



Revelation of Coupling Biogenic with Anthropogenic Isoprene by Highly Time-Resolved Observations

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ABSTRACT

Inter-annual variations of atmospheric isoprene in a major metropolis, Taipei, were reported based on a two-year continuous measurements of non-methane hydrocarbons (NMHCs) with an hourly resolution. It is by far the largest dataset ever collected in the urban subtropical environment with thriving vegetation and traffic flows. The dataset revealed the detailed interplay between the two major sources of biogenic and vehicular throughout the year. To separate the vehicular contribution from the biogenic one for the ambient isoprene, ethylene was used as an indicator of traffic emissions. While dramatic surge of isoprene was observed at noontime in hot months with the highest average peak mixing ratio of 1.6 ppbv in August, its abundance decreased to 0.2 ppbv on average in cold months. The vehicular contribution to ambient isoprene was largely masked over by the noontime surge of isoprene in hot seasons, but was still able to be vaguely observed on the slopes of the isoprene peaks mimicking the rush-hour features of ethylene. In winter, the diurnal variations of isoprene were very similar to those of ethylene, which suggests that ambient isoprene in cold months was almost of traffic origin.

This study based on the continuous dataset could enhance the key findings in previous flask studies in the same metropolis. While canister sampling had a major advantage of area coverage, the highly time-resolved fixed-site monitoring could better reveal the evolution process from a biogenically overwhelmed condition in hot months to the condition where the biogenic source weakened to reveal the traffic source in cold months.

Keywords: Photochemical assessment monitoring stations (PAMS); Ozone formation potentials (OFP); Secondary organic aerosols (SOA).

INTRODUCTION

The atmospheric abundance of a volatile organic compound (VOC) is controlled by the combination of its source strength and removal efficiency (sink). Although selected VOCs can pose direct adverse health effects, the indirect adverse effect can be even more alarming as they can undergo photochemical reactions in the atmosphere to form secondary pollutants such as ozone and fine particles. VOCs are released to the atmosphere from a variety of anthropogenic and biogenic sources (Williams, 2004). Unlike anthropogenic VOCs, which can be mitigated through regulatory policies, biogenic VOCs are difficult to be controlled and; thus, the forge of any control strategy to improve air quality should take into account their potentials as precursors to form secondary pollutants. Of all the biogenic compounds present in the atmosphere, isoprene was the

most studied and reported one because of its ubiquity, significant abundance and extremely high reactivity, creating strong potentials to form secondary oxidants, e.g., organic peroxy radicals (RO₂), ozone, and secondary organic aerosols (SOA). As a result, the isoprene's emissions are of particular importance from the perspectives of atmospheric oxidant capacity, urban air quality and even regional climates (Chameides *et al.*, 1988; Atkinson, 2000; Ryerson *et al.*, 2001; Hallquist *et al.*, 2009; Pacifico *et al.*, 2009; Rollins *et al.*, 2009).

Approximately 90% of the atmospheric isoprene is produced by terrestrial plants (Guenther *et al.*, 2006; Arneth *et al.*, 2008), with the rest contributed from automobile exhaust (McLaren *et al.*, 1996; Borbon *et al.*, 2001). In the past, most of the geographic regions chosen for isoprene study were in temperate, tropical, boreal forests, etc., and the objective was to provide temporal variability of biogenic isoprene. These types of studies are of particular relevance for model validation and further estimates of the potential magnitude of the associated climate feedbacks (Pacifico *et al.*, 2009). Perennial plants growing in populated urban habitats constantly suffer from multi-stressed conditions (Calfapietra *et al.*, 2013). For example, the heat-island effect

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raises the urban temperatures much more (up to 10°C) than the surrounding rural temperatures (Chen *et al.*, 2006). It is commonly acknowledged that the primary environmental controls on the release of biogenic isoprene are light and temperature (Guenther *et al.*, 1993; Shao *et al.*, 2001; Sharkey and Yeh, 2001). With the noontime temperature in summer often approaches 40°C in many megacities worldwide, the release of biogenic isoprene can be even more dramatic (Guenther *et al.*, 1993). High levels of nitrogen oxides meeting with strong isoprene production in urban environments can give rise to substantial production of peroxyacetyl nitrates (PAN), alkyl nitrates and possibly SOA (Ryerson *et al.*, 2001; Fan and Zhang, 2004; Shirley *et al.*, 2006; Hallquist *et al.*, 2009; Rollins *et al.*, 2009). By contrast, isoprene emitted into unpolluted atmospheres by terrestrial vegetation is much less harmful (Lelieveld *et al.*, 2008). Therefore, tropical and subtropical cities with high temperatures and intense sunlight are good incubators for biogenic isoprene emissions, as well as photochemical oxidants.

