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Biogenic isoprene and implications for oxidant levels in Beijing during the 2008 Olympic Games

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Abstract

As the host of the 2008 Summer Olympic Games, Beijing implemented a series of stringent, short-term air quality control measures to reduce the emissions of anthropogenic air pollutants. Large reductions in the daily average concentrations of primary pollutants, e.g., non-methane hydrocarbons (NMHCs) and nitrogen oxides (NO_x) of approximately 50 % were observed at the air quality observatory of Peking University. Nevertheless, high levels of ozone were present during the control period. Although anthropogenic precursors were greatly reduced, the meteorological conditions in summer, including high temperature and light flux, are conducive to the production of large amounts of biogenic isoprene, which is extremely reactive. The diurnal pattern of isoprene showed daily maximum mixing ratios of 0.83 ppbv at noon and a minimum at night, reflecting its primarily biogenic properties. Using the ratio of isoprene to vehicle exhaust tracers, approximately 92 % of the daytime isoprene was estimated from biogenic sources, and only 8 % was attributed to vehicular emissions. In terms of OH reactivity and the ozone formation potential (OFP), biogenic isoprene with its midday surge can contribute approximately 20 % of the total OFPs and 40–50 % of the total OH reactivities of the 65 measured NMHCs during the midday hours. The discrepancy between decreased precursor levels and the observed high ozone was most likely caused by a combination of many factors. The changes in the partition among the components of oxidation products (O_3, NO_2 and NO_z) and the contribution of air pollutants from regional sources outside Beijing should be two primary reasons. Furthermore, the influences of biogenic isoprene as well as the non-linearity of O_3-VOC-NO_x chemistry are other major concerns that can reduce the effectiveness of the control measures for decreasing ozone formation. Although anthropogenic precursors were greatly reduced during the Olympic Games, sufficient biogenic isoprene and moderate NO_x were still present in the conditions of high radiation flux and temperature during midday and early afternoon, which can still contribute a significant fraction of midday and early afternoon O_3.

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1 Introduction

Beijing, the capital of China, is a major urban center located on the North China Plain. The rapid growth of the city and surrounding areas is accompanied by worsening air quality; ozone and particulate matter are the most serious contaminants in recent years (Shao et al., 2006; Wang et al., 2006; Beijing EPB Environmental Quality Communique, 2010). As the host of the 29th Olympic Games, the Beijing government implemented a series of stringent, short-term air quality control measures on major air pollution sources from 1 July to 20 September 2008 to reduce the emissions of air pollutants during the Olympic period (Wang et al., 2010a); this provided an opportunity to investigate the responses of secondary and primary pollutants to the control measures. The target sources included motor vehicles, gas stations, paint and solvent use, petrochemical factories, steel factories, power plants, etc. Emission inventory studies revealed that the traffic emissions of volatile organic compounds (VOCs), carbon monoxide (CO), nitrogen oxides (NO_x), and particulate matters (PM_{10}) were estimated to be 50 % less than their normal levels in Beijing (Zhou et al., 2010; Wang et al., 2010b). The reductions in these pollutants have also been validated by ground-based observations (Liu et al., 2009; Wang et al., 2009a, b, 2010a, c). Wang et al. (2010c) reported that ambient concentrations of vehicle-related NO_x and VOCs near the Olympic Stadium dropped by 25 % and 20–45 % in the first two weeks after the full controls were implemented. Chou et al. (2011) compared the summer data of 2008 with 2006 at an air quality observatory of Peking University; the non-methane hydrocarbons (NMHCs), CO, NO_x, and total odd reactive nitrogen (NO_y) were decreased by 49.7, 27.8, 42.2, and 56.5 %, respectively. Wang et al. (2009a) studied the changes in on-road air pollutants using a mobile laboratory, and the results show obvious reductions in gaseous pollutants of up to 54 % for CO, 41 % for NO_x, 70 % for SO_2 and 66 % for the sum of benzene, toluene, ethylbenzene and xylene (BTEX).

Evidently, the air pollution control measures successfully reduced the ambient levels of the primary air pollutants in Beijing during the Olympic Games. In contrast to the substantial reduction of primary air pollutants, the mitigation of ozone (O_3) in Beijing during the Olympic period was not as expected, although the precursors to ozone production, i.e., NMHCs and NO_x, were decreased (Wang et al., 2010c; Chou et al., 2011). In particular, the ozone formation potentials (OFPs) of the anthropogenic NMHCs had been reduced by 48 % (Wang et al., 2010a). The phenomenon of the decreased precursors and the observed high O_3 is interesting; thus, several proposals regarding the cause of the inconsistency were published (Wang et al., 2010c; Chou et al., 2011). A basic reason for the inconsistency was the reduced NO-O_3 titration, which was a result of the reduction in NO_x emissions. Chou et al. (2011) reported that the daily average total oxidants (defined as $O_x = O_3 + NO_2 + 1.5NO_z$, and $NO_z = NO_y + NO_x$) were reduced by 21.3 %, although O_3 increased by 42.2 %. Wang et al. (2010c) suggested that the weather conditions and the regional sources influenced and contributed significantly to the secondary pollutant levels in urban Beijing. All of these proposals as well as the non-linearity of O_3-VOC-NO_x chemistry are very likely the causes of the discrepancy between the decreased levels of precursors and the observed high ozone levels during the control period. Another significant factor which cannot be ignored is the biogenic VOCs, as biogenic sources were not targets of the control measures.

