer and autumn) and similar diurnal patterns with temperature and sunlight intensity indicate that the source of isoprene was primarily biogenic. In comparison, the irregular profile of the measured isoprene in the winter indicates isoprene may have contributions from different sources.

Fig. 2. Diurnal variations of (a) total NMHCs, (b) isoprene, (c) 1,3-butadiene, (d) temperature, (e) PAR and (f) wind speed in the four seasons. The range of ±1/2σ (standard deviation) is indicated by the error bars.
The pattern of the anthropogenic tracer 1,3-butadiene is shown in Fig. 2 to provide a contrast to that of the biogenic species. There were two obvious humps during rush hour traffic, which conform to the characteristics of traffic emissions. Furthermore, 1,3-butadiene was well correlated with many of the other exhaust tracers (e.g., 1-butene, isobutene, 1-pentene, trans-2-pentene and cis-2-pentene) with $R^2 > 0.95$, which reveals that the 1,3-butadiene at the urban site was almost exclusively from traffic emissions, therefore it can be used as a tracer representative of traffic emissions. Our previous study have investigated the ratio of anthropogenic isoprene to 1,3-butadiene in on-road vehicular emissions at a typical road site in Taipei (Wang et al., 2013a), and the ratio of isoprene to 1,3-butadiene was 0.42 ± 0.04 (average ± standard deviation), which could be exploited as a gauge to separate the biogenic contribution to ambient isoprene from traffic emissions in the study city.

3.2. Seasonal and diurnal characteristics of biogenic and anthropogenic isoprene

Fig. 3 shows the distributions of isoprene/1,3-butadiene ratios at the urban site for the four seasons. The dashed line denotes the ratio of 0.42 characteristic of pure traffic emissions, which serves as a “baseline” condition for isoprene only released from anthropogenic emissions (traffic emissions). When biogenic isoprene was present, it caused ratios to rise above the line. In spring, the ratios of isoprene/1,3-butadiene for most of the samples were higher than the characteristic ratio, indicating that the extra biogenic contribution to the ambient isoprene was common in the season. The average ratio of isoprene/1,3-butadiene was 1.21, which was on average 2.9 times higher than that of pure traffic emissions (ratio = 0.42). Therefore, approximately 65% of the ambient isoprene in spring was estimated to be released by biogenic sources and 35% could be attributed to vehicular emissions. The spread of the isoprene/1,3-butadiene ratio in summer was much larger than the other three seasons, and the notably high isoprene/1,3-butadiene ratios were well above the characteristic ratio of pure traffic emissions (dashed line), which indicates large biogenic emissions contributing to the excess isoprene. The average ratio is 15.8 times higher than that of the vehicular sources; therefore, approximately 94% of the ambient isoprene was estimated to come from biogenic sources in the summer. The spread of the isoprene/1,3-butadiene ratio in autumn was smaller than that in summer but higher than that in spring. It was estimated that approximately 81% of the ambient isoprene in autumn was released by biogenic emissions. Among the four seasons, data in winter showed the smallest spread of the isoprene/1,3-butadiene ratio, and biogenic contribution accounted for approximately 29% of the ambient isoprene. The seasonal characteristics of the biogenic and anthropogenic contributions to isoprene in the tropical—subtropical city are somewhat different from those in temperate cities. Studies in temperate urban areas have reported that isoprene was mostly contributed by anthropogenic emissions in the winter months (Borbon et al., 2001; Hellen et al., 2012), and biogenic sources dominated the contribution in summer. Both anthropogenic and biogenic isoprene emissions were significant for isoprene in summering the periods between winter and summer (Hellen et al., 2012; Legreid et al., 2007). The study in the tropical—subtropical city revealed that the biogenic contribution overwhelmed the anthropogenic counterpart in summer and biogenic emissions were also predominant in autumn and spring. Despite wintertime, biogenic sources still contributed a non-negligible fraction to isoprene.

Regarding isoprene sources during daytime, the biogenic contribution was noticeably large in summer and overwhelmed the anthropogenic isoprene despite heavy traffic in the city. It was estimated that approximately 97% of the daytime (defined as 6:00 to 18:00) isoprene was released by biogenic sources in summer. In spring and autumn, the biogenic sources also dominated the daytime isoprene levels and comprised approximately 80% and 89% of the daytime isoprene, respectively. The biogenic contributions to isoprene in spring and autumn in the city were relatively significant compared to the cities in temperate zones and likely caused by the abundant evergreen trees and relatively high temperature and radiation flux in spring and autumn as a result of the city's tropical—subtropical climate. In winter, the average temperature varied from 11 °C to 27 °C and the solar intensity was weaker than in the spring and autumn (Fig. 2e). Although the weather conditions were not as conducive as in spring and autumn, the biogenic sources still contributed approximately 44% of the daytime isoprene, which is different from cities in temperate zones where isoprene in the winter months is almost contributed from anthropogenic sources.

