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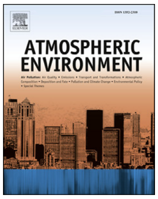

Seasonal characteristics of biogenic and anthropogenic isoprene in tropical–subtropical urban environments

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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.

1. Introduction

Isoprene reacts actively with the hydroxyl radical (OH) and nitrate radical (NO_3), leading to the production of diverse secondary oxidants, e.g., organic peroxy radicals (RO_2), ozone (O_3), 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;

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Chameides et al., 1988; Pacifico et al., 2009). Recently, an increasing number of studies of urban atmosphere and air quality have indicated a significant influence of biogenic isoprene on secondary pollutant formation in urban areas and areas downwind (Li et al., 2007; Wang et al., 2013a; Situ et al., 2013; Lee and Wang, 2006; Xie at al., 2008; Hellen et al., 2012). In a polluted atmosphere with high levels of complex pollutants, the addition of biogenic isoprene might substantially enhance the levels of secondary pollutants through diverse types of anthropogenic–biogenic interactions (Shilling et al., 2013; Pöschl et al., 2000). In contrast, isoprene that is emitted into unpolluted atmospheres is much less of a threat than that released into polluted urban areas (Lelieveld et al., 2008).

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 conditions that are conducive 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 form 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) consisting of both 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 of 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 (CH_4). 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,