Wang et al. (2003) estimated that large amounts of 1.6×10^{10} g C of total annual biogenic VOCs were emitted from vegetation in Beijing, and biogenic isoprene accounted for half of these emissions. Isoprene has drawn attention because of its pervasive sources and extremely high reactivity, which leads to the production of secondary oxidants (Atkinson, 2000; Ryerson et al., 2001; Hallquist et al., 2009; Rollins et al., 2009; Pacifico et al., 2009). In contrast to most other precursors of secondary oxidants, which almost exclusively originate from anthropogenic sources, a significant fraction of isoprene is biogenic in origin. Studies of enclosure and above-canopy flux measurements have shown that the primary environmental controls on isoprene emission are light and temperature (Guenther et al., 1993; Shao et al., 2001; Sharkey et al., 2001). Biogenic isoprene increases dramatically as the temperature rises, and the highest mixing ratios usually occur during the midday hours. High temperature and light flux during summer in Beijing provide conditions that are conducive for biogenic isoprene emissions. The coherence with the OH diurnal pattern accentuates the significance of biogenic isoprene and its potentially large impact on photochemistry and secondary pollutant formation. Although anthropogenic precursors were decreased greatly during the control period, biogenic isoprene might still be reactive enough to support and even dominate secondary pollutant formation.

This study aims to provide a clearer understanding of the role of biogenic isoprene in Beijing during the Olympic period when the emissions of anthropogenic precursors were stringently controlled. Hourly data for 65 NMHCs, including isoprene, during the Campaign for Air Quality Research in Beijing and Surrounding Region-2008 (CAREBeijing-2008 campaign) are presented to assess the relative significance of biogenic isoprene and anthropogenic NMHCs in secondary pollutant formation. Regression analyses for the concentrations of isoprene and some common exhaust tracers are used to separate biogenic isoprene from its anthropogenic counterpart. Furthermore, factors responsible for the discrepancy between the decreased anthropogenic precursors and observed high ozone levels are also investigated in terms of the precursors, photochemistry and dynamics.

2 Methodology

2.1 Site description and instrumentation

To investigate the air quality and atmospheric chemistry during the Olympic Games, the CAREBeijing-2008 campaign was conducted in Beijing and the surrounding region in the summer of 2008. During the campaign, an integrated observatory with a variety of instruments was set up on the campus of Peking University (PKU). PKU is in the northwest section of downtown Beijing and is surrounded by major traffic arteries, business buildings, busy streets, shops and residential apartments, which is representative of the urban environment in Beijing (Song et al., 2007; Cheng et al., 2008). The air inlets of the instruments were set up on the roof of a 6-story building (~ 25 m above ground). Over 700 hourly-average data points for 65 NMHCs, CO, NO, NO_2, NO_y, O_3 and the meteorological parameters during 1 August through 30 August 2008 were integrated for the study. The instruments relevant to the study are described in the following sections.

2.1.1 NMHCs

The continuous VOC measurement during the CAREBeijing-2008 campaign was conducted by an automated GC-MS/FID (Varian Saturn 2200 ion-trap mass spectrometry, MS and flame ionization detector) system using parallel columns and two detectors to simultaneously analyze a large variety of VOCs, including the C_2-C_{11} NMHCs (listed in Table 1), ≥ C_1 halocarbons, chlorinated compounds, etc. with each injection (Wang et al., 2012; Chang et al., 2003). A glass Y-splitter split the flow of thermal desorption to two columns, i.e., a PLOT column (30 m × 0.32 mm, $d_f = 5\,\mu m$, Chrompack) connected to FID for separating and detecting the extremely volatile C_2-C_4 NMHCs and a DB-1 column (60 m × 0.3 mm, $d_f = 5\,\mu m$, J&W) connected to MS for a larger variety of VOCs. Four internal standards, i.e., bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5, and 1-bromo-4-fluorobenzene, were blended with each sample aliquot to check the stability of the MS and to ensure the data quality. The precision (repeatability, 1σ) for most species was in the range of 0.5–2 %, and the limits of detection for most of the species were below 30 pptv. A standard gas mixture, 65 C_2-C_{11} NMHCs (Scott Marrin Inc., Riverside, CA, USA), was employed for concentration calibrations of target NMHCs, and another standard gas mixture, C_2-C_{12} NMHCs (Spectra gases, Branchburg, NJ, USA), was used for quality control.

2.1.2 NO, NO_2 and NO_y

NO was measured using a chemiluminescence detector (Model 42C-TL, Thermo Scientific). NO_2 was measured with a system consisting of a chemiluminescence detector

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(Model CLD 88p, ECO Physics) and a photolytic converter (Model PLC 860, ECO Physics). The efficiency of the converter kept at ~ 66 % throughout the campaign was determined using the gas titration method. A NO_y converter (ECO Physics) was employed to reduce the NO_y species to NO with CO on the surface of a gold tube at 300 °C. The efficiency of this converter was ~ 100 %, and the efficiency was checked by HNO_3 measurement in the laboratory before the field experiment and was consistent with the literature (e.g., Fehsenfeld et al., 1987). Daily calibration of the chemiluminescence detectors was performed during 19:00–20:00 LT. The detection limits of the instruments were estimated by 3 times the standard deviation of the signals of zero-air measurements, which were 0.3, 0.1, and 0.3 ppbv for NO, NO_2, and NO_y, respectively.

2.1.3 CO, O_3 and meteorology

In addition to the VOCs and $NO/NO_2/NO_y$ instruments for the intensive experiments, the PKU observatory was equipped with a general air quality station. All the instruments were calibrated regularly at midnight each day during the campaign. The CO and O_3 data from the station is included in the following analysis and discussion. In addition, the total short-wave irradiance, SWI, (0.3–3.0 µm) was measured using an Eppley precision spectral pyranometers (PSP).

2.2 Assessment of biogenic and anthropogenic contributions to isoprene

In urban areas, isoprene has both biogenic and anthropogenic sources (Borbon et al., 2001; Wang et al., 2013). Several studies have quantified isoprene in vehicle exhaust (Duffy et al., 1999; Borbon et al., 2001), and measurements in temperate urban winter periods have revealed a strong correlation between isoprene and common vehicle exhaust tracers, such as 1,3-butadiene, alkenes and carbon monoxide (Reimann et al., 2000; Borbon et al., 2001; McLaren et al., 1996). The results indicate that anthropogenic sources of isoprene in the investigated cities were mainly a result of vehicle exhaust. Considering that anthropogenic isoprene has a strong correlation with vehicle

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exhaust tracers, simple regression analyses for the concentrations of isoprene and exhaust tracers can be used to estimate the contributions of anthropogenic and biogenic sources to ambient isoprene levels (Borbon et al., 2001; Reimann et al., 2000; Wang et al., 2013).