Regarding the nighttime (defined as 18:00 to 6:00) sources of isoprene, Fig. 4 reveals different results from the daytime sources. The nighttime isoprene mostly originated from traffic emissions except in summer. Fig. 4 indicates that it had still large biogenic contributions to the nighttime isoprene in summer. In theory, the biogenic isoprene emissions should fall to negligible rates because of the lack of illumination at night. Presumably the biogenic isoprene at night was the remainder from daytime. The weather in the tropical—subtropical city during daytime hours in the summer...
months was rather favorable to high biogenic isoprene, and it is likely that the residual isoprene (nearly biogenic) after daytime photochemical loss persisted into nighttime (Wang et al., 2013a). The remaining isoprene would enhance the level of nighttime isoprene, as shown in Fig. 2b; therefore, the level of nighttime isoprene in summer was obviously higher than the levels in the other three seasons. Approximately 77% of the nighttime isoprene in summer was estimated to be contributed by the remainder from daytime, which indicates that biogenic isoprene might also have a large impact on the summer nighttime chemistry (Starn et al., 1998).

### 3.3. Relationship between biogenic contributions, temperature and radiation flux in urban environments

Fig. 5 shows the plot of isoprene/1,3-butadiene ratios versus ambient temperature at noon (11:00–14:00) for four seasons. The same time data (noon) was used because the emissions of 1,3-butadiene could serve as a reference to offset the dilution effect on isoprene and facilitate the data comparison under different dilutions. The dashed line in Fig. 5b is the same as in Fig. 3 and represents the ratio of 0.42, which is characteristic of pure traffic emissions and presents a baseline condition when isoprene was only contributed from traffic sources. When biogenic isoprene was present, the ratios would rise above the line. Shown in Fig. 5, the differences in the correlation between the biogenic contribution and ambient temperature between seasons were apparent. The biogenic contribution increased slowly with increased temperature in winter when the temperature was low, whereas it increased dramatically in summer when the temperature was high. Integration of the four seasons’ data showed a high correlation ($R^2 = 0.88$) between the biogenic contribution and ambient temperature. An exponential increase in isoprene/1,3-butadiene ratio with ambient temperature can be found in Fig. 5a, showing that the biogenic contribution increased dramatically with increased ambient temperature. Furthermore, a temperature threshold appeared to be at approximately 17–21 °C, as shown in Fig. 5b; beyond this threshold, the biogenic sources began to significantly contribute isoprene. The threshold obtained from the field study represented an integrated value of many kinds of isoprene emitting plants in the vicinity. Several studies in urban, rural and remote areas at temperate latitudes revealed that biogenic isoprene became pronounced when the local temperature was generally higher than 10–15 °C (Borbon et al., 2001; Lee et al., 2006; Jobson et al., 1994). In comparison, the threshold of biogenic isoprene emissions in this tropical–subtropical city made from mostly broad-leaved trees was obviously higher than that of cities and areas at temperate latitudes. The most widely held explanation for isoprene production and emissions from isoprene emitting plants is as protection against heat stress. Other explanations may include serving as an antioxidant in leaves, flowering hormone, and a metabolite overflow to reduce excess carbon (Sharkey and Yeh, 2001). The different temperature thresholds indicate that the adaptation of plants growing in the tropical–subtropical urban setting to ambient temperatures and environmental conditions via isoprene emissions may be quite different from plants growing at temperate latitudes. Although the temperature threshold was higher, the favorable weather conditions of high temperatures and light flux in tropical and subtropical cities in combination with the characteristics of an abrupt increase in biogenic isoprene emissions with increased temperature (Fig. 5a) are still conducive to the production of large amounts of biogenic isoprene.