In an urban setting with significant biogenic isoprene emissions, the inter-annual variations can be rapid owing to its sensitivity to the seasonal and diurnal changes in source strength and reactivity. Although studies of isoprene with in-situ measurements made in the temperate zones were sufficiently extensive and thorough (Borbon *et al.*, 2001; von Schneidmesser *et al.*, 2011; Hellén *et al.*, 2012), vegetation and climate in other latitudinal zones are known to be significantly different, making direct adoption of the temperate findings to subtropical or tropical climates prone to errors. In the past, flask samples were collected in a major city of subtropical climate and found dramatic seasonal/diurnal variations and high temporal variability of terrestrial dependence (Wang *et al.*, 2013; Chang *et al.*, 2014). Although flask sampling can provide the general knowledge of isoprene's abundance and variability in a given region, the on-site continuous monitoring of isoprene can complement flask sampling to provide better details of variability and longer time span in profiling isoprene's inter-annual variations with superb resolution. Such observation is highly desirable in terms of helping solidify isoprene's budget estimates or emission inventory in 3-D photochemical modeling to generate realistic distribution of isoprene with sufficient tempo-spatial resolution in the given climate zone, which in return can complement in-situ measurements which are limited by cost in deployment and operation.

To complement the flask sampling (Wang *et al.*, 2013; Chang *et al.*, 2014), which previously stressed more on spatial variability than temporal resolution, this study attempts to perform the opposite; that is to focus on the temporal variability of isoprene with superb resolution. Isoprene and other selected VOCs with hourly resolution were monitored in the same major metropolis of subtropical climate by an automated monitoring station. Two-year worth of uninterrupted measurements spanning over hot and cold seasons were used to observe the inter-annual variations of atmospheric isoprene with great details in a large metropolis where the source types, land-use and climate may be typical and representative in the warm climate regions.

METHODS

Compounds with molecular size from C₂ to C₁₂ are generally a good representation of the volatility range in defining VOCs. Thus, speciated non-methane hydrocarbons (NMHCs) were continuously monitored by photochemical assessment monitoring stations (PAMS) on the island operated by Taiwan Environmental Protection Administration (EPA) since 2002 to provide hourly mixing ratios of 54 C₂ to C₁₂ species by automated GC with flame ionization detection (FID) (Yang *et al.*, 2005; Chang *et al.*, 2010). The PAMS NMHCs were calibrated every five days by analyzing a gas mixture at sub-ppb levels (Scott Specialty Gas, U.S.). The precision (1σ) for majority of the PAMS species was better than 4% (see Table S1 in Supplementary Information). More analytical details of the PAMS measurements in Taiwan can refer to our previous studies (Wang *et al.*, 2004; Chang *et al.*, 2010; Chen *et al.*, 2014). The PAMS measurements were validated via inter-comparison with various techniques. For instance, the combined total mixing ratios of the 54 PAMS species with a hourly resolution obtained by auto-GCs were inter-compared with non-speciated NMHC measurements (APHA-360, HORIBA, Japan) and found extremely consistent results (Chen *et al.*, 2014). In addition, both flask sampling inter-comparison and a third-party auto-GC validation with the PAMS sites also demonstrated superb consistency (Wang *et al.*, 2004; Chang *et al.*, 2010). Isoprene is a C₅ compound listed as one of the 54 PAMS species analyzed on the hourly basis by the PAMS network. Although 1, 3-butadiene was commonly used as the indicator of vehicular emissions in an urban setting to separate the contributions of biogenic vs anthropogenic sources (Reimann *et al.*, 2000; Borbon *et al.*, 2001; Wang *et al.*, 2013; Chang *et al.*, 2014), it was not targeted by the PAMS list of the 54 target compounds. Instead, ethylene was used as the surrogate of vehicular source (McLaren *et al.*, 1996; Reimann *et al.*, 2000; Borbon *et al.*, 2001) (See Fig. S1 for the peaks of isoprene and ethylene for a typical analysis of ambient air).

Of the nine PAMS sites across the island, the Wanhua PAMS site, situated in the great Taipei metropolis with a population of over six million, was chosen to represent a typical urban setting with vegetation and vehicular emissions being the two dominant sources of biogenic and anthropogenic, respectively (Fig. 1). The Wanhua site used in this study was one of the nine stations of the PAMS network across the island (Chen *et al.*, 2014), and is one of the two stations in Taipei primarily influenced by vehicular, residential and biogenic sources. No apparent industrial sources were in the surroundings. The station was placed on a two-story building in an elementary school, and had been operated continuously since 2006. Two-year worth of data from 2008 to 2010 for the Wanhua site were used for the study, which included approximately 5×10^5 data points. This highly temporally resolved dataset from a fixed site revealing very detailed features in variations of the PAMS species, including isoprene and ethylene, is hardly achievable by the flask sampling method (Wang *et al.*, 2013; Chang *et al.*, 2014).