2.3 Relative potentials of VOCs for secondary pollutant formation

The photochemical reactivity differs greatly among various VOCs (Carter and Atkinson, 1989; Atkinson, 2000; Atkinson and Arey, 2003). Several reactivity scales of VOCs have been proposed for the evaluation of ozone formation potentials (OFPs) and their relative reactivities in the atmosphere (Carter, 1994; Atkinson and Arey, 2003; Dimitriades, 1996). A common reactivity scale, maximum increment reactivity (MIR), based on calculating effects of VOCs on O_3 formation under various NO_x conditions in model scenarios (Carter, 1994) provides convenient indices for quantifying ozone-forming impacts imposed by precursors. In addition, the k_{OH} reactivity method is another means of referencing VOC reactivities with OH radical (Chameides et al., 1992; Dimitriades, 1996; Atkinson and Arey, 2003). Oxidation of VOCs by OH leads to formation of organic peroxy radicals which are important intermediates in the secondary pollutant formation. In addition to participation in O_3 formation, organic peroxy radicals also take part in other oxidation reactions in the atmosphere, which can lead to the formation of diverse oxidants, e.g., NO_2, organic nitrates, peroxyacyl nitrates (PANs) and HNO_3. The MIR and k_{OH} reactivity methods are defined differently and Wang et al. (2013) used the two methods to address different purposes. The MIR method can be used to estimate the potentials of individual VOCs for O_3 formation. Although the initial reactivity of a VOC with OH in the k_{OH} reactivity method does not directly reflect OFP, it is involved in the production rate of organic peroxy radicals and implies the potential for formation of subsequent products. In the study, both the MIR method and the k_{OH} reactivity method were utilized. The OFPs and OH reactivities of individual VOCs were calculated by multiplying individual VOC concentrations measured at PKU by their corresponding MIR and k_{OH} (reaction rate constants of VOCs with OH radical), as shown in Table 1.

3 Results and discussion

3.1 Characteristics of isoprene during the 2008 Olympic Games

3.1.1 Diurnal variations of isoprene, temperature and radiation

To investigate the diurnal emission characteristics of isoprene and assess the influence of temperature and solar radiation on isoprene during the 2008 Olympic Games, air sampling and meteorological observations were conducted synchronously at the PKU site to obtain the diurnal variation of isoprene, 64 other NMHCs, CO, NO, NO_2, NO_y, O_3 and the meteorological parameters (e.g., temperature, solar radiation and wind speed). The trace gas data during the CAREBeijing-2008 campaign were representative of those under stringent control measures. To draw a contrast, the data observed at the same air quality observatory of Peking University during the CAREBeijing-2006 summer campaign (Xie et al., 2008) that did not include stringent control measures were utilized for comparison.

Diurnal variations in the mixing ratios of isoprene, temperature, radiation and wind speed are shown in Fig. 1. During the two campaigns, the meteorological data showed similar patterns. The temperature varied with the regular diurnal patterns of maximum temperatures at approximately 14:00 and minima at dawn. The ambient temperature and radiation flux during CAREBeijing-2008 were slightly higher than those during CAREBeijing-2006, and the average wind speed decreased by $\sim 40\,\%$. In general, the weather conditions of 2008 were more favorable for the emission and accumulation of biogenic isoprene.

The isoprene measured during the two campaigns showed similar patterns, with the daily maximum isoprene of $0.8 \sim 0.9$ ppbv occurring during midday. After that, the isoprene decreased gradually to its minimum level before dawn. The sensitivity of isoprene to sunlight intensity and temperature indicate the source of isoprene to be primarily biogenic. However, both campaigns showed isoprene leveling off from approximately 09:00 to 15:00, which was very different from the sharper maximums of isoprene in rural environments (Biesenthal et al., 1997; Montzka et al., 1993; Goldan et al., 1995). Because the diurnal variation of isoprene is influenced by a wide range of biological, chemical and dynamical processes, one reason for isoprene leveling off at the urban site may be attributed to larger dilution effect of raising mixing layers and higher wind speed at and after noon. Another possible reason for the pattern different from those in rural environments is the potentially larger consumption of isoprene due to extensive chemical reactions with other complicated pollutants and/or oxidants in polluted urban settings (Shirley et al., 2006; Ryerson et al., 2001; Hallquist et al., 2009).

As shown in Fig. 1a, there is a larger difference in isoprene levels between the two campaigns during the early morning and evening rush hour periods and at nighttime. As mentioned in Sect. 2.2, isoprene has both biogenic and anthropogenic sources in urban areas. Some studies in business-oriented cities have indicated that anthropogenic isoprene was strongly related to traffic-related sources (Borbon et al., 2001; Wang et al., 2013). Ambient isoprene during rush hour periods and at nighttime may partially result from traffic emissions. Because of the stringent controls on traffic emissions during the Olympic period, the lower isoprene levels during these periods may be caused by the large reduction in anthropogenic isoprene, which originated from motor vehicles.

3.1.2 Biogenic and anthropogenic contributions to isoprene

Anthropogenic isoprene can be reduced by traffic control measures, whereas biogenic isoprene is hard to control. Investigations on the biogenic and anthropogenic contributions to isoprene are essential to the understanding of their respective significance for secondary pollutant formation. Provided that anthropogenic isoprene has a strong correlation with vehicle exhaust tracers, simple regression analyses on the concen-

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trations of isoprene and exhaust tracers can be used to estimate the contributions of anthropogenic and biogenic sources to ambient isoprene levels.

In this study, three common exhaust tracers, i.e., propene, 1-butene and isobutene, with higher observed mixing ratios in Beijing and chemical properties similar to isoprene were employed for the source apportionment of isoprene. Figure 2 shows the diurnal variations in the ratios of isoprene to the three different tracers during CAREBeijing-2008. Isoprene has no (or negligible) emissions from biogenic sources without illumination (Shao et al., 2001; Sanadze, 2004); thus, the isoprene/tracer ratio at night can generally be considered the value characteristic of traffic emissions. Shown in Fig. 2, from late night (22:00) to 05:00 the next day, the flat ratios of isoprene/tracers reveal that isoprene was strongly correlated with the three exhaust tracers, which indicates that isoprene during this period was almost from vehicular emissions.