In addition to temperature, light flux is another highly regarded parameter. Fig. 6 shows a three-dimensional (3D) plot of isoprene/1,3-butadiene ratios, temperatures and PAR for the noontime (11:00–14:00) data from the four seasons. The temperature threshold can be seen by the isopleths at approximately 17–21 °C. As the ambient temperature passed the threshold, the biogenic contribution increased rapidly with increasing radiation flux and was saturated at higher radiation flux levels (upper right corner of Fig. 6). When the ambient temperature was lower than the threshold, the biogenic contribution to ambient isoprene was no or...
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negligible, regardless of the intensity of the radiation flux (lower left corner of Fig. 6). These results were similar to those of the enclosure measurements and above-canopy flux studies with more controlled or simplified environmental conditions (Guenther et al., 1993; Sanadze, 2004; Sharkey and Yeh, 2001). The difference is that this study investigated the composite characteristic of the response of biogenic isoprene to ambient temperature and radiation flux in a tropical–subtropical urban setting with a large variety of thriving plant species, heavy traffic and complex pollutants.

3.4. Spatial characteristics of biogenic isoprene

Fig. 7 shows the concentration contours of isoprene and 1,3-butadiene, which are extrapolated from the data of the 38 sampling sites at noon (11:30–12:30) in summer and dawn (5:00–6:00) in winter. The summertime data at noon showed that the isoprene levels were much higher than the levels of 1,3-butadiene (Fig. 7a), which indicates that isoprene was almost entirely contributed by biogenic emissions. In contrast, the wintertime data at dawn exhibited a high consistency in the contours of isoprene and the anthropogenic tracer 1,3-butadiene (Fig. 7b), indicating that isoprene was mostly contributed from anthropogenic sources. The relative emission potentials of anthropogenic and biogenic sources in the different regions of the city can be obtained from the two contour plots of isoprene during the two contrasting periods of winter dawn and summer noon in which isoprene was almost exclusively from anthropogenic and biogenic sources, respectively. Areas with high anthropogenic emission potentials, such as the densely populated and highly urbanized areas, showed higher concentrations of 1,3-butadiene and isoprene (Fig. 7b). Furthermore, 1,3-butadiene in metropolitan Taipei was well correlated with many other alkenes (e.g., isobutene, 3-methyl-1-butene, 1-pentene, trans-2-pentene, cis-2-pentene and 2-methyl-2-butene), which are among the main species found in vehicle exhaust, revealing 1,3-butadiene with anthropogenic isoprene in the city were dominated by traffic emissions.

Areas with high biogenic isoprene emission potential, such as the suburban sites near the mountains, generally revealed high concentrations of biogenic isoprene (Fig. 7a). However, biogenic isoprene was also significant in the city exhibiting medium- to high-levels. During the summer sampling period, ambient temperatures at the urban sites were 1–3 °C higher than the temperatures at the suburban sites near the mountains, which may partially offset the lower density of plants in the urban area. The contour plot of summer noontime data reveals that high levels of biogenic isoprene was generally a widespread phenomenon in the city, although certain spatial differences in isoprene emission existed as shown in Fig. 7a and indicated by the standard deviations in Table 1. Furthermore, the isoprene levels and source apportionment at the urban NTU site, which was selected for the four season sampling, were close to those at the 38 sites during similar periods, reassuring the urban NTU site to be representative of the general urban conditions.

In addition to revealing the spatial characteristics of isoprene and its sources in the city, the emissions and sources of anthropogenic VOCs are also included for comparison. Anthropogenic emissions can be indicated by common tracers, such as methyl tert-butyl ether (MTBE), toluene, propane and methane. MTBE has been proven to be a good indicator of vehicular emissions, including tailpipe exhaust and gasoline evaporation (Chang et al., 2003). The sources of toluene include solvents, chemical intermediates and

Fig. 5. Plots of isoprene/1,3-butadiene ratios versus ambient temperature for noon-time (11:00–14:00) data from four seasons; (a) normal y-axes and (b) zoomed-in y-axes. Superimposed in (a) is the regression line fitting to all data, with $R^2 = 0.88$. The red dashed line in (b) denotes the ratio of 0.42 characteristic of pure traffic emissions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. Three dimensional plot of isoprene/1,3-butadiene ratios, ambient temperatures and PAR. The surface is a fit to the data (black dots), $R^2$ is the correlation coefficient of the fitting. Vertical lines between the black dots and the surface denote the deviation from the fitting surface.
vehicular emissions (Chang et al., 2006; Guo et al., 2007). Propane and methane are the major components of liquefied petroleum gases (LPG) and natural gas (NG), respectively. Fig. 8 shows the concentration contours of these tracers and the total NMHCs extrapolated from the summer noontime data of the 38 sites. Among these tracers, toluene, propane and methane have strong area dependence, and they revealed higher concentrations in the western part of the city, which is consistent with the major distribution of factories and residential areas there. MTBE showed higher concentrations at the sites in the downtown area, which was consistent with the highly populated and urbanized areas. The suburban sites near the mountains showed relatively low levels of the total NMHCs, whereas high concentrations of the total NMHCs were observed in the urban areas, especially in the western part of the city.