The climate of Taipei is typical of a subtropical city with

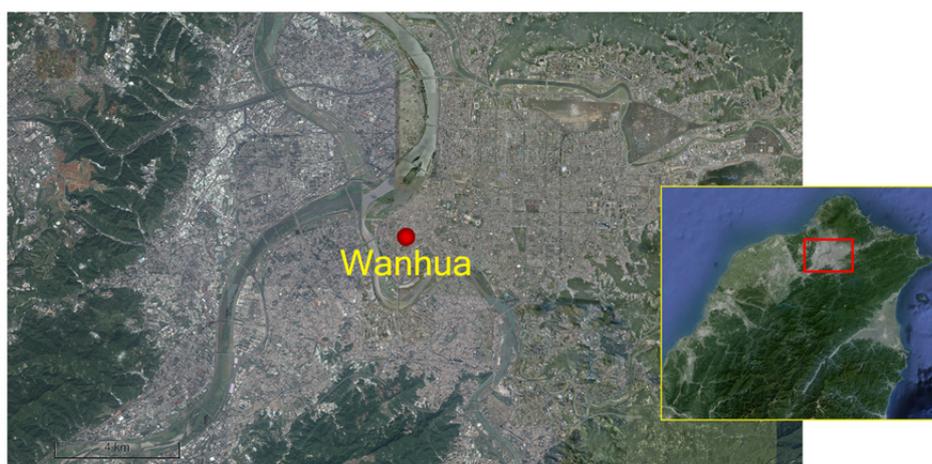


Fig. 1. Location of the PAMS site, Wanhua, used in this study.

high humidity and mild climate with an average annual temperature about 23°C. Its coldest months are from January to February and the warmest months are from July to August. During winter, the city is often dominated by the continental high-pressure systems from Mongolia and Siberia to experience multiple cold fronts and monsoonal winds with an average temperature of 17°C and minimum temperature of 10°C for January. In summer, the weather is controlled by the marine high-pressure system in the Pacific, prevailed by humid, southwestern winds with an average temperature of 30°C and maximum temperature of 38°C for July and August. The generally warm climate and ample precipitation facilitate the growth of vegetation on the island, as well as in and around the city as a basin type of terrain. Different from the temperate climate where coniferous and deciduous forests dominated the vegetation, thick evergreen broad-leaved forests dominated the vegetation of the city and the hills surrounding the basin.

RESULTS AND DISCUSSION

Statistics of Ethylene and Isoprene

Fig. 2 illustrates the time-series mixing ratios of both isoprene and ethylene with the hourly resolution at the Wanhua site from 2008 to 2010. The data of ethylene are also shown to represent the vehicular source arising from incomplete combustion and to pose a contrast to the data of isoprene. The very dense dataset shows the “raw” condition prior to any data averaging or analysis. Compared to ethylene, isoprene appeared to show a much more dramatic seasonality. In addition, rather large variability associated with the seasonal profile was noticed. The much clearer seasonal profiles for the two species are shown in Fig. 3 as box plots with each month averaged over two years of data for that month. Despite large data variability in both Figs. 2 and 3, notably the mixing ratios of isoprene elevated in summer, but subsided in winter. By contrast, ethylene showed opposite seasonality despite a less dramatic one. Since the traffic source can be assumed to be non-seasonal, the observed seasonality for ethylene and most of the other target PAMS species (data not shown), can be attributed to the lower

mixing height in winter and stronger photolysis in summer. Although isoprene is also subject to the same meteorological factors, the intense emissions of isoprene in summer (hot seasons) outweighed other factors in shaping its distinct seasonality (Lee and Wang, 2006; Chang *et al.*, 2014). While seasonality is clearly revealed in Figs. 2 and 3, the rather large variability with the data is mostly arising from the diurnal behaviors of the two species.

Scatter Plots of Isoprene vs. Ethylene to Reveal Biogenic Contributions

The scatter plots of isoprene versus ethylene provide another way to look at the biogenic contribution in addition to the anthropogenic one. The notion is that there exists a common source if both species are correlated with each other. In Fig. 4, the data were divided into daytime (from 08:00 a.m. to 04:00 p.m.) and nighttime (from 08:00 p.m. to 04:00 a.m.) periods for four seasons to show the excess concentrations of isoprene besides vehicular contribution. In summer, a large percentage of the daytime samples showed large excess concentrations contributed by the biogenic source in addition to the automobile contribution, which accounted for most of the nighttime concentrations. The data points of excess concentrations were either lower in concentration or less spread-out for spring and fall compared to those of summer, whereas almost no excess concentrations and thus no biogenic contributions were found in winter, since the daytime and nighttime observations showed similar isoprene-to-ethylene ratio.