In contrast to the flatter ratios at night, the ratios of isoprene/tracers started increasing at dawn and gradually reached a maximum in the early afternoon (14:00). The enhanced ratios during the daytime indicate the large additional contribution of biogenic sources to daytime isoprene. The ratios of isoprene to the three tracers show similar patterns except for isoprene to propene in the morning (08:00 to 10:00). The lower average ratios of isoprene to propene resulted from a few data with high propene levels. In these data with high propene levels, propene did not correlate well with other vehicular exhaust tracers, which indicates that propene occasionally had large emissions from sources other than vehicular exhaust; thus it is not suitable as an exhaust tracer to discriminate isoprene sources. In this study, 1-butene, the compound measured during both the CAREBeijing-2008 and CAREBeijing-2006 campaigns, was employed as the tracer to estimate the contributions of anthropogenic sources to isoprene.

Figure 3 shows the estimated anthropogenic and biogenic isoprene during the CAREBeijing-2008 and CAREBeijing-2006 campaigns. The calculated anthropogenic isoprene was estimated by the measured 1-butene multiplied by the characteristic ratio of isoprene to 1-butene representative of vehicular emissions (flat ratio in Fig. 2). Biogenic isoprene was calculated by subtracting the anthropogenic isoprene from the

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observed ambient isoprene. As shown in Fig. 3, both campaigns indicated similar contributions for biogenic sources to ambient isoprene. However, the contribution of anthropogenic sources during CAREBeijing-2008 was much lower than that during CAREBeijing-2006 as the stringent controls on anthropogenic sources were conducted during CAREBeijing-2008.

During the daytime, biogenic isoprene overwhelmed anthropogenic isoprene. It is estimated that approximately 92 % and 86 % of daytime (defined as 06:00 to 19:00) isoprene was released by biogenic sources during CAREBeijing-2008 and CAREBeijing-2006, respectively. In other words, only 8 % and 14 %, respectively, of daytime isoprene could be attributed to vehicular emissions. Regarding the nighttime pattern during CAREBeijing-2008, isoprene was almost emitted from vehicular sources except for the evening period (19:00 to 22:00). From 19:00 to 22:00, there was a transitional period that the fraction of biogenic isoprene gradually decreased and anthropogenic isoprene gradually increased. In theory, biogenic isoprene emissions should fall to negligible rates without illumination, i.e., when night falls. The reason that a fraction of biogenic isoprene existed at night is that a little residual isoprene persists into the nighttime after daytime photochemical loss. A similar phenomenon involving residual daytime isoprene persisting into nighttime was also observed during CAREBeijing-2006, as shown in Fig. 3. In conclusion, biogenic isoprene dominated the isoprene levels during the daytime, whereas isoprene levels from late night (22:00) to dawn the next day almost originated from vehicular emissions.

3.2 Relative potentials for secondary oxidant formation

Of the 65 measured NMHCs during CAREBeijing-2008, Fig. 4 shows the daytime and nighttime average concentrations and standard deviations. Among these species, ethyne (acetylene), ethene and C_2-C_4 alkanes, which originate nearly exclusively from anthropogenic sources, were the most abundant species. Ethyne and ethene in the urban atmosphere are generated primarily from incomplete combustion, particularly vehicle exhaust. C_2-C_4 alkanes result mainly from the leakage of liquefied petroleum

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gases (LPG), natural gas (NG) and gasoline evaporation. In comparison with daytime levels, the concentrations of most NMHCs were slightly higher at night, except for isoprene. Isoprene revealed notably higher daytime concentrations, indicating that it had larger emissions during the day, which is interpreted as being associated with biogenic sources, as discussed in the previous section.

Although the concentrations of isoprene were relatively low compared to other main species in urban Beijing, it still deserves attention due to its extremely strong photochemical reactivity and primarily biogenic sources during the day in summer. Especially for the stringent control period of anthropogenic pollutant sources during the Olympic Games, the significance of isoprene for atmospheric chemistry may be emphasized since anthropogenic pollutants were controlled. To further assess the relative importance of isoprene and other NMHCs in secondary pollutant formation, the MIR method and k_{OH} method (reactivity of NMHC with OH radical) were used for rapid, convenient evaluation. Figure 5 shows the diurnal patterns of the relative OFPs and OH reactivities of isoprene and four categories of alkanes, alkenes (excluding isoprene), aromatics and ethyne during CAREBeijing-2008. With respect to the OFP results estimated by the MIR method, aromatics and alkenes were the categories with the highest OFPs and accounted for 31–45 % and 28–36 %, respectively, of the total OFPs in the daytime. Although the contribution of isoprene to the total OFPs was lower than those of aromatics and alkenes, it still accounted for 20 % of the total OFPs during the midday hours. In terms of the OH reactivity, it is surprising that isoprene accounted for 33 % of the total reactivities during the day and its maximum can reach approximately 40–50 % of the total reactivities during midday and early afternoon, which implies its significance for atmospheric chemistry in the summer daytime. Figure 5 shows that the fraction of isoprene in total OH reactivities was much larger than the fraction of isoprene in the total OFPs. The MIR value of isoprene listed in Table 1 is close to that of other reactive species, such as xylene, ethene and propene, which reveals their approximate potentials for ozone formation on a per-gram-of-VOC basis. Nevertheless, the reaction rate constant of isoprene with OH radical is much higher than the rate constants of other compounds by a factor of 5 to 10.