To assess the relative importance of biogenic isoprene for atmospheric photochemistry in different areas of the city, the reactivity of isoprene and other 65 NMHCs with the OH radical was used. The reactivity of NMHCs with the OH radical implies NMHC’s potentials for photochemical pollutant formation (Chameides et al., 1992; Dimitriades, 1996; Atkinson and Arey, 2003). The reactivity of individual NMHCs was calculated by multiplying individual NMHC concentrations measured at each urban site by their corresponding \( k_{OH} \) (reaction rate constants of NMHCs with the OH radical). Fig. 9 shows the contour plot of fractional reactivity of isoprene to total NMHC extrapolated from 38 summer noontime samples. Overall, isoprene was the top species with the highest reactivity, accounting for on average 54% of the total NMHC reactivity at noon in the summer. Isoprene contributed large fractions of 50–75% to the total NMHC reactivity at the suburban sites near the mountains because of the higher isoprene levels and lower concentrations of anthropogenic species there. In comparison, it showed relatively small fractions of approximately 30–50% of the total reactivity at the downtown sites. However, isoprene at the downtown sites still ranked first in reactivity among the 66 NMHCs, indicating the remarkable potential of biogenic isoprene to affect urban atmospheric chemistry and air quality in summer in this tropical–subtropical city.

4. Conclusions

Atmospheric isoprene and selected volatile organic compounds (VOCs) were measured by flask samples and GC–MS/FID to address both temporal and spatial characteristics of biogenic

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Average mixing ratios of isoprene in urban and suburban areas; units ppbv (average ± standard deviation).</th>
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<tbody>
<tr>
<td></td>
<td>Urban area</td>
</tr>
<tr>
<td>Summer (noon)</td>
<td>1.51 ± 0.88</td>
</tr>
<tr>
<td>Winter (dawn)</td>
<td>0.19 ± 0.10</td>
</tr>
</tbody>
</table>

* Suburban area includes sites No. 1, 4, 7, 19, 23, 34, 36, and the rest sites are included in urban areas (see Fig. 1).

Fig. 7. Concentration contour plots of isoprene and 1,3-butadiene extrapolated from 38 samples collected at (a) summer noontime and (b) winter dawn. Topography of metropolitan Taipei (Fig. 1) is superimposed on the contour plots. The darker green areas are mountainous terrain on the outskirts of the city basin (see Fig. 1). Suburban area includes sites No. 1, 4, 7, 19, 23, 34, 36, and the rest sites are included in urban areas.
isoprene in a tropical–subtropical metropolis (Taipei). Several important findings were resulted which are summarized as follows: 1. The biogenic contributions overwhelmed their anthropogenic counterparts in summer and dominated the daytime isoprene levels in spring and autumn. Even in winter, a significant fraction of approximately 44% of the daytime level still existed. 2. The contour plots calculated from 38 samples throughout the city revealed that high levels of biogenic isoprene were generally a widespread phenomenon in summer. 3. The relationship between isoprene/1,3-butadiene ratio and ambient temperatures and radiation flux showed a temperature threshold, beyond which the biogenic contribution began to increase exponentially with temperature. However, when the ambient temperature was below the threshold, there was no or negligible biogenic contribution to the ambient isoprene, regardless of the radiation intensity. 4. The temperature threshold (approximately 17–21°C) of isoprene emissions in the tropical–subtropical city was higher than the thresholds at temperate latitudes, indicating that the adaptation of plant physiology to different temperature zones via isoprene emission may be characteristic. 5. Different from the enclosure measurements and above-canopy flux studies with relatively controlled simplified environmental conditions, our findings indicate a composite response of biogenic isoprene to ambient temperature and radiation flux in a metropolis with a large variety of thriving plant species, heavy traffic and complex pollutants.
Fig. 9. Contour plot of fractional reactivity of isoprene to total NMHC extrapolated from 38 summer nocturnal samples.

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