Interplay between Biogenic and Anthropogenic Sources

Although the strong biogenic contribution of isoprene in warm seasons is well recognized in this climate zone (Lee and Wang, 2006; Chang *et al.*, 2014), the dynamic transition for the biogenic source to be turned on and thrive in hot months, and then to gradually weaken and be even completely turned off in coldest months can be closely visualized from the continuous data. In Fig. 5, the two-year data were calculated into a monthly diurnal form without discarding any data points to reveal both seasonal and diurnal variations. A large seasonal difference is noticed for isoprene

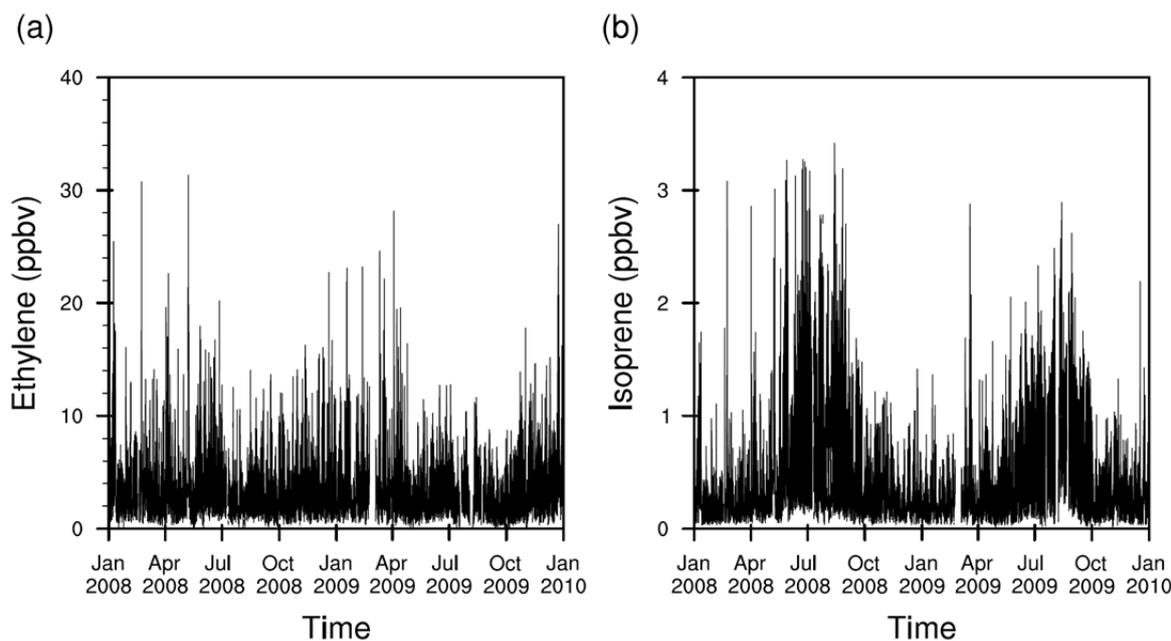


Fig. 2. Time-series observations of ethylene and isoprene with hourly resolution for the Wanhua dataset to demonstrate the raw condition prior to any data analysis or averaging.

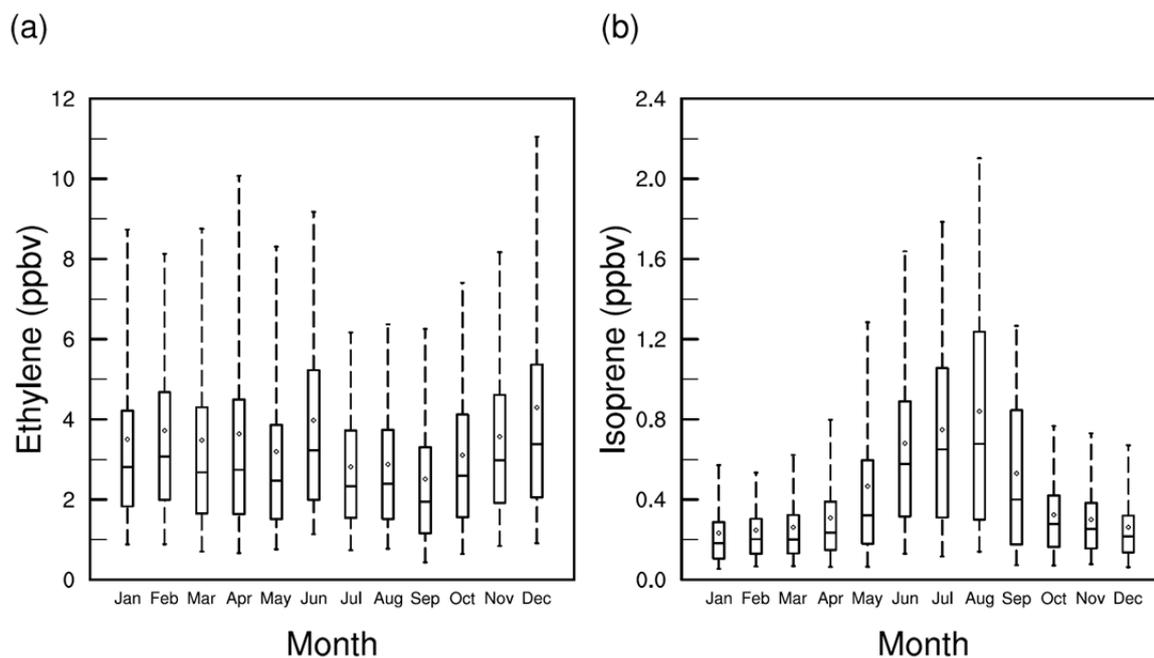


Fig. 3. Box plots of the Wanhua data to show seasonal variations and data spread for (a) ethylene, and (b) isoprene. Medium (short bar within the box), average (round circle), 75 and 25 percentiles (upper and lower ends of the box), as well as 95 and 5 percentiles (two extremes) are shown for each month.