The OFP and OH reactivity of a NMHC are estimated and determined by its concentration level and corresponding MIR and k_{OH} values. Although the emission strength and reactivity of a precursor are important for the secondary pollutant formation potential, the timing of release is also critical from the perspective of photochemistry. The midday surge of biogenic isoprene could produce a much larger loss and more efficient production of midday ozone and/or secondary pollutants because the midday peak of isoprene is almost concurrent with the peak of OH, a condition that could maximize photochemical reactions (Lee and Wang, 2006). The observed high levels of midday isoprene would result in even higher potentials for the production of secondary pollutants when coupled with the period of intense photochemical reactions. Furthermore, the observed daytime profile of isoprene should be regarded as the net concentration of isoprene after taking emissions and photochemical loss into account (Lee and Wang, 2006); this indicates that the originally emitted isoprene at noon must be greater than the observed isoprene. Xie et al. (2008) derived the mixing ratios of initial isoprene by employing the observed isoprene and its photoproducts, methyl vinyl ketone (MVK) and methacrolein (MACR); the OFP for initial isoprene at the PKU site during the CAREBeijing-2006 campaign accounted for 23 % of the total OFPs in the daytime, compared to 11 % using observed isoprene. In conclusion, the high levels of biogenic isoprene during the daytime in summer, and its coherence with OH diurnal cycle accentuate the significance of biogenic isoprene and its potentially great impact on atmospheric chemistry, OH reactivities and secondary pollutant formation.

3.3 Discrepancy between the decreased levels of primary air pollutants and high observed levels of O_3 during the 2008 Summer Olympics

In contrast to the substantial reduction of the primary air pollutants, the mitigation of O_3 in Beijing during the Olympic period was not effective, although the precursors to ozone production, i.e., anthropogenic NMHCs and NO_x were decreased. As shown in Fig. 1,

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the reduction in the levels of primary pollutants was significant in that the average daily mixing ratios of NMHCs, NO, NO_2 and CO were reduced by 49.7, 76.5, 31.0 and 27.8 %, respectively, by comparing the data observed during CAREBeijing-2008 with those during CAREBeijing-2006. However, the average daily mixing ratio of O_3 increased by 42.2 %. To explain this interesting phenomenon, we combine the possible causes proposed by other groups and analysis of biogenic isoprene to resolve the inconsistency. Regarding the influence of meteorology, the weather conditions in 2008 showed higher temperature, slightly larger radiation flux and lower wind speed and were more conducive to the formation and accumulation of O_3. The enhancement in the mixing ratios of O_3 might be partially explained by the difference in the meteorological conditions between the two campaigns.

Considering the possibly significant contribution of regional sources to secondary pollutant levels in Beijing, Streets et al. (2007) estimated that approximately 35–60 % of ozone during high ozone episodes at the Olympic Stadium site can be attributed to sources outside Beijing based on the US EPA's Models-3/CMAQ model simulation over the Beijing region. Furthermore, Wang et al. (2010c) proposed that the enhanced O_3 at an urban site in north Beijing was strongly associated with the transport of chemically processed air masses from the North China Plain by southerly winds. These studies indicate that the significance of regional sources for the secondary pollutant levels in Beijing and O_3 would not be abated proportionally by the large decrease in precursors inside Beijing alone.

Furthermore, the effectiveness of the emission control measures on the secondary oxidants can be very different due to various definitions of oxidants. O_3 and NO_x are rapidly exchanged via NO titration under intense photochemical conditions (Liu, 1977; Levy et al., 1985; Sillman, 1999). Using the sum of O_3 and NO_2 provides more accurate estimates of ozone formation during photochemical processing. The mean daily $O_3 + NO_2$ were only increased by 11.8 % if NO titration was considered (Fig. 1k). The reduced NO-O_3 titration due to the reduction in NO_x emissions was a reason for the increased O_3 during CAREBeijing-2008, especially during rush hour traffic (06:00–09:00

and 18:00–22:00) and at nighttime. Furthermore, Chou et al. (2011) compared the difference in the average daily total oxidants (defined as $O_x = O_3 + NO_2 + 1.5NO_z$) between the CAREBeijing-2008 and CAREBeijing-2006 campaigns. In contrast to the increased O_3 and $O_3 + NO_2$ during CAREBeijing-2008, the average daily total oxidants were reduced by 21.3 % due to substantially lower NO_z in 2008 (Fig. 1l).

In addition to the factors discussed above, the biogenic isoprene is another concern that can reduce the effectiveness of the control measures for decreasing ozone formation. By comparing the data during CAREBeijing-2008 with those during CAREBeijing-2006, the level of biogenic isoprene (Fig. 3) did not decrease although anthropogenic precursors were greatly reduced. In the period of intense photochemical reaction around noon and early afternoon, i.e., 11:00–15:00, biogenic isoprene contributed significantly to the atmospheric OH reactivity and accounted for 40–50 % of the total OH reactivities, which was still able to provide a large amount of organic peroxy radicals for subsequent atmospheric reactions, e.g., oxidation of NO to NO_2 and formation of organic nitrates, PANs and O_3.

Besides, the discrepancy can be attributed, in part, to the non-linearity of O_3-VOC-NO_x chemistry. The complicated photochemical reactions in the atmosphere lead to the formation of diverse oxidants. The levels of individual oxidants produced in various environments can be quite different, and they depend on conditions of reaction kinetics and environment, including radiation flux, temperature, precursor species and precursor levels. With respect to the NO_x levels during the two campaigns, Fig. 1g and h shows that the large reduction in NO and NO_2 occurred in the morning, evening and at nighttime but not as significantly during midday and early afternoon. The major products of atmospheric NO_x oxidation are HNO_3, PANs and organic nitrates, which are involved in NO_z. As shown in Fig. 1i, lower NO_z was observed during CAREBeijing-2008. The lower NO_z levels and the non-decrease of midday NO_x levels implies that most NO and NO_2 during midday might persist in the cycle that catalyzes ozone formation; therefore, less NO_x was transformed to NO_z. The High radiation flux and temperature at midday were more conducive for the photo-dissociation of NO_2 to NO and

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$O(^3P)$ radical and for the oxidation of NO to NO_2 by organic peroxy radicals than for radical combination reactions, e.g., formation of PANs, organic nitrates and HNO_3. During midday, isoprene accounted for approximately 40–50 % of the total OH reactivities. Although organic peroxy radicals originated from anthropogenic VOCs were largely reduced during CAREBeijing-2008, the high levels of midday isoprene (mostly biogenic) and its reactive photoproducts can still supply large amounts of reactive peroxy radicals for the oxidation of NO to NO_2. This factor in combination with the high radiation flux and temperature during midday and early afternoon might support and keep the levels of midday NO and NO_2 and maintain the NO_x cycle that resulted in abundant O_3 but lower levels of NO_z.

Ryerson et al. (2001) studied the production rates and yields of ozone from power plant NO_x sources in rural area with low anthropogenic NMHCs but high biogenic isoprene. High ozone was observed after a diluted NO_x plume into a high ambient loading of reactive biogenic isoprene. This indicates that under conditions of high biogenic isoprene and moderate NO_x, high ozone can be produced although the levels of other anthropogenic NMHCs are low. Furthermore, model studies indicate that the ozone response to biogenic emissions varies greatly, showing more sensitivity in relatively high NO_x areas (i.e., urban areas) and less sensitivity in relatively low NO_x areas (Han et al., 2005). It accentuates the significant role of biogenic isoprene in urban areas. Although anthropogenic precursors were reduced greatly during the Olympic Games, sufficient biogenic isoprene was present and NO_x levels were maintained during midday and early afternoon, which can still result in a large amount of midday and early afternoon O_3.

4 Conclusions

The measured isoprene during the Olympic Games showed a pattern with daily maximum mixing ratios of 0.83 ppbv at noon and a minimum at night. The sensitivity of isoprene to sunlight intensity and temperature indicate that the sources of isoprene were primarily biogenic. Using the ratio of isoprene to vehicle exhaust tracers, approximately 92 % of daytime isoprene was estimated from biogenic sources, and only 8 % was attributed to vehicular emissions. The midday surge of biogenic isoprene in the period of intense photochemical reactions could result in the efficient production of midday ozone. During midday and early afternoon, biogenic isoprene can contribute approximately 20 % of the total OFPs and 40–50 % of the total OH reactivities of the 65 measured NMHCs.

The discrepancy between the decreased precursor levels and the observed high ozone levels was most likely caused by a combination of many factors. The changes in the partition among the components of oxidation products (O_3, NO_2 and NO_z) and the contribution of air pollutants from regional sources outside Beijing should be two primary reasons. Furthermore, the influences of biogenic isoprene as well as the complicated non-linearity of O_3-VOC-NO_x chemistry can be other significant factors that reduced the effectiveness of the control measures in decreasing ozone formation. Although anthropogenic precursors were greatly reduced during the Olympic Games, sufficient biogenic isoprene was present. During midday and early afternoon, large numbers of organic peroxy radicals resulting from biogenic isoprene and its reactive photoproducts as well as the conditions of high radiation flux and temperature may support and maintain the cycle and levels of NO_xthat resulted in abundant O_3 and lower levels of NO_z. In the study, the midday surge of biogenic isoprene during summer and its coherence with OH diurnal cycle accentuate the significance of biogenic isoprene and its potentially large impact on atmospheric chemistry, OH reactivity and oxidant levels in urban atmosphere, particularly when anthropogenic NMHCs were reduced.

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Table 1. Photochemical properties and average daily mixing ratios of the 65 measured NMHCs during CAREBeijing-2008.

Compound[a]	MIR[b]	$k_{OH} \times 10^{12c}$	Average daily mixing ratio (ppbv)
Alkane			
ethane	0.3	0.3	2.78
propane*	0.5	1.2	2.17
isobutane*	1.2	2.3	1.52
n-butane*	1.1	2.5	1.60
isopentane*	1.4	3.9	1.21
n-pentane*	1.2	3.9	0.44
2,2-dimethylbutane*	1.1	2.2	0.03
cyclopentane*	2.2	5.2	0.06
2,3-dimethylbutane	1.1	6.2	0.07
2-methylpentane*	1.4	5.6	0.32
3-methylpentane*	1.7	5.7	0.23
n-hexane*	1.1	5.6	0.31
2,4-dimethylpentane*	2.1	5.7	0.02
methylcyclopentane*	1.5	5.1	0.17
cyclohexane*	1.1	7.5	0.06
2-methylhexane*	1.1	6.9	0.11
2,3-dimethylpentane*	1.3	5.1	0.04
3-methylhexane*	1.5	5.1	0.13
2,2,4-trimethylpentane*	1.2	3.7	0.02
n-heptane*	1.0	7.2	0.12
methylcyclohexane*	1.6	10.4	0.06
2,3,4-trimethylpentane	1.0	7.0	0.01
2-methylheptane*	1.1	8.3	0.04
3-methylheptane*	0.8	8.6	0.04
n-octane*	0.7	8.7	0.04
n-nonane*	0.6	10.2	0.04
n-decane*	0.5	11.6	0.05
n-undecane*	0.5	13.2	0.04
Alkenes			
ethene	7.4	8.5	1.98
propene*	11.6	26.3	0.43
trans-2-butene*	15.2	64.0	0.19
1-butene*	9.6	31.4	0.50
isobutene	5.3	51.4	0.19
Alkenes			
cis-2-butene*	14.3	56.4	0.16
3-methyl-1-butene	6.2	31.8	0.03
1-pentene*	7.1	31.4	0.05
isoprene*	**10.5**	**101.0**	0.45
trans-2-pentene*	10.5	67.0	0.06
cis-2-pentene*	10.3	65.0	0.03
2-methyl-2-butene	6.4	68.9	0.04
cyclopentene	7.7	67.0	0.01
4-methyl-1-pentene	6.7	63.0	0.01
2-methyl-1-pentene	6.7	63.0	0.02
trans-2-hexene	6.7	63.0	0.01
cis-2-hexene	6.7	63.0	0.01
alpha-pinene	3.3	53.7	0.08
beta-pinene	4.4	78.9	0.01
Alkyne			
ethyne	0.5	0.9	3.52
Aromatics			
benzene*	0.7	1.2	0.95
toluene*	3.9	6.0	1.15
ethylbenzene*	3.0	7.0	0.43
m, *p*-xylene*	8.5	20.5	0.61
styrene*	1.7	58.0	0.06
o-xylene*	7.6	13.6	0.22
isopropylbenzene*	2.5	6.6	0.03
n-propylbenzene*	2.0	5.7	0.04
m-ethyltoluene*	7.4	18.6	0.10
p-ethyltoluene*	4.4	11.8	0.04
1,3,5-trimethylbenzene*	11.8	56.7	0.04
o-ethyltoluene*	5.5	11.9	0.04
1,2,4-trimethylbenzene*	8.8	32.5	0.13
1,2,3-trimethylbenzene*	11.9	32.7	0.03
m-diethylbenzene*	7.1	15.0	0.01
p-diethylbenzene*	4.4	10.0	0.02