compared to ethylene. While the diurnal features of ethylene remained the same throughout a year, namely the double humps corresponding to the morning and evening rush-hour traffic, the diurnal features of isoprene are distinctly different between the hot and cold months (Fig. 5). Very intense biogenic production of isoprene was noticed in the summer months contributing to the noontime maxima; however, biogenic activity appeared to weaken as the time

elapsed into colder months and revealed the double humps similar to those of ethylene. The magnitude of diurnal variations for ethylene was less than two fold throughout the year, whereas it could reach as high as eight fold in summer, but decreased to about two fold in winter for isoprene, which is similar to the magnitude of ethylene. The noontime maximum mixing ratios for isoprene can reach 1.6 ppbv in August compared to only 0.2 ppbv in January, which are very

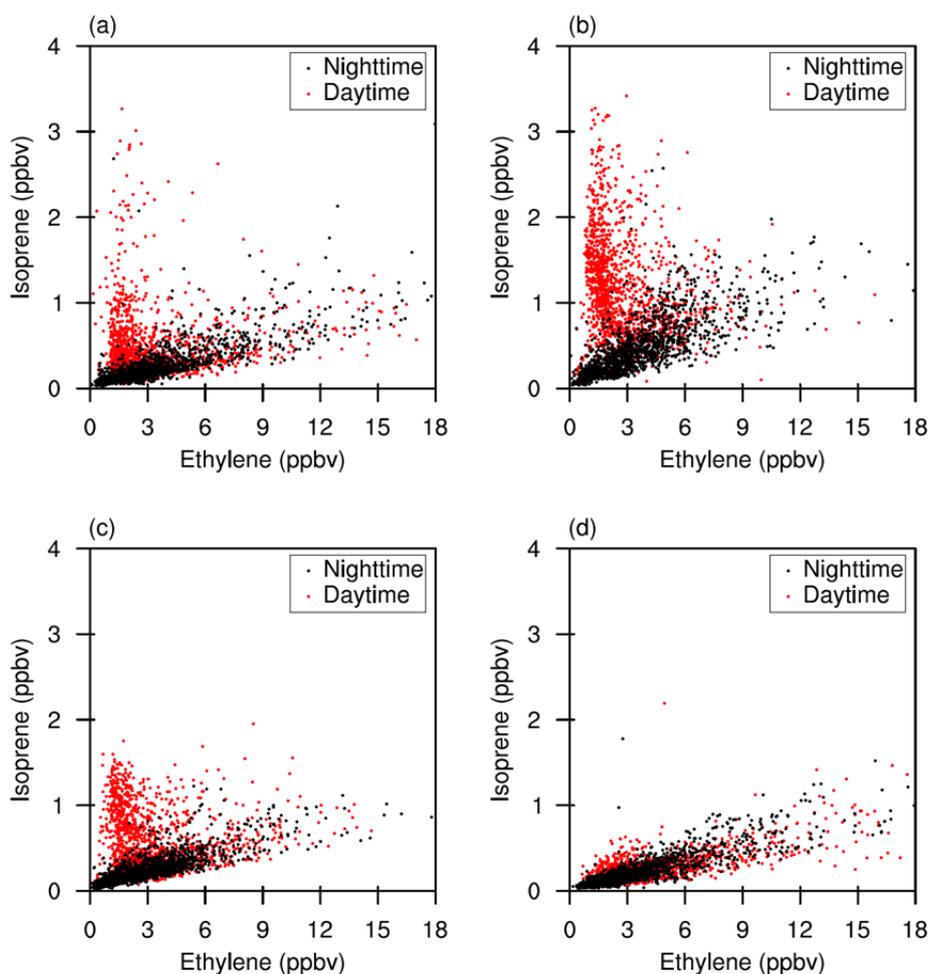


Fig. 4. Scatter plots of isoprene vs. ethylene for four seasons to show excess concentrations of isoprene besides vehicular contribution. Only two periods of data were used for this purpose: daytime (from 08:00 a.m. to 04:00 p.m.) and nighttime (from 08:00 p.m. to 04:00 a.m.) for four seasons. (a) Spring; (b) summer; (c) fall; (d) winter.