[a] * denotes the species measured in the CAREBeijing-2006 (49 species).

[b] MIR denotes maximum incremental reactivity ($g(O_3)\,g(VOCs)^{-1}$), Carter, 1994.

[c] k_{OH} denotes rate constant of VOCs react with hydroxyl radicals at 298 K (Atkinson and Arey, 2003).

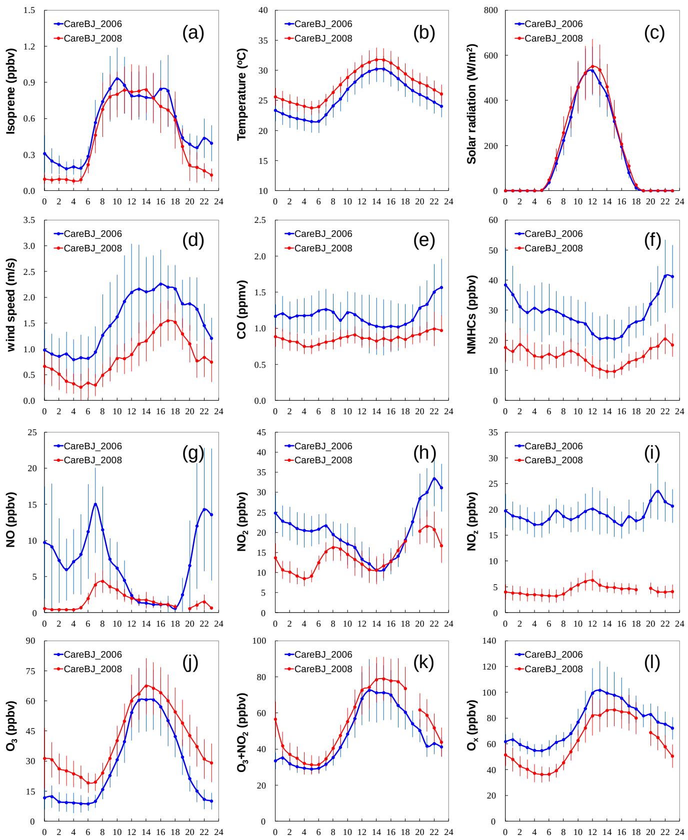

Fig. 1. Diurnal variations in the mixing ratios of trace gases and meteorological parameters during CAREBeijing-2008 (1–31 August 2008) and CAREBeijing-2006 (12 August–9 September 2006). The ranges of ±1/2σ (standard deviation) are indicated by the error bars. **(a)** Isoprene; **(b)** temperature; **(c)** total short-wave irradiance (SWI); **(d)** wind speed; **(e)** CO; **(f)** NMHCs (49 common species); **(g)** NO; **(h)** NO_2; **(i)** NO_z; **(j)** O_3; **(k)** $O_3 + NO_2$; **(l)** O_x.

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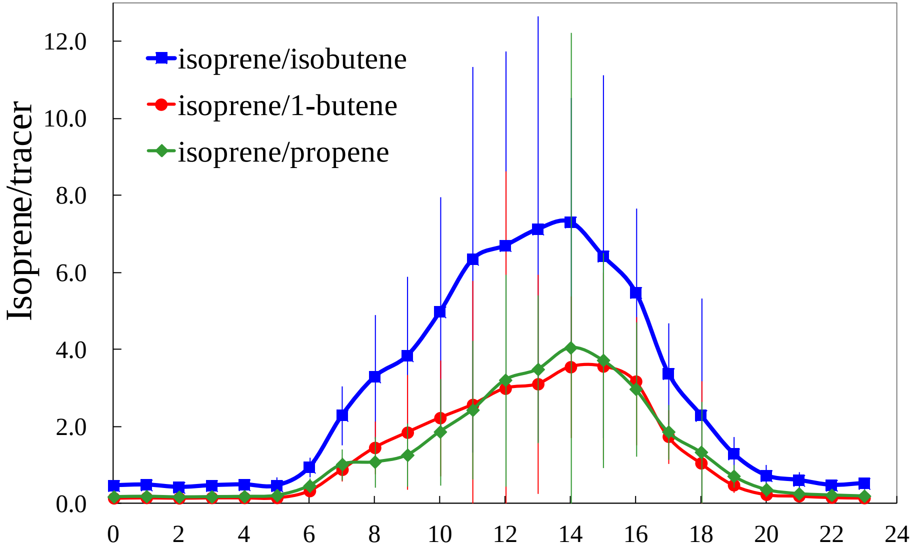

Fig. 2. Diurnal variations in the mixing ratios of isoprene to different tracers during CAREBeijing-2008. The ranges of ±1/2σ (standard deviation) are indicated by the error bars.