close to the flask measurements of about 1.8 and 0.2 ppbv, despite different sampling and analytical methods (Chang *et al.*, 2014). The nighttime mixing ratios for isoprene throughout the year were rather uniform (around 0.2 ppbv) compared to the daytime mixing ratios. Presumably, the “left-over” from daytime photolysis in addition to the traffic emissions are responsible for the observed nighttime abundance of isoprene. The rush-hour features of isoprene were largely masked over by the intense noontime biogenic peaks in summer months, and only began to reveal when the biogenic source subsided or was turned off. As shown in Fig. 5, the rush-hour humps of isoprene were almost identical to those of ethylene in the winter months of January and February, suggesting that in cold months little biogenic emissions existed and the vehicular emissions became the only major source of ambient isoprene. Despite that the large noontime peaks of isoprene in summer overshadowed the rush-hour traffic emissions; however, on closer look, the morning and afternoon rush-hour emissions of isoprene can still be spotted on the two slopes of the peaks, as indicated by the arrows in Fig. 5 as a few examples.

Such a detailed evolution of atmospheric isoprene over

time exhibiting the interplay between the biogenic and anthropogenic sources was rarely reported in the literature, particularly at the tropical-subtropical latitudes. The evolution of interplay could not be as clearly revealed, if there had not been the highly temporally resolved measurements.

Ozone Formation Potential (OFP) and OH Reactivity

The observed midday peak of isoprene should be regarded as the concentrations of equilibrium resulting from the balance of emissions and photochemical loss; this indicates that the originally emitted daytime isoprene is greater than the actually observed. Since the midday peak of isoprene is aligned in time with the peak of OH, a condition that is conducive to photochemical loss (Lee and Wang, 2006), the midday thrive of biogenic isoprene could add fuel to photochemistry to enhance formation of secondary pollutants, such as ozone and secondary organic aerosols (SOA). The dramatic difference between the warm and cold months in isoprene emissions could translate into an air quality issue resulted from biogenic contribution in warm months.

Several reactivity scales of VOCs have been proposed for the convenient evaluation of ozone formation potentials

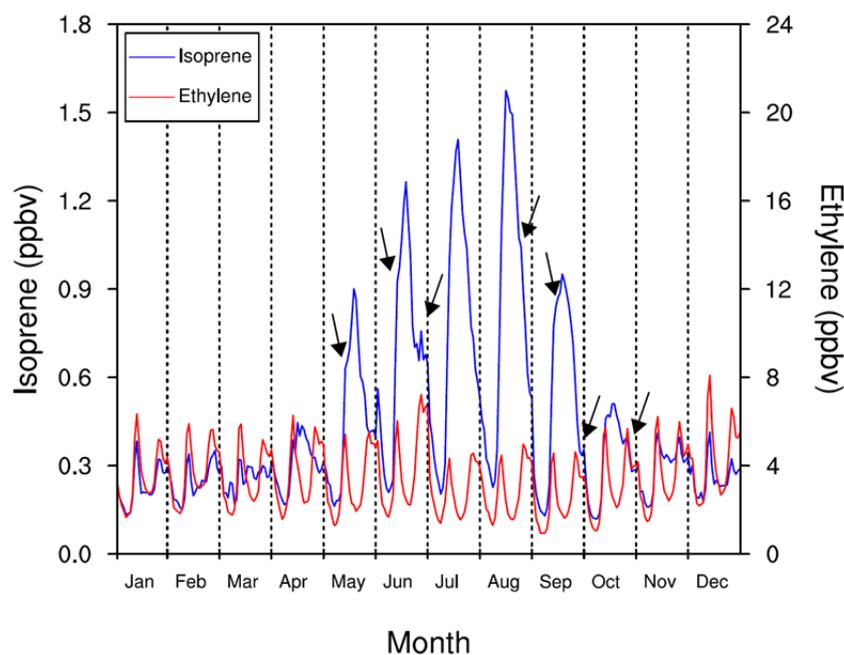


Fig. 5. Monthly diurnal variations for isoprene and ethylene throughout the year. Arrows indicate the rush-hour emissions that can be vaguely seen on the slopes of the isoprene peaks in warm seasons.

(OFPs) or their relative reactivities in the atmosphere. In the study, both the methods of maximum incremental reactivity (MIR) method and reactivity based on k_{OH} were used to calculate the OFPs and OH reactivities of the 54 NMHCs, respectively (see Table S2 in Supplementary Information). After the initial reaction of VOCs with OH, peroxy radicals are formed, and the ensuing reactions with NO_x generate photochemical smog. In addition, these oxidation reactions also produce secondary products in addition to ozone. Oxidation of VOCs and its products may introduce additional functional groups that tend to make the subsequent products less volatile and more water soluble or that lead to fragmentation of the carbon chains to form oxygenates of lower molecular weight (Hallquist *et al.*, 2009). The MIR method is used to estimate the OFPs of individual VOCs for ozone formation. Although the initial reactivity of a VOC with OH in the k_{OH} method does not directly reflect OFP, it implies the potential for subsequent product formation after reaction with OH.

To grasp a rapid estimate of the ozone-forming abilities resulted from precursors in urban-suburban environments, the MIR method was used to predict the highest incremental reactivity of the VOC mixture by adjusting the NO_x concentration (Czader *et al.*, 2008). Fig. 6 shows both the relative OFPs and k_{OH} reactivities of the 54 VOCs at the Wanhua site for the midday hours (11:00 a.m. to 02:00 p.m.) by grouping the target compounds into four categories of alkanes, alkyne (containing only one species of acetylene), alkenes, aromatics and isoprene. The fraction of isoprene in the total NMHC abundance is small (max. = 5% in August); however, its importance in photochemistry was amplified after taking into account of the MIR. Its OFP was 10% of the total in August and about 8% for the summer midday average, which is close to the results of

canister sampling in the same district of the city (Wang *et al.*, 2013). Due to the much smaller MIRs compared to other functional groups alkanes, although alkanes abundance amounted to nearly 70% of total abundance, their OFPs contributed to less than 20% of the total. Since both alkenes and aromatics are mainly released from vehicles, their combined OFPs of > 70% of the total, suggesting that vehicular source was still the dominant factor to control air quality in this city based on the MIR calculation.

The reactivities of individual NMHCs were calculated by multiplying individual NMHC concentrations by their corresponding k_{OH} (reaction rate constants of NMHCs with the OH radical). The much simpler method of k_{OH} led to an even a greater amplification in photochemistry for isoprene, showing more than 30% in total reactivity in August and approximately 27% for the summer midday average, which is similar to what the canister has observed at the downtown area (Wang *et al.*, 2013).

Temperature Sensitivity

Fig. 7 shows the plot of isoprene/ethylene ratios versus ambient temperature for the midday hours (11:00 a.m. to 02:00 p.m.) in four seasons. The ratios of isoprene to ethylene instead of the absolute concentrations of isoprene were used to cancel off the factors of air mixing and the vehicular contribution. Thus, the data points in Fig. 7 directly reflects the source characteristics of biogenic isoprene responding to the ambient temperature. An exponential increase for the ratio vs. temperature was apparent, suggesting a rapid acceleration of isoprene emission at an onset temperature of approximately 30°C. The winter ratios (blue dots) are concentrated on the left bottom of the plot and remain flat, while the summer ratios (red dots) are mostly on the upper right of the plot with a very steep curvature. The