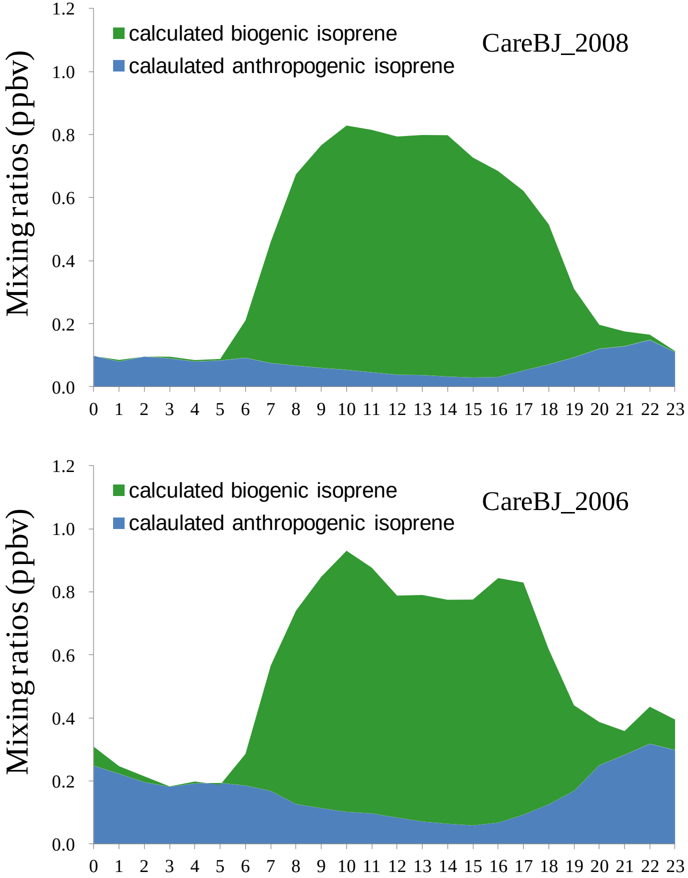

Fig. 3. Diurnal patterns of the estimated anthropogenic and biogenic isoprene during CAREBeijing-2008 (upper panel) and CAREBeijing-2006 (lower panel).

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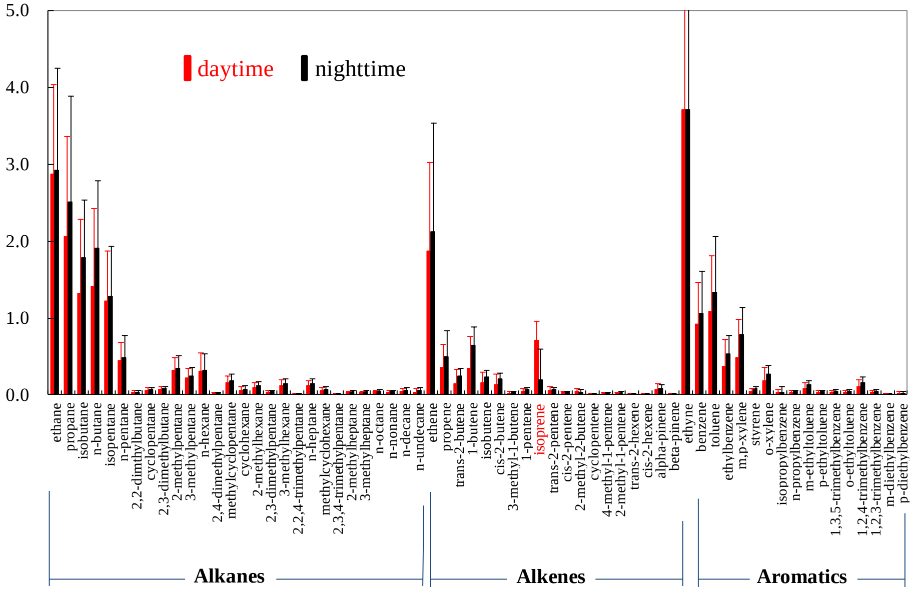

Fig. 4. Daytime and nighttime average concentrations of 65 NMHCs during CAREBeijing-2008 (unit: ppbv). Error bars represent the standard deviations (1σ).

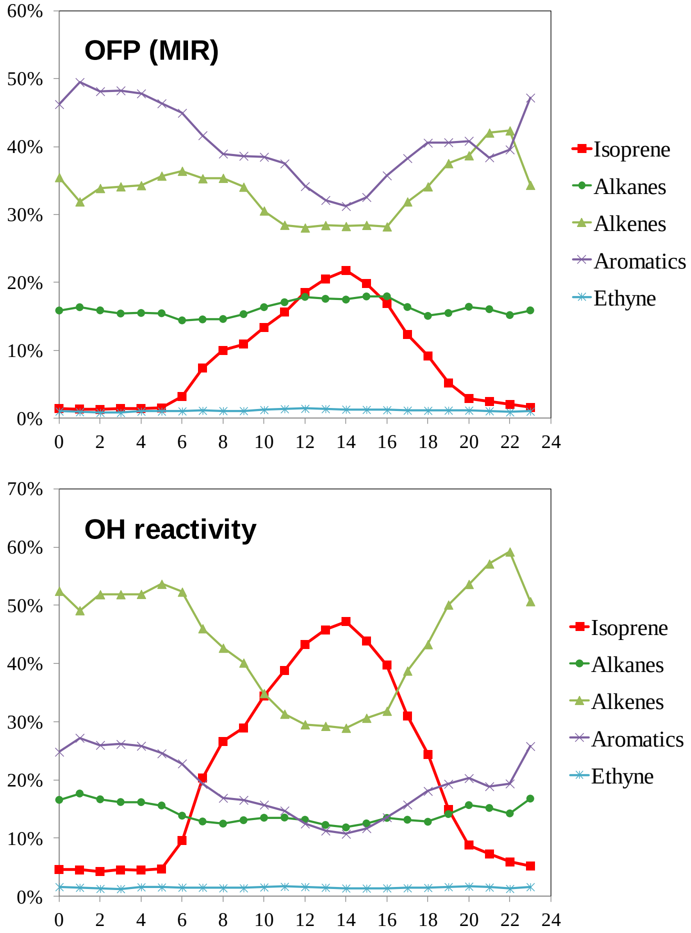

Fig. 5. Fractional contributions of isoprene and four categories of alkanes, alkenes (excluding isoprene), aromatics and ethyne to the total OFP (upper panel) and the total OH reactivity (lower panel) during CAREBeijing-2008.