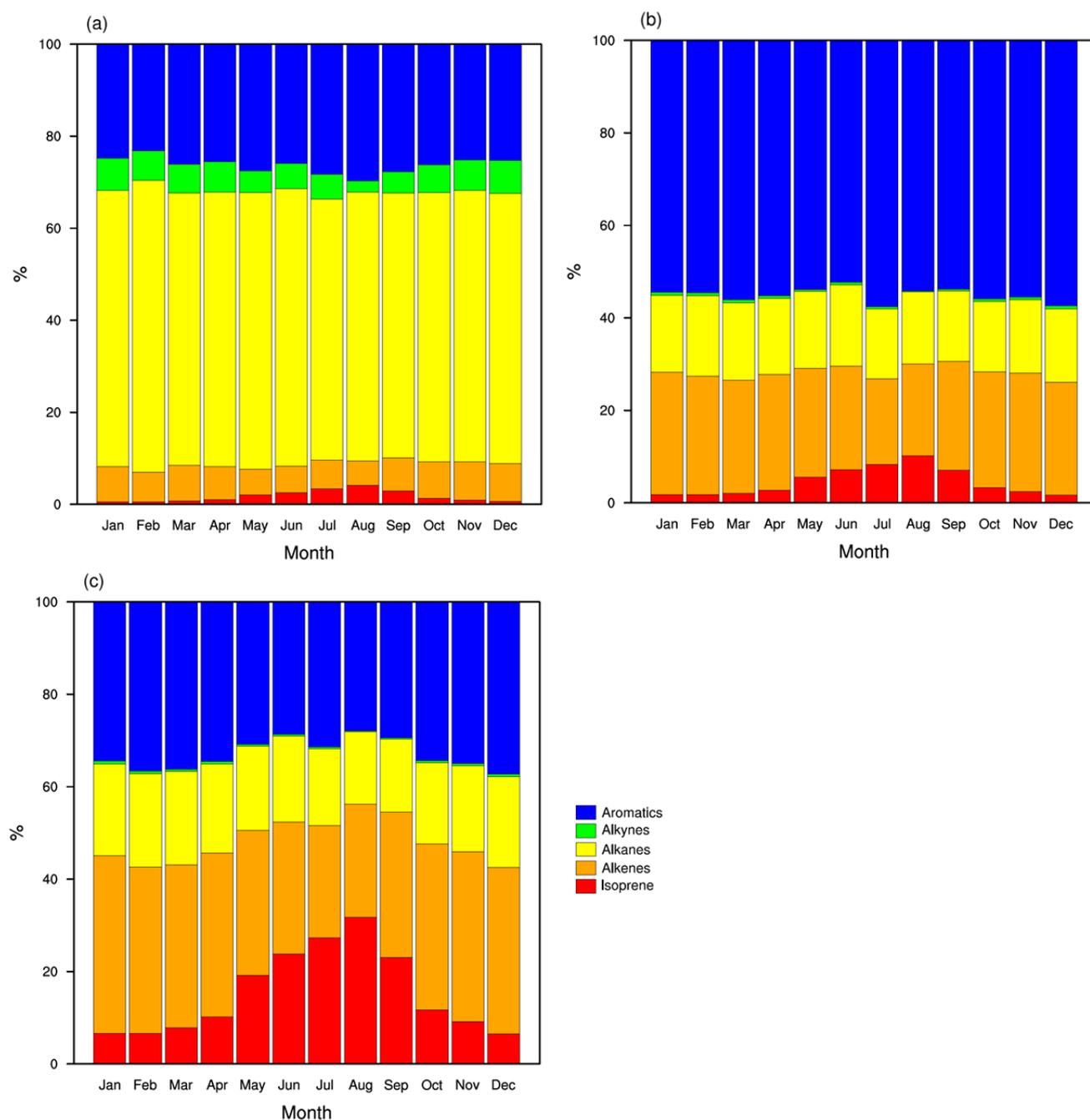


Fig. 6. OFPs and reactivities for five groups of compounds. (a) Percent contributions in abundance, (b) percent contributions in OFP based on MIR calculation, (c) percent contribution in reactivity based on k_{OH} calculation.

rather flat section of the curve fitting the winter data in Fig. 7 are an analogy of Fig. 4(d) with a regression slope of 0.06 (Fig. S2 in Supplementary Materials). This result is in support of the previous finding reported by the flask sampling study (Chang *et al.*, 2014), except that the highly temporally resolved dataset in this study can further reinforce the findings from the flask sampling in visualizing the emission acceleration with temperature. The extremely high sensitivity of biogenic isoprene production towards the high temperature zone could be of a concern in urban areas where the land use and climate change have significantly

elevated the urban temperature. The urban heating can add additional stress to vegetation to produce excess biogenic VOCs, which further worsens air quality in the presence of ample oxidants such as hydroxyl radicals, ozone and NO_x (Ghirardo *et al.*, 2016).

CONCLUSIONS

Based on a two-year dataset of NMHCs including isoprene and ethylene measured from a PAMS site in Taipei, a subtropical metropolis with thriving vegetation and congested

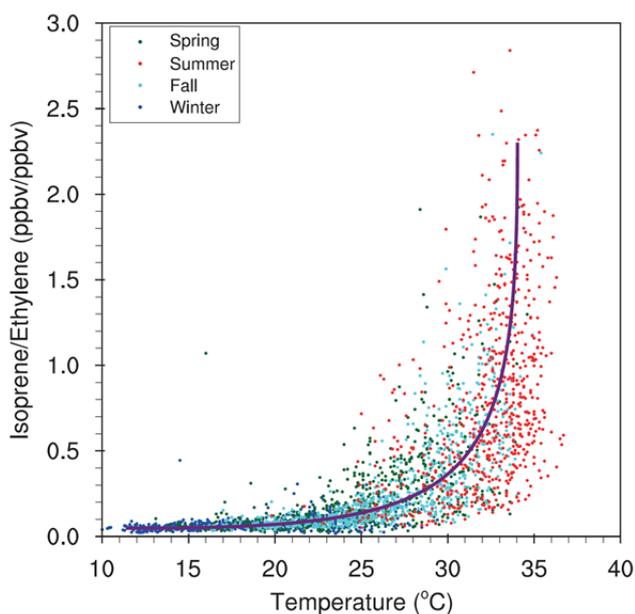


Fig. 7. Midday ratios of isoprene to ethylene vs. temperature for the noontime hours from 11:00 to 14:00. Four colors correspond to different seasons.

traffic, the detailed inter-annual variations of seasonal and diurnal cycles of the two species with an hourly resolution were reported. It was found that the biogenic isoprene overwhelmed the anthropogenic counterpart (vehicular emissions) in warm seasons, but it subsided to a negligible level to only reveal the anthropogenic features similar to those of ethylene. The high temporal resolution of the fixed-site dataset allowed the revelation of the very dramatic seasonal variations of isoprene and the detailed dynamic transition from a biogenic dominant condition in hot months to an anthropogenic dominant condition in cold months. The rapid acceleration of emissions of biogenic isoprene surpassing the onset temperature of approximately 30°C suggests that a full-blown supply of isoprene as a strong reducing agent can fuel photochemistry in hot weather to enhance potentials to form secondary pollutants including ozone and SOA